

WATTS

DICTIONARY OF CHEMISTRY

RAVISED AND ENTIRELY REWRITTEN (1884)

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ASSISTED BY EMINENT CONTRIBUTORS

IN FOUR YOLUMES
VOL. IV.

WITH ADDENDA

NEW IMPRESSION

LONGMANS, • GREEN, AND CO.

39 PATEBNOSTER BOW, LONDON

FOURTH AVENUE & NOTE STREET, NEW YORK

BOMBAY, GALGUITTA, AND MADRAS

1920

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INTRODUCTION*

TO THE ARTICLES ON INORGANIC CHEMISTRY.

IT has been thought advisable to include in an Addenda brief accounts of the chief work done in descriptive inorganic chemistry since the publication of Vols. I., II., and III., and the printing off the final proofs of Vol. IV.

Nothing bearing on organic chemistry has been included in the ADDENDA, as to give an account of what has been done in this department since the various volumes were published would occupy many hundred pages.

Dates are attached to the references made to original memoirs in the ADDENDA; and references are frequently made to abstracts of the memoirs in the Journal of the Chemical Society.

M. M. PATTISON MUIR.

INTRODUCTION

THE ARTICLES RELATING TO ORGANIC CHEMISTRY.

THE names used to denote ring formulæ are given below for convenience of

Since the publication of the last volume I have been assisted in the work of reading and making abstracts of original memoirs by Drs. T. Cooksey, T. A. Lawson, Samuel Rideal, Messrs. J. Wilkie, G. N. Huntly, and J. T. Norman. I have also been existed by Mr. Arthur G. Green and Mr. Cecil W. Cumhington in the work of revising the proof-sheets. I have great pleasure in thanking these gentlement for the energetic and Miscient manner in which they have carried out their share of the work.

H. FORSTER MORLEY.

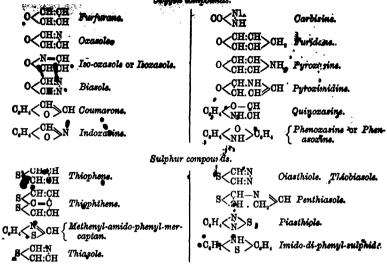
Nomenclature of Ring Formulæ.

Hydrocarbons.

OH, CH, Tri	imethylens.	•сн<сн Он Он	Tetramethenyl.
$CH_2 < CH_2 > CH_2$	Tetramethylene.	CH₂ <ch:ch< td=""><td>Pentamethenyl hydride.</td></ch:ch<>	Pentamethenyl hydride.
OH ₂ CH ₂ OH ₂ Pe	entamethylene.	с"н"<Сн >он	Indonaphthene.
	Nitrogen o	empounds.	
ин<сн:он	Pyrrole.		OH Pyridasine.
NH <n=ch< td=""><td>Pyrazole.</td><td>N≪CH:⊕H></td><td>N Pyrasins.</td></n=ch<>	Pyrazole.	N≪CH:⊕H>	N Pyrasins.
NH CH: N	Glyoxaline.	N≪CH:N CH.CH	CH Pyrimidine.
n≪ ^{oh.oh} ,	Metapyrasole.	n≪ch. n >	CH Triazoline.
$NH < \stackrel{OH:N}{\underset{CH:N}{\text{OH}}} \stackrel{\bullet}{\text{or}} N < \stackrel{OI}{\underset{CI}{\underset{CI}{\text{OH}}}}$	H.NH H:N <i>Triazole.</i>	$N \leqslant_{N:CH} N :_{CH}$	CH Osotetrasole.
$NH <_{N:CH}^{N:CH}$	Osotriasole.	C.H. CH:CH	- Quinolins.
$\mathbf{nH} <_{\mathbf{CH}:\mathbf{N}}^{\mathbf{N}=\mathbf{N}}$	Tetrasole.	CH:CH	Isoquinolins.
$NH <_{CH:N}^{CH:N}$	Pyrrodiasols.	O.H. N :OH	Quinozaline.
$c_H <_{NH}^{NH} > c_H$	Indole.	O.H. CH:N	Quinasoline.
$\mathbf{C}^{\mathbf{H}} < \stackrel{N}{\overset{C}{\overset{H}}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}}{\overset{H}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}{\overset{H}}}{\overset{H}}}}{\overset{H}}}}}}}}}$	Indasine.	CH CH:CH	Cinnoline.
$C_H < NH > N$	Pseudo-indasins.	C.H. CH:N	Phentriasine.
$c_H <_{OH}^N >_{OH}$	Acridine.	C.H. C(NH).OH:O.N	Ph C.H. Rosindulins.
$0^{4}H' < \frac{N}{N} > 0^{4}H'$	Phenasine.		PhO H. { Naphthoros indulins.
MCOHOH OH	Pyridine.	,	•

DELLO VOTON

Daygon compounds.



INITIALS OF SPECIAL CONTRIBUTORS.

- SOLUTIONS I.
- J. W. C.
 J. W. CAPSTICK, D.Sc., M.A., Fellow of Prinity College, and Demonstrator in Physics in the University, Cambridge. Contributes Capillaryty, Methods Based on; and Viscosity of Liquids.
- G. G. GEORGE GLADSTONE, Esq. Configibutes Optical methods, section Refraction and Dispersion.
- W. D. H. W. B. HALLIBURTON, M.D., F.R.S., Professor of Physiology at King's College, London. Contributes Proteids.
- W. N. H. W. N. HARTLEY, F.R.S., Professor of Chemistry in the Royal College of Science Dublin. Contributes Optical methods, section Spectroscopic methods.
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- S. R. SAMUEL RIDEAL, D.Sc. Contributes TANNIN.

Contributes ELECTRICAL METHODS.

w. o.

- W. A. T. WILLIAM A. TILDEN, D.Sc., F.R.S., Professor of Unemistry at the Royal College of Science, South Kensington. Contributes Terrense.
 - F. E. T. T. E. THORPE, D.Sc., Ph.D., F.R.S., Head of the Government Laboratories, Somerset

 House. Contributes Sprayro volumes.

Articles by Mr. MUIR are initialed M. M. P. M.

Ummaned Arricles are by Dr. MORLEY, except those in the Addenda, which are by Mr. MUIR.

ABBREVIATIONS

I. JOURNALS AND BOOKS.

When an author has then mentioned in an article, he is usually referred to thereafter in that article by his initial only.

U	<i>y</i> 3
4	Liebig's Annale) der Chemie.
Z. A	Annales de la Séciedad Cientifica Argentina.
19 Oh. 0.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences.
Am	American Chemical Journal.
Ann. M.	Annales des Mines.
Amus.	American Journal of Science
A. O. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am, J .	1
a Pharm.	nimerican ocurran or i zarmacj.
An	The Analyst.
A. Ph. S.	Proceedings of the American Philosophical Society.
	Archives neerlandaises—The Hague.
Ar.N	Mémoires de l'Académie des Sciences.
Ar. Ph.	Archiv der Pharmacie.
Ar. Sc.	Archives des Sciences phys. et nat.
70	Berichte der deutschen chemischen Gesellschaft.
B. A	Reports of the British Association.
יוסד דסד	Bulletin de la Société chimique de Paris.
B. B	Berliner Akademie-Berichte.
B. C	Biedermann's Centralblatt für Agricultur-Chemie.
B.J.	Berzelius' Jahresberichte.
В. М.	Berliner Monatsberichte.
C. Mem.	
$C.J_{\lambda}$.	Journal of the Chemical Society of London.
O.J. Proc.	
C. N.	Chemical News.
0. R	*Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences
	Paris.
O. C	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fr	Fresenius' Zeitschrift für analytische Chemie.
G	Gazzetta chimica italiana.
G. A	Gilbert's Annalen der Physik und Chemie.
H	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
T	Proceedings of the Royal Irish Academy.
J	Jahresbericht über die Fortschritte der Chemie und verwa
	anderer Wissenschaften.
J. O. T	Jahresbericht für Übemische Technologie.
J. M	Jahrbuch für Mineralogie.
J. de Ph.	Journal de Physique et des Sciences accessoires.
J. Ph	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
J. Th	Jahresbericht über Thierchemie.
J. R	Journal of the Russian Chemical Society.
7. Q	Jenaische Zeitschrift für Medicin und Naturwissenschaft.
L. Fo	Landwirthschaftliche Versuchs-Stationen. Monatshefte für Chenile und verwandte Theile anderer Wissensphaften.
X	Le Moniteur Scientifique.
Y. S. Y. Mon. 8.	Mémoires de la Société d'Arcueil.
ďA,	SECULIATION NO NA PROGRAM & STANDAN
Hem. B.	Mémoires couronnés par l'A adémie de Bruxelles.

ARRESTATION

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N.Ed.P.J. New Edinburgh Philosophical Journal.
N. J. P. Neuery Jahresbericht der Pharmacie.
N. R. P. Neuery Sahresbericht der Pharmacie.
N. J. P.
N. R. P.
N. J. T.

Neues Journal von Trommsdorff.

P. M.

Philosophical Magazine.

Poggendorff's Annalen der Physik und Chemie.
P...
P. B.
                  Beiblätter zu den Annalen der Physik und Chemie.
                  Beiblatter 20 den Annaten der ruysig und Gescherberger's Archiv für Physiologie.
Proceedings of the Royal Society of Edinburgh.
Pharmaceutiscal Journal and Transactions.
Pharmaceutisches Central Blatt.
Pf. E.
 Ph. O. .
Pr. .
P. R. I. .
                   Proceedings of the Royal Society.
                   Proceedings of the Royal Society.

Proceedings of the Royal Institution of Great Britain.
Phaymaceutische Zeitahriff für Russland.
Recueil des gravaur chimiques des Pays-Bas
 P. Z.
B. T. C.
 R. P.
Q. J. S.
S.
                   Repertorium für die Pharmacie.
                   Quarterly Journal of Science. Schweigger's Journal der Physik.
  Scher. J.
                   Sonweiger's Journal der Lysik.
Scherer's Journal der Chemie.
Journal of the Sociéty of Chemical Industry.
Sitzungsberichte der K. Akademie zu Wien.
Transactions & the Royal Society.
  8. C. I. .
  Sits. W. .
  T. or Tr.
T. E. . .
                    Transactions of the Royal Society of Edinburgh.
Wiedemann's Annalen der Physik und Chemie.
  ₩.
₩. J.
                    Wagner's Jahresbericht.
  Z.
                    Zeitschrift für Chemie.
 Z. B. c.
                    Zeitschrift für Biologie.
                    Zeitschrift für die gesammten Naturwissenschaften.
  Z. f. d. g.
Natur-
     wiss.
  Z. K..
Z. P. C.
                     Zeitschrift für Krystallographie und Mineralogie.
                    Zeitschrift für physikalische Chemie.
                    Handbuch der organischen Chemie: von F. Beilstein, 2te Auflage.
  Bn. .
E. P.
                    English Patent.
  G. P.
                    German Patent.
  Gm.
                    Gmelin's Handbook of Chemistry-English Edition.
  Gm. K.
                    Gmelin-Kraut: Handbuch der anorganischen Chemie.
                   Traité de Chimie organique: par Charles Gerhardt.
Lehrbuch der organischen Chemie: von Aug. Kekulé.
Graham-Otto: Lehrbuch der anorganischen Chemie [5th Ed.]
  Gerh.
  Stas.
                    Stas' Recherches, &c.
                                                                          Aronstein's German translation are ferred to as Chem. Proport.
      Rech.
                    Stas' Nouvelles Recherches, &c.
  Stas.
   Nouv. R.
  Th. . . Thomsen's Thermochemische Untersuchungen.
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II. TERMS AND QUANTITIES, &C., FREQUENTLY USED.

```
Water; e.g. NaOHAq means an aqueous solution of caustic sods.
                   18 parts by weight of water.
                  Residues of mono, di., and tri-basic acids. Thus, in describing the salts of a monobasic acid NaA', CaA', AlA', may be written, HA' standing for the acid. For a dibasic acid we should write Na,A'', CaA', Al,A', &c. Stand for bases of the ammonis type, in describing their salts. Thus the
Ã‴
                   Stand for bases of the ammonia type, in describing their salts. Thus the hydrochloride would be B'HCl or B"2HCl, according as the base is
B'B" etc.
                          monacid or discid, &c.
                   Concentrated.
cone..
dil. .
                   Dilute.
                   gram.
g. .
                   milligram.
møm.
                  millimetre.
mm. .
mol. .
                   molecule.
oil.
                  liquid, nearly, or quite, insoluble in water.
                  precipitate.
to precipitate
precipitating.
pp. .
to ppt.
                  precipitated.
```

Santa in

AREKEVELTIONS.

```
soluble in.
 insol.
 we sol. .
                 very easily
 y. sol.
                very
moderatel
 Ŷn. sol.
                                    soluble in.
                slightly
very slightly
 sl. sol.
 v. sl. sol.
                800.
                 compare.
 [°)
                 about.
                a melting-point.
                a boiling-point.

Hardness (of minerals).

Atomic weight.
 Ħ.:
 At. w.
                Molecular weight.
 Mol. w. or
    M.ew.
 D....
                Density.
 uncor.
                corrected.
                uncorrected.
 i.V. •.
                in vapour.
 Ÿ.D. .
                vapour-density, i.e. density of a gas compand with hydrogen or air
 8.G. 19
8.G. 19
8.G. 11
8.G. 11
                Specific gravity compared with water.
                                    at 10° compared with water at 02.
                             **
                                     ,, 15°
                             ,,
                                     ,, 12°; compared with water of which the temperature is
                             ,,
                    not given.
 S.H. .
                Specific heat.
                             " of a gas at constant volume.
 S.H. p. .
                Quantity of heat, in gram-units, produced during the complete com-
bustion of the mass of a solid or liquid body represented by its
                                                           pressure.
 H.C.
                      formula, taken in grams.
 H.C. v. .
                Heat of combustion in gram-units of a gram-molecule of an element or
                      compound, when gaseous, under constant volume.
H.C. p. .
                The same, under constant pressure.
                Quantity of heat, in gram-units, produced during the formation of the mass of a solid or liquid body represented by its formula, taken in
H.F.
                      grams, from the masses of its constituent elements expressed by
                    • their formulæ, taken in grams.
               Heat of formation of a gram-molecule of a gaseous compound from the gram-molecules of its elements under constant volume.
 ■.F. v. ..
H.F. p.
H.V.
                The same, under constant pressurce
               Heat of vaporisation of a liquid, i.e. gram-units of heat required to change
                     a gram-molecule of the liquid compound at B. P. into gas at same temperature and pressure.
T.C. .
                Thermal conductivity (unit to be stated).
8.V. .
                Specific volume; or the molecular weight of a gaseous compound divided
                      by the S.G. of the liquid compound at its boiling-point compared with
                      water at 4°.
               Specific volume of a solid; or the mass of the solid expressed by its formals, taken in grams, divided by its S.G.
S.V.S. .
E.C. .
               Electrical conductivity (the unit is stated in each case).
C.E. (10°
to 20°)
                Coefficient of expansion (between 10° and 20°).
                                           of a gas = volume dissolved by 1 volume of water.
of a liquid or solid = number of grms. dissolved by
               Solubility in water
S. (alco-
                             ,, alcohol 100 grms. of water. In both cases the temperature is stated.
   hòl)
               Index of refraction for hydrogen line $\beta$.

", sodium a, p, &c.

Molecular refraction for sodium light, i.e. index of refraction for line a
\mu_{\rm p}, &c. B_{\rm B} V.
                     minus one, multiplied by molecular weight, and divided by S.G. at 15°
                     compared with water at 0°.
               The same; S.G. being determined at 15^{\circ}-20^{\circ} and referred to water at 4^{\circ}. The same for line of fininite wave-length, index being determined by
Roo
               Cauchy's formula (Brühl's R<sub>A</sub>).
Specific rotation for sodium light.
(a)a
                  , , , neutral ting. [s] =\frac{100}{p} \times \frac{s}{d}, s=observed rotation for 100 mm. of liquid. d=S.G. of liquid. p=no. of grammes of active analysis of liquid.
[a]<sub>j</sub>
```

```
Molecular magnetic rotatory power = \frac{m \times n}{d \times d \times m}, where m = molecular
M. M.
              weight of the body of $3. = d, a = angle of rotation under magnetic influence, we angle of rotation of water under same influence, and memory and memory of the same influence, and Acet 1 G.H.O.

Bensoyl C.H.O.
ia
Bs
          •
Cy
Etc
He
Ph
                Cyanogen CN.
Ethyl C.H..
Methyl CH..
        ċ
                 Phenyl C.H.
                                                               in Grmule.
                 Normal Propyl CH4, CH4, CH4, Isopropyl CH(CH4),
Pr ،
R, R' do.
                 Alcohol radicles or alkyls. Opimary.
tori
n
                 tertiary.
 v., o, p
                 meta-ortho-para.
                 consecutive.
   .
                 irregular.
   .
                 symmetrical
                 unsymmetrical.
    .
    •
                 attached to nitrogen.
                 Employed to denote that the substituent is attached to a carbon atom
                        which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined
        40
8
    .
                        by the nature of the compounds. Thus CH2.CHBr.CO2H is a-bromo-
                        propionic acid.
                  denotes that the element or radicle which follows it is attached to a ter-
                        minal carbon atom.
 α,β,γ,&ο.
                  indicate position in an open chain, only. .
 1,2,8, &c.
                  indicate position in a ring only.
                  Used when a, $, &c. are employed in a sense different from the above,
 (α), (β),
&c.
                  e.g. (a)-di-bromo-camphor.
Baeyer's Nomenclature:
 (B.) . . (Py.) . .
                        benzene ring.
                        pyridine ring
                        pyridine ring.

Thus (B. 1:8) dichloroquinoline, means a meta-dichloroquinoline in which the chlorine atoms are both in the benzene ring.

While (Py. 1:8) dichloroquinoline, means a similar body, only the chlorine atoms are in the pyridine ring. The numbers are counted from two carbon atoms which are in different rings; but both united
                         to the same carbon atom.
                  denotes the central ring in the molecule of afithracene, acridines, and
 (4.) . .
                         azines.
                  means that the element or radicle it procedes is in a closed ring.
 480-
                                                                                       not in a benzene ring.
                   denotes isomerism that is not indicated by ordinary formulæ; thus maleïe
 allo- .
                  acid may be called allo-fumaric acid.
denotes displacement of oxygen by sulphur.
 thio. .
                             the group 80.H, except in the word sulphocyanide.
 sulpho-
 sulphydro-
                             the group SH.
                  Tribromonitrobenzene sulphonic acid [2:2:3:4:5] means that the three bromines occupy positions 1, 2, and 8; the nitro-group the position 4,
```

and the sulpho- group the position 5. " Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulæ without this mark are those

analysed compounds.

All temperatures are given in degrees Centigrade unless when specially stated

Wavy-lengths are given in 10-' mm.
Formulas, when used instead of names of substances, have a qualitative meaning only.

Thomsen's potetion is used in thermochemical data.

DICTIONARY OF CHEMISTRY

PHENYL - AZOXAZOLE CH: NO. [30°]. (OPh: NO. [30°]. (OPh:

PHENYL - BENZAMIDINE C₁₈H₁₈N₁ i.e. C.H₁C(NH).NHPh or C₁H₁C(NPh).NH, [112°]. Formed from benzonitrile and aniline hydrochloride at 230° (Bernthsen, A. 184, 848; 192, 83). Formed also from benzimido ether and aniline, and from CPhCl:NPh and NH, (Kobbert,

**Manufacture of the state of t 8. CS, at 100° forms thio-benzanilide and phenylbenzamidine sulphocyanide.-4. Reduced by sodium-amalgam to C.H., CH(NH₂). MHPh. — 5. Nitrous acid forms benzanilide (Mieran,

4. 265, 141). The derivatives The derivatives C.H.C(N.SO.Ph).NHPh [189°] and C.H.(SO.N.C(NHPh).C.H.), [196°] have been prepared (Wallach, A. 214, 214;

Jackson, Am. 9, 846).

s - Di - henyl - bensamidine • C₁₁H₁₄N₂ i.s.

C.H. C(NPh) NHPh. [144°].

Formation.—1. From benzamilide by treat-

Formation.—1. From benzanilide by treatment with PCl, and aniline (Gerhardt, A. 108, 219; Hofmann, 5-1866, 161; Wallach, A. 184, 88).—2. From Ph.CCl, and aniline with or without ZnCl, (Limpricht, A. 135, 82; Döbner, B. 15, 283).—3. A produce of the action of aniline hydrochloride at 250° on benzonitrile, thiobenzamide, or phenyl-benzamidine (Bernthsen, A. 184, 352).-4. By heating benzanilide with phenyl cyanate at 190° (Kühn, B. 18, 1476)...5. By heating the hydrochloride of benzimido-ether in alcohol with aniline for a long time (Kobbert, A. 265, 155).

Properties.—Needles (from alcohol), m. sol.

beasene. Its alcoholic solution is neutral to litmus. Not affected by nitrous acid. Split up into aniline and benzanilide when boiled for a

leng time with alcohol.

Rections.—1. Dry H.S at 160° forms thic-Realtions.—1. Dry H.S at 160° forms thickness and the second of the seco

Its alcoholic solution turns litmus blue. Conc. H₂SO₄ gives a violet blue colour on warming.

Reactions.—1. Dilute HClAq as 180 forms.

NPh.Bs.—2. The free base and its hydrochloride yield benzonitrile and diphenylamine on heating—3. Nitrons soid forms Ph_Bs (Klobbert, A. 265, 157).—4. H₂S at 130° forms Ph.CS.NH₂, dippenylamine, Ph.CS.NPh₃ and NH₄₅—5. CS, at 140° forms Ph.CS.NPh₃ and HNOS.—Salts.—B'HCl. [c. 228°]. Moncolinia

Saits.—B'HCl. [c. 225°]. Moncelinie crystals, a:b:c=529:1: 507; \$=85°52'. V. sol. water, sol. alcohol, insol. ether.—B-H-2PtCl.—B'HNOS. [208°]. Yellow prisms.
PHENYL-BENZAMIDOXIM

PHENYL-BENZABIDULIE

C.H.,C(NOH).NHPh. [188°]. Formed by boi
ing C.H.,CS.NHPh with an alcoholic solution a
hydroxylamine (Müller, B. 19, 1669). Needles
(from water). Yields BERGI. CICO.Et forms

CI.H.,N.O. [187°].

DI.PHENYL-BENZAZIDINE C.H.,N. d.c.

H. C. MEDEL NH NHPH. [170°]. Farmed by

C.H.C(N.MHPh).NH.NHPh. [179°]. Termed by the action of phenyl-hydrasine on PhCQl, or on the hydrochloride of benz-imide-ether dissolved in absolute alcohol-(Pinner, B. 17, 182; Marckwald, C. C. 1888, 1410). Dark-red needles. PHENYL-BENZENE v. DIPHENYL.

p.Di-phenyl-bensene C.H. i.e. C.H.Ph. Mol. w. 290. [207°]. (c. 405°). Formation.—1. A product of the action of sodium on an ethereal solution of p-di-bromobenzene, or, better, of a mixture of p-di-bromo-benzene with bromine (Riese, Z. [2] 6, 192, 785; A. 164, 168).—2. Tegether with its isomeride, and other products, by passing the vapour of benzene, or of a mixture of benzene. and toluene, through a red-hot tube (G. Schultz, B. 6, 415; A. 174, 280; 208, 118; Carnelley, C. J. 37, 712).—8. Together with the isomerida and other products, by the action of AlCl, on a mixture of MeCl and diphenyl (Adam, Bl. [2] 49, 97; A. Ch. [6] 15, 241).
Properties.—Needles (from bensene), or iri-

descent laminæ (by sublimation); insol. alcohol, v. al. sol. HOAc. Its solution in benzene shows blue fluorescence. Conc. H,SO; gives a dirty The fluorescence. Conc. H₂SU₂ gives a dirty green solution changing to purple. GrO, in HOAc oxidises it to diphenyl p-earboxylic [3167] and terephthalic scids. Does not form a compound with piorie acid. Not volatile with stearity lields C₁₆Cl₁₆ on exhaustive chilerination with SbCl₁ (Mern a. Weith, B. 16, 2884).

References. — Brown and Tax-critical. Dt.

PRENTL-BUNKENS Iso-di-phenyl-benzene C, H,, [85°]. (c. 870°). Formed as above. Slander prigns, v. sol. al. Rormed from benzamidine hydrochloride, phenyl cyanate, and NaOHAc (Dispute of the control of the Nacias, and NaOHAq (Pinner, B. 22, 1607).
Nacias, inc.). water, v. sl. sol. hot alcohol.
PHENYL-BENZIMIDO-ETHEE C, H, NO i.e. OPh(NPh).OEt. A product of the action of aniline on bensimido-ether (Lossen, A. 265, 138). Oil. Decomposed by conc. HClAq into EtCl and benzanilide. PHENTL BENZOATE v. Benzoul derivative of PHENOL PHENYL. RENZOIC ACID of DIPHENYL-CARR-OXYLIC ACID. ONTLICATION.

PHENYL-BERZOPHENOME C₁₂H₁₁O.i.e. [1:4]

C.H., C.H., C.H., ClO4*]. V.D. 9*0. Formed by oxidation of p-benzyl-diphenyl with chromic acid (Goldschmiedt, M. 2, 487; Köller, M. 12, 10).

ENTLY Parad also from diphenyl Bell, and 501). Formed also from diphenyl, BzCl, and AlCl. (Wolf, B. 14, 2032). Scales, sol. alcohol. Yields benzophenone-p-carboxylic scid on further oxidation by CrO.

Oxim. [1946]. Needles. When HCl is passed into its solution in HOAc containing and the mixture heated in sealed tubes Ad 0 and the mixture nearest in scales successions. 100°, it is converted into the isomeric O.H., C.H., CO.N.H.C.H., 1224°]. The oxim is reduced by sodium-amalgam to the corresponding amine C.H., C.H., C.H.(N.H.), C.H., [77°]. Bensoyl derivative of the Oxim [198°]. Needles (from alcohol). Phenyl-hydraside. [144°]. medies (from dilute alcohol).

10 - phanyl. benzophenone (C,H,C,H,),CO.

120 - Rormed by the action of COCl. on
diphenyl in presence of AlCl. (Adam, Bl. [2] 47,
638]; A. Gh. [6] 15, 259). Got also by oxidising
CH-(C,H,Ph), (Weiler, B. 7, 1188). White needles,
sol. acctone, v. sl. sol. alcohol. Not attacked by
toming HNO, or by H,SO, and HNO, at 100°.
By adding Na to its solution in alcohol-benzene
life reduced to (C,H,C,H,),CH,OH, [151°], S.
(chert) 5; S. (Scohol) 1:25 at 15°. Potash-fusion
mile, diphenyl.-p-carbof-pile acid [218°].

**CHERTL BENZOPHENONE CARBONYLIO

**ACCHILL BENZOPHENONE CARBONYLIO

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de blos allowed about the

Arti-phenyl-beasene C.H., i.e. C.H.M., Mol. v. 866. [13°]. (shows 860°). Formed from actiophanone by treatment with F.O., with alcoholie NH., or with dry HCl (Engley, B. 6, 688; 7, 1128). Formed also by heating O.H.(O.H., CO.H.), tith KOH (Gabriel a. Michael, B. 11, 1007). It is also a by-product in the action of actiophenone on dimethylaniline in presence of 2nCl? (Dopper a. Petachoff, A. 242, 389). Trimetricerystals; a: to = 566:1: 766, affsol. alcohol. Yields benzole acid on oxidation by Cro. in HOAc (Mellin, B. 28, 2583). By exhaustive chlorination with SbCl, it yields penchloro-triphenyl-benzene (Merz a. Waith, B. 18, 2883). On heating with I and red R at 27%; it yields the crystalline dodeca-hydride C.H., and finally oily C.H., (Mellin, B. 28, 2584). Fuming H.SO, at 100° forms a disulphonic acid, which yields the Bastl C.H.S.O.Ba crystallising immedles.

Ba salt C.H.S.O.Ba crystallising inmeedles. •.
PHENYL BENZENE SULPHAZIDE Phonyl-hydraside of Benzene aulphonic acid. DE-PHENYL-BENZENYL-DI-URBA

PHENYL-BERZOYL IS HERSOFFERD
PHENYL-BERZOYL AGENTO AGEN
CHBerh.CO.H. Wethyl sther MeA'. Form
from de-oxybensoin, McOEt, and CIOO,
(Rattner, B. 21, 1816). Oil, decamposed by d
tillation into C.H.Ph., CO., and HOBs.
PHENYL-BERZOYL-BUTYRIC ACID CHBzPh.OH., CH., CO.H. (B) Beyl-propion acide [186°]. Formed from deoxybenzoi NaOEt, and \$\text{Biodo-propionic ether (Knoevenag B. 21, 1344). Needles. Bields MeA' [64 and EtA' [84°].

PRENTL BENZOYL is BENZOPHENOMA.

The isomeric acid CHBzPh.CHMe.CO, [215°], formed from \$\theta\$-bromo-propionic acid, less sol, alcohol and ether.

PHENYS-BENZOYL-CARBINGL v. BENZOÏ

PHENYL-BENZOYL-PROPIONIC ACID CHBzPh.CH. CO.H. [186°]. Formed from d oxyberzoin, NaOEt, and chloro-acetic eth (Meyer a. Oelkers, B. 21, 1295; Knoevenage 21, 1344). Small tables (from alcohol). Di-phenyl-benzoyl-propionic acid CH,Bz.CPh,CO,H. [183°]. Got by the action (

alcoholic potash on the lactone of oxy-tri-pheay crotonic acid (Japp a. Klingemann, B. 22, 2882 Yields a phenyl-hydrazide C₂₂H₂₁N₂O [185° and an oxim C₂H₂₁N₂O, [152°].

**PHENYL-EENZYL ALCOHOL C₁₂H₁₂O i.

C₄H₂Ph.CH-OH. Got from C₄H₂Ph.CH, by trea

ment with Br and alcoholic potash; the resultin syrupy C.H.Ph.CH.OEt being treated with H (Adam, Bl. [2] 49, 97). Syrup. PHENYL-BENZYL-AMIDO-DI-PHENYI

METHANE C. H., N. i.e. CH., Ph.C., H., NPh.C., H. Formed by heating NPh,H (1 mol.) with bens; chloride (2 mols.) and ZnCl, at 210° (Meldols C. J. 41, 200). Solid; s. sol. ether, insol. alcoho and HOAc. PHENYL-BENZYL-AMINE v. BENZYL-ANIL

Nitrosamine C.H.NPh.NO. [58°]. Needle (Antrick, A. 227, 8860). Yields benzyl-anilinand benzyliden-aniline on treatment with alcoholic HCl (O. Fischer, A. 241, 378). Phenyl-di-bensyl-amine v. DI-BENZYL-ANL

Di-phenyl-benzyl-amine NPh, CH,Ph. [87°] Ot from C.H., CSNPh., zinc-dust, and HCla'd (Bernthsen a. Trompeter, B. 11, 1761; cf. Wilm a. Girard, B. 8, 1196). Needles, al. sol. cold alcohol. Yields a green dye on heating with HClAq and arsenic acid (Meldola, B. 14, 1885). DI-PHENYL-DI-BENZYL-TETRAZONE

NPh(CHPh).N:N.NPh(CH.Ph). [109]. Formed from (a)-phenyl-benzyl-hydrazine. CHCl., and HgO (Michaelis a. Philips, A. 252, 290). Needles. PHENYL-BENZYL-CABBINOL C. H.O. i.e. CH.Ph.(H(OH).C.H., Toluylene hydrate. [62°]. Formed by reducing deoxybenzoln, and by the action of alcoholic potath on the same body action of alcoholic potash on the same-body (Limpricht a. Schwanert, A. 185, 62; Golden-berg, A. 174, 882; Zagoumenny, A. 184, 185; Anschütz, A. 261, 298). Formed the (827) by the action of nitrous acid on CH.Ph.CHP.R.H., (Leuckart, B. 32, 1410). Long similar modelles (from alcohol), inkol. water. Reduced by Hida to dibensyl. Yields a liquid accept derivative. PHERYL RESINIL EXPER a Plengle of the of Bennyl. Access. of Brauer, Appelion. C. J. 1919. Formed from ethyl-thio-cartonide and bensyl-atiline in alcohol (Dixon, O. J. 50, 568). Rectangular frams, insol. cold vater, v. e. sol. boiling alcohol.

An isomeride [91] uncor.] formed from bensyl-thiocartonide and ethyl-aniline crystallises in oblique frisms grouped in rosettes.

PHENYL-MENYL-HYDRAZINE C.H.H.N. CH.Ph.NPh.NH. [269]. Formed from

i.s. CH_Ph.NPh.NH. [26°]. Formed sodium phenyl-hydrazine and benzyl chloride, and got also by reduction of phenyl-benzyl mitrosamine (Antrick, A. 227, 661; Michaelis a. mitrosamine (Antrick, A. 227, 501; Michaells a. Philips, A. 252, 286). Needles (containing aq), decomposed by heat. Benzoic aldehyde forms CH,Ph.NPh.N:CHPh. [111°]. In benzene solution it gives with SOCl, the thiony compound C,H,NPh.N:50Z[65°] (Michaelis a. Ruhl, A. 270, 122). C,HPCl, forms C,H,NPh.N:PC,H, [147], crystallising from ether in needles.—EHCl. [167]: colourless needles. Benzene phosphinate B'O.H.,PH₂O₂ [108°] (Michaelis, A. 270, 185).

Acetyl derivative. [121°]. Scales. Bensylo-chloride (C,H,),NPhClNH,

PHENYL-BENZYLIDENE-ALLYL-HYDRA-ZINE NPh(C,H₄).N:CHPh. [52°]. Formed from phenyl-allyl-hydrazine and benzoic ablehyde (Michaelis a. Claesson, B. 22, 2237). s, v. sol. ether and hot alcohol

PHENYL-BENZYLIDENE-AMINE v. BENZ-YLIDENE-ANILINE.

Phenyl-benzylidene-diamine C.H. CH(NH.)(NHPh). [115°]. Formed by reduction of phenyl-benzamidine with zinc and Hol (Bernthsen a. Szymanski, B. 13, 917).

Small crystals.—B'HCl. (224°). Thick prisms.

—B',H,PtG; : spikes or plates.

DI-PHENYL-BENEYLIDENE. ETHYLENE.

DIAMINE CHPh NPh C.H. [187°]. Formed from benzoid aldehyde and di-phenyl-ethylene-

from cenzous agenyae and up-puenya convented diamine (Moos, B. 20, 432). Needles, split up by the convented from the parent bodies.

PHENYL - BERZYLIDENE - ETHYL
RYDRAZINE PHNELN:CHPh [59°]. Formed the convented for the conven

from benzoio aldehyde and phenyl-shyl-hydrazine (Michaelis a. Philips, A. 252, 272). PHENYL-BENZYLIDENE-HYDRAZINE v.

Phenyl-hydraside of Benzhio Aldehyde.
DI-PHENYL-BENZYLIDENE-DI-INDOLE CHPh(C14H16N)2. [268° uncor.]. Formed from CHPh(C₁,H₁,N)₂. [200 uncor.]. Formed to bensoic aldehyde and C₂H, CH CPh (E.

Fischer a. Schmidt, B. 21, 1074). Slender leaflets, v. sl. sol. hot alcohol. PHENYL-BENZYL-INDOLE

AlCl, on a mixture of phenyl-acetyl chloride and benzepe (Graebe a. Bungener, B. 12, 1879). 6. From phenyl-acetic acid, benzene, and P.O. (Zincke, B. 0, 1771).—7. By the action of alcoholic ammonium sulphide (or KHS) on bensil (Zinin, J. pr. 38, 35; Jena, A. 155, 87).—8, By dissolving s-di-phenyl-acetylene in H. SO, and adding water (Béhal, Bl. [3] 49, 387).

Properties—White plates (from alcohol); al. sol. hot water, volatile with steam.

Reactions.—1. On heating with alcoholic potagh it yields phenyl-benzyl-carbinol and diethyl carbobenzonic acid C₁₈H₁₀(100°), which gives Eth' (309° at 11 mm). (Zagoumenny, A. 184, 163; Anschütz, A. 261, 298). The acid C₁₈H₁₀O₁ is converted by P and HI into an isomeric acid (184°), by HNO, (S.G. 1.18) into C₁₈H₁₀O₂ (196°), by conc. HNO, into C₁₈H₁₆(NO₂O₂ (156°), and by potashrusion into β-benzyl-isobutyric acid.—2. KOH in propyl. alcohol at 150° forms C₂₈H₂₆O₂ (90°) and also an isomeride (139°) which yields C₂₈H₂₆(NO₂)O₂ (176°).—3. KOH in isobutyl alcohol at 140° forms dissobutyl-carbobenzonic acid C₂₈H₂₆O₂ (148°), S. Reactions .- 1. On heating with alcoholic isobutyl-carbobenzonic 'acid C,H,O, [148°], S. (alcohol) 5. The homologous isoamyl compound S₂H₂O₂ [160] may be got in like manner.—4. Reduced by HI to di-phenyl-sthylene and di-phenyl-ethane.—5. Sodium-amalgam reduces it to O₂H₂O₂ and finally to phenyl-benzyl-agrinol.— On Ing. Og and many to pneny - pensy compounds yield oxims melting at 107° and 141° respectively. Fuming HNO₂ (S.G. 1-51) at 0° forms three isomeric di-nitro derivatives at 0° forms three isomeric ol-niero- univasaves [116°], [126°] and [155°] (Golubeff, B. 18, 2408; J. R. 18, 23).—7. Bromine forms C_{1,}H₁,BrO [55°] (Knoevenagel, B. 21, 1355) and C₁H₂,Co.OBr.C.H₁ [112°].—8. PCl. yields CHPh:CClPh.—9. Alcoholic potesh and bensoic aldehyde form benzamarone C, H, O, (215°] (Japp a. Klingemann, B. 21, 2984; cf. Zinin, Z. 1871, 127).-10. NaOEt and nitrous said yield the mono- oxim of benzil.—11. NaOEt and CSCl. yield golden (C.H.C(CS).CO.O.H.).
[2869] (Bergreen, B. 21, 850).—12. NaOEt and MeI yield phenyl phenyl ethyl ketone C.H. CO.OHMePh. Other alkyl fodides act in like manner (V. Meyer, B. 21, 1295).— PHENYL BENZYL INDOLE Unit of discounting the phenyl-hydraxide of d 13. Sodium acting on a bensens solution in absence of air forms C.H., CO.CHRa.C.H., a very hygroscopic yellow substance converted by CO.

anilha yisis ibanyi baniyi ketone, tri-phanyi-ganidine, and H.S.
Osim C.H.CR. C(NOH.C.H., [98°].

Phanyi-Nydraside
CH.Ph.C(N.HPh.Ph. * [108°]. Needles (from sleadhol) (May B. 21° 2447).

PHENYI BENZYI INTONE-c-CARBOXYLIC ACID C_{1.H.1}Co : s. C.H., CO.C.H., C.H., CO.H.
Decrybersolm-carboxpilic acid. [168]. Formed by heating isobenzylidene-phthalide with NaOH (Gabriel, B. 18, 2448). Needles, sol.
dlacohol. Reduced by sodium-amalgam to C.H., CH.(OH). CH., C.H. Ammonia forms isobenzylidene-phthalimidine. Hydroxylenine hydrochloride in Stocholic solution at 100°

ALTO OFFICE OFFICE AND A STATE OF Anhydride v. Isobenzylidene-phthalide.

Methylamide CH,Bz.C,H,CO.NHMe. od methylamine in alcohol at 100° (Gabriel, . 20, 2866). White needles.

Phenyl benzyl ketone o-carboxylic acid

Phenyl bensyl ketone o-componytic acia H. CH. CO.C. H. CO.H. Decaybenzoin-ecarb-iglio acid. [75]. Formed by boiling benz-idene-phthalide with KOHAq (Gabriel a. ichael, B. 11, 1018). Prisms (containing aq). AgA': Crystalline pp. Anhydride v. BENZYLIDENE-PHTHALDE.

Amide CH,Ph.CO.C,H,.CO.NH, [166°]. ormed from benzylidene-phthalide and alcoilio NH, at 100° (Gabriel, B. 18, 2434).

iedles, sol. hot water, converted into henzyl-iedles, sol. hot water, converted into henzyl-idene-phthalimidine by boiling with HOAc. Ethylamids OH_Ph.CO.C.H.,CO.NHEt. [140°]. Formed from benzylidene-phthalide and alcoholic NEtH, at 100° (Gabriel, B. 18, 1258, 2484). Converted by boiling HOAc into C.H. CO(CHPh) NEt. [77°]. Hydroxylamine

forms C,H, C(CH,Ph) N [177°], which is also formed by the action of hydroxylamine on

phenyl benzyl ketone carboxylic acid.

Phenyl benzyl ketone dicarboxylic acid.

C_tH₁(CO_tH).CO.CH₁.CJ.H..CO_tH. [239°]. Formed together with an isomeride [250°] by heating phenyl-acetic-o-carboxylic acid with phthalic anhydride and NaOAc at 190° (Ephraim, B. 24, 2621). Needles. Gaseous HCl acting on its alcoholic solution forms the anhydride O_*H_* COH, COO, $O_*O_*H_*$. [260°]. Hydroxyl-

C,H,<CO,H,.CO,H yields [280°] crystallising in needles. Alcoholic NH, forms crystalline C, H, NO. PHENYL-BENZYL-METHYL-AMINE

FHENYL-BENZIL-MEINIL-AMANA G.H.N i.e. NMePh.CH.Ph. [306°] (Nölting, M. S. [8] 18,88). Methylo-chloride B'MeClaq. [110°]. Formed from di-methyl-aniline and benzyl wormed from di-metayl-aniline and beinsyl abloride (Michler, B. 10, 2079). Tables, v. sol.
water and alcohol. Converted by successive freatment with Ag,80, and baryta into a syrupy bydroxide, which is split up on distillation into Sensyl alcohol and dismethyl-aniline.

FRENTL BENZYL-BENZYL-BENZYL-WETHYL-TRIO-URBA

O.H. N.S. i.a. NPhMc.CS.NHC.H.. [85] Formed from bensyl-thiocarbimide and methyl-sniline (Dizon, C. J. 59, 568). Prisms.

Inqueries NEME CENTRO H. (MI) Formed by boiling methyl-thiocarbimide with bensyl-aniline in alcoholic solution (D.). Talks of white prisms, L. sl. sol. hot water. PHENYL-BENEZYL-METHYL-UREA

CH.Ph.NH.CO.NPhMe. 847. Formed from CH.Ph.NH.COCI and methyl-miline (Kühn a. Riesenfeld, B. 24, 8817). V. sel. alcohol.

EENZYL-PHENYL-NITEOSAMINE
C.H.NPh(NO). Nitrosamine of bensyl-amiline. (10 g.).

[589]. Formed from bensyl-amiline (10 g.).

salobio (126 c.o.), H.SO. (6 c.o.), and NaNO, in the cold, the product being poured into water (500 c.o.) (Antrick, A. 227, 860). Pale-yellowish needles, v. sol. alcohol and ether.

PHENYL-BENZYL-OXIDE v. Phenul ether

of BENZYL LOCHOL.

PHENYL BENZYL-PHOSPHLER?

CH-Ph.PHPh or C. H., P. [171°]. Formed by heating C.H., PCl., with benzyl chloride and zinc (Michaelis a. Gleichmann, B. 15, 1961). Needles, believe the state of the shoring of the state of

converted by successive treatment with chlorine

conversed by successive treatment with chlorine and slikelis into C,H,PO or C,H,P,O, [156].

Di-phenyl-bensyl-phosphine dichloride C,H,PCL,(C,H,), [187°]. Formed from (C,H,PCl and benzyl chloride at 180° (Dörken, B 21, 1506; cf. Michaelis, B, 18, 2117). Priams.

Di-phenyl-bensyl-phosphine oxide
C.H.PO(C.H.). [198°]. Formed by decomposing the preceding body with water. Yields a

tri nitro- derivative [206°].
DI-PHENYL DI-BENZYL-SUCCINIC ACID. Nitrile. CN.CPh(CH,Ph).CPh(CH,Ph).CN. [235°]. Formed from CN.CNaPh(CH,Ph) and I

(235). Formed from UN.UNAFII(CH₂FI) and I (Chalanay a. Knoevenagel, B. 25, 290). White crystalline powder, sl. sol. alcohol.

PHENYL BENZYL SULPHONE C₁₂H₁₂SO₂₆

£. C₂H₂SO₂CH₂Ph. [148°]. Formed from C₂H₃SO₂O₃Na and benzyl chloride (Knoevenagel, B. 21, 1344). Sl. sol. ether₂m.*sol. alcohol.

DI.PHENYL-BENZYL-THIOSENIGAEBAZ-TENDEL (H. N.N. C. N. DE).

DI-PHENNI-BENZYI.-THIOSEMICARBAZ-IDE NPh(C,H.),NH.CS.NHPh. [1509]. Formed from phenyl-benzyl-hydrazine in alcohol and phenyl-liflocarbinide [Michaelis a. Philips, A. 252, 289). Crystals, v. sol. test alcohol. PHENYI.-BENZYI.-THIO-UREA C_{1.}H.,N.S. i.e. NHPh.CS.NHCH.Ph. [154°]. Formed by mixing alcoholic-solutions of benzylamine and phenyl-thiocarbimide (Dixon, C. J. 55, 300). Prisms (from alcohol), sl. sol. Cs. Phenyl-di-benzyl-thio-urea C_{1.}H.,N.S. i.e. NPh(C,H.),CS.NH.C,H., [103°]. Formed from phenyl-thiocarbimide and benzyl-aniline (D.). White prisms, v. sl. sol. hot water.

pnenyi-mocarounde and benzyi-aniline (D.). White prisms, v. sl. sol. hot water.

PHENYL-BENZYL-p-TOLYL-BIURET

C₃H₁₁N₄O₂. [95°-104°]. Needles (from dilute alcohol) (Kühn a. Henschel, B. 21, 504).

PHENYL-BENZYL-UREA C₁H₁N₄O i.e.
NHPh.CO.NHOH.Ph. [168°]. Formed by mixing benzyl cyanate with aniline (Letts, C. J. 25, 448). Needles, v. sol. alcohol.

Phanyl-di-henzyl-urea C. H. N.O. [1980]

A48). Needles, v. sol. alcohol.

Phenyl-di-bensyl-ures C₂₁H₂N₁O. [128°].

Got from (O,H₂), N.COCI and spiline (Hammerich, B. 25, 1819). Silky medies (from

alcohol).

PHENYL-BISMUTHINE v. vol. i. p. 517.

PHENYL-BIURET C.H.N.O. t.a. 2.

NHPh.CO.NH.CO.NH... Formed from phenylures and POL. (Weith, B. 10, 1744). Crystals.

s.Diplenyl-biuret NH(CO.NHPh). [310].

Formed by boiling alloghants asher, biums, or

Sales other, with aufline (Hofmann

And Scher, 188 aniline (Hofmann, R.S. 250; Lauchart, J. pr. [2] 21; 27). Formed also by the action of phenyl syanate on phenyl-ures (Rühn a. Henschei, B. 21, 504). Needles. 4-Di-phenyl-biaret NH, CO.NPh.CO.NHPh. [165°]. Got from di-phenyl disyanate and alcoholic NH, (Hotmann). Prisms, sol. alcohol. a-Tri-phenyl-biaret NPh(CO.NHPh), [148°]. Formed from di-phenyl disyanate and aniline (H.) and by heating phenyl syanate with di-phenyl-ures at 150°. Prisms (from alcehol). An isomeride [165°] was gog by Schiff (B. 3, 651) by distilling phenyl-carbamb ether. References.—Di-Bromo-Dr. and Oxy- PHENYL-

References .- DI-BROMO-DI- and OXY- PHENYL-

BIURET.

PHENTI-BORATE C.H.BO. Formed by heating phenol (3 pts.) with B.O. (2 pts.), or, better, by heating tri-phenyl borate with alcohol at 150° (Sahiff, A. Suppl. 5, 202). Sticky mass. Tri-phenyl borate (C.H.), B.O. Formed by boiling phenol with B.O. Glassy mass, decomposed by hot water.

posed by hot water.

Tetra-phenyl diborate (C.H.), B.O. S.G. 1124. Formed, with the preceding body, by heating C.H.BO, at 350°. Thick oil, quickly de-

composed by water.

Phanyl-boric acid C.H.,B(OH), [204°].

Formed from C.H.BCl, and water (Michaelis a. Becker, B. 15, 181). Needles, sol. alcohol, ether, and hot water. Powerful antiseptic, with ether, and hot water. Powerful antiseptic, with but slight physiological action. With HgCl, it gives a pp. of PhHgCl. Reduces ammoniacal AgNO₃, forming a mirror. On heating, it yields the oxide C₄,BO [190°] (above 860°), which forms crystals, sol. alcohol.

Salts.—NaA": dimetric tables.—CaH₂A"₃: crystals.—AgHA": yellow pp.

Ethyl ether Et,A". (176°). Oil.

Chlorida v. volai. p. 581.

Chloride v. vol. i. p. 531. PMENYL BROMIDE v. BROMO-BENZENE. PHENYL BROMO-ALLYL OKIDE v. Bromoallyl derivative of Phenol.
PHENYL BROMO-BENZYL KETONE

C.H., CO.CHBrPh. [55°]. Set by brominating phenyl benyl lessone (Knoevenagel, B. 21, 1856).

PHENYL BROWO BUTYL KETONE
C.H., CO.CH., CH., CH., CH., E. [61°]. Formed

from phenyl oxy-butyl ketone anhydride or its carboxylic acid and cone. HBrAq (W. H. Perkin, jun., C. J. 51, 732; B. 19, 2559). Six-sided plates, v. sol. alcohol. Converted by warm alcoholic potash into the parent

CH, CH, CH, O.

Phonyl di-bromo-butyl ketone C.H. CO.CH. CH. CHBr. CH.Br. Formed from

allyl-acetophenone and Br (Perkin, C. J. 45, 188). Oil. Bromine yields C, H, Br. 0 [122°] esystallising from dilute alcohol in prisms.

PHENYL BROMO-ETHYL KETONE C.H., CO.C.H.Br. Formed from phenyl ethyl strone and Br in CS, (Pampel a. Schmidt, B. 19, 2897). Oil with pungent odour.

PHENEL ROBO-ETHYL OXIDE v. Bromo-

ethyl derivative of PHENOL.
PHENYL BROMG-ETHYL SULPHONE C.H.SO.CHMEBr. [50°]. Formed by boiling an aqueous solution of the Na salt of the acid C.H.SO.CMEBr.CO.H [184°], which is got by bromination of C.H.SO.CMEH.CO.H (Otto, 27 [2] 49, 550). Rectangular takes. PHENYL BROMO-IMESATIN O. ISATIN.

PHENYL - BROMO-MATHEMYL-DI-ETHYL. FHENTL-SEWEU-BERTHEN IN-DI-BUNG.
TRI-SULPHONE C.H. SO. CORTSO, CARL.
[1357]. Formed by bromination of the sulphone
CH(SO,Ph)(SO,Et), (Leves, B. 25, 884). Plates
(from alcohol) or needles (from Aq).
TRI-PHENTL-BROWG METHERYL

SULPHONE OBr(SO,Ph), (255°). Got by brominating CH(SO,Ph), (Laves, B. 25, 851). Amorphous insoluble pp.

PHENYL BROMO-METRYL KETONE v. w-Bromo-acetorhienone.

PHENYL BROMO-METHYL SULPHONE

PHENYL BROMO-METHYL SULPHONE
C.H., SO., CH.Br. [48°]. Formed, together with
C.H., SO., CH.Br. [78°]. From C.H., SO., CH.C.O.H
and Br (Otto. J. pr. [2] 40, 542). Both compounds
form monoclinic tables, v. sol. hot alcohol.

PHENYL BROMO-(a)-NAPHTHYL RETONE
C.B., CO.C., C.H.Br. [98°]. Formed by brominatien of paenyl (a)-naphthyl ketone (Eibs a.
Steinike, B. 19, 1966). Yields a crystalline dinitro. derivativa decomposing at about 90°. nitro derivative decomposing at about 90°.
Yields C, H, Br(SO, H) [116°] on sulphonation.
PHENYL - BROMO - NITRO - METHANE v.

BROMO-NITRO-TOLUENE

PHENYL-BROMO - DI - NITRO - PHENYL -AMINE v. Bromo-di-nitro-di-phenya-amine.

AMINE v. BROMO-DI-NITRO-DI-PHENWI-AMINE.
PHENYL - BROMO - NITRO - PHENYLHYDRAZINE C₄H₂, N₂H₂C₄H₂Br(NO₂), [3:14],
[165°]. Formed from phenyl-hydrazine and
C₄H₂Br(NO₂), (Willgerodt, J. pr. [2] 87, 458).
PHENYL-p-BROMO-PHENYL-HYDRAZINE
C₄H₂N,H₂C₄H₂Br. [115°]. Formed by reduction of C₄H₂N,C₄H₃Br. [115°]. Formed by reduction of C₄H₂N,C₄H₃Br. [115°]. Tables.
PHENYL BROMO-PHENYL FETONE **

PHENYL BROMO-PHENYL KETONE .

Bromo-benzophenone.

DI-PHENYL BROMO-PROPYLENE DISUL. PHONE C.H.Br(SO.Ph). [160°]. Got from CH.Br.CH.Br and NaSPh in alcohol (Stuffer, B. 28, 1411). Needles.

PHENYL BROMO-PROPYL KETONE

C.H. CO.CH. OH. CH.Br. [89°]. Formed from benzoyl-trimethylene carboxylic acid and fuming HBr (W. H. Perkin, jun., C. J. 47, 844). Crystalline mass, v. sol. alcohol.

PHENYL-BUTANE v. But A. Benzene Di-phenyl-butane CH,Ph.CH,.CH,Ph. [52°]. Formed by heating di-phenyl-butylene with HI and P at 250° (Freund a. Immerwahr, B. 25, 2858). Crystals, v. sol. alcohol. Di-phenyl-butane CHMePh.CHMePh.

[128.5°]. Formed by the action of sinc-dust or [123°5]. Formed by the action to annual state of the American Ma on CHMePhBr (Radziszewski, B. 7, 142; Engler, B. 7, 1127). Needles (from ether). Di-phenyl-butane CPh.MeEt. [128°].

Formed from CPh, Me.CO.OH., phosphorus, and HI (Zincke a. Thorner, B. 11, 1990). Tables or prisms, m. sol. alcohol.

prisms, m. sol. alcohol.

De pheryl-butane CH, CH(CH,Ph), (800°).

Formed by heating acetophenone with HIAq and P at 180° (Graebe, B. 7, 1037). Oil.

References.—Amido-, Tel-chilono-, and The CHLORO-DI-MITRO- and OIL-PREMIS-BUTAMES.

PHENYL-BUTAME FRICAR BOXYLIG ACTD.

Ethyl sther C.H.,CH.,C(CO,Rt), CHMs.CO,Rt. (388° cor.). S.G. \$9 1.1008. \(\mu_2\) 1.4850 at 20°.

Four 2 from sodium-propens tri-carboxylie ether and benzyl chloride (Bischoff a. Minty.)

Insol. water. Combines with Br. Excess of Br added to a glacial acetic acid solution forms

promo-phenyl-butenyl ketone dibromide, [120°].
PHENYL-BUTINENE C, L., i.e. OPh:CRt.
Phenyl-sthyl-acetylene. (202°). S.G. 21 923. Premyl-stray-acetylene. (202"). 5.9. 2020. Formed from sodium phenyl-acetylene and EtI (Morgan, O. 7. 29, 162). Liquid. Phenyl-butinene CieHip. (185°—190°). Got from CH.Ph.CH.CH.Br.CH.Br and alcoholic potash at 180° (Aronheim, A. 171, 231). Liquid.

Di-phengl-butines CHPh:CH.CH:CHPh. [148°]. (820°-840°). Obtained by heating CHPh:CH.CH:CPh.CO.H (Rebuffat, G. 15, 107; 20, 154). Micaceous plates.

References .- AMIDO - and OXY - PHENYL -

PHENYL - BUTINENE DICARBOXYLIC ACID CHPh:CH.CH:C(CO.H), [208°]. Formed by heating cinnamic aldehyde with malonic acid and HOAc at 100° (Stuart, C. J. 49, 366).
Needles; gives off CO, when melted.
DI-PHENYL-DI-BUTINYL KETONE

CO(OH:CH:CHPh), [142°]. Formed from colonionioning, laws, rothed from einnamic aldehyde, acctone, and NaOHAq (Diehl a. Einhorn, B. 18, 2825). Needles.

PHENYLBUTINYL METHYL KETONE
CH., CO.CH.CH.CH:CHPh. [68°]. Formed from

sinnamic aldehyde, acetone, and NaOHAq (Diehl a. Einhorn, B. 18, 2821). Plates (from ather). Yields a dibromide [174"] and a phenyl-

sther). Yields a dibromide [174°] and a phenyl-bydrazide [180°] crystallising in plates. DLPHENYBBUTONENE C₁₈H₁₈. Phenyl-naphthalene? [101°]. (846°). Formed from di-oxy-sthyl-benzene (styrolene alcohol) by treatment with H₂SO₂ (16 pts.) and water (9 pts.) Zincke a. Breuer, A. 226, 23). Plates, v. sol. alcohol. Oxidised by K₂Cr₂O₂, and HOAc to C₁₈H₁₈O₂ [110°], which crystallises in golden needles, m. sol. alcohol, and is readily poly-merised by exposure of its solution to light, yielding two polymerides [207°] and [225°-229°]. merised by exposure of its solution to light, yielding two polymerides [2077] and [2265-2229]. The quinone C₁₄H₁₆O₄ is reduced by SnCl₄ to the hydroquinone C₁₄H₁₆O₄D₃ [93°] which gives C₁₄H₁₆OAO₂ [152°]. The quinone C₁₄H₁₆O₄ is reduced by squeous SO₄ at 120° to the quinohydrone C₁₄H₁₆O₄ [138°]. On heating the animone with NaOHAQ it is converted into the cry quinone C₁₄H₁₆O(H)O, [144°], which gives D₁₄H₁₆OAO₂ [111°], and may be reduced to the cry quinhydrone [188°], and the cry quinhydrone [18°]. The oxydininene is suitaised by alkaline KMnO₄ to an acid A₁₄H₁O₄ [177°-197°] whence BaA"2aq, R₂A", OxyGH₁A"6sq, and Ag₄A". Alcoholic NH₂

by water (Popoff, B. 8, 768). Needles.

Tri-pheng-tert-butyl-alcohol CPh, CMe, OH, (above 260°). Formed from CCl. CMe, OH, (benzene, and AlCl. (Willgerode a., Genieser, J. pr. [2] 87, 868). DI-PHENYL-DI-ISOBUTYL-TETRAZONE

C.H.,NPh.N:N.NPh.C.H. [107°]. Got from phenyl-isobutyl-hydrazine in ether by treatment with HgO (Michaelis a. Philips, A. 252, 284).

1062; A. 171, 219). The same hydrocarbon 106§; A. 171, 219). The same hydrocarbon appears to be formed by distilling the lactonic acid of γ-oxy-γ-phenyl-s-di-methyl-succinic acid (Penfield, A. 216, 125). Oil, yielding a liquid dibromide. KNO₂ and HOAc form C₁₀H₁₂N₂O₃, which gives on reduction a base O₁₀H₁₃NO, whence B'HCl and B'₂H₂PtCl₄ (Tōnnies, B. 11, 1211). 1511).

(a) Phenyl-butylene C₄H₁CH:CH.CH.CH.(CH₂CH) (186°). Formed by distilling C₁₆H₁₁Br obtained by bromination of n-butyl-benzene (Radziszawski, B. 9, 260). Forms a dibromide C₁₆H₁₂Br₂ [71°] crystallising in white needles. Probably identical orystallaing in white needles. Frobably identical with the phenyl-butylene (187°) obtained by Perkin (C. J. 33, 567; 35, 140 from phenylangelic acid by successive treatment with Histand Na CO.Aq or with HI and ROLE Perkin's phenyl-butylene corms a crystalline dibromide

phenyl-duylene during a cypesanine during (68°) converted by alcoholic potash into oily C_{1,6}H_{1,1}Br, which forms oily C_{1,6}H_{1,6}Br, (185°). Formed by heating benzoic aldehyde with sodium isobutyrate and isobutyric anhydride for 8 hours with inverted condenser (Perkin, C. J. 35, 138), and by distilling 8-cxy-phenyl-valeric acid (Fittig and by distilling B-CKy-Pnenyi-valence and (Fitting a. Jayne, A. 216, 11d). Oil. Forms an oily dibromide converted by alcoholic potash into C₁₈H₁₁Br, which forms crystalline C₁₈H₁₁Br, (53-5). Yields benzoic and scetic acids en oxidation. Nitrous acid forms C₁₈H₁₈N₂O₈[1127] (Angeli, B. 25, 1962).

DI-PHENYL-BUTYLEHE C. H., 4.6.
C.H., CH.CH.CH.CH.C.H. [39°]. Formed by reduction of the nitrile of e-phenyl-f-styryl-acrylic acid (Freund a. Immerwahr, #. 22, 2858).
Crystals, v. sol' alcohol. Yields a dibsomide [88°].

DI-PHENYL-BUTYLENE-DIAMINE O.H. (NHPh). • Formed from isobutyline dibromide and aniline (Colson, C. R. 105, 1014; Bl. [2] 48, 900). Oil. Yields a nitrosamine [90°].

—B'H.Oi. [98°]. S. 10 at 15°. B'H.Bs. [122°]. S. 10 at 15°; 30 at 100°.

TOPEN IL-DONE CANADADA CPh.NH >C.CH.Pr. [2230]. Formed from benzil, isovaleric aldehyde, and NHAQ (Japp a. Wynne, C. J. 49, 468).—
B"H.PtOl.: orystalline
FHENYL-120BUTYL-HYDRAZINE
C.H.NPh.NH, (240°-245°). Formed from iso-

butyl bromide and sodium phenyl-hydrazine (Michaelis a. Philips, B. 20, 2485; 2. 252, 282; 270, 122). Liquid, which reduces hot Fehling's

solution. Converted by thionyl-aniline into oily C.H.NPh.N:SO.—B.H.SO.: Blates. Acetyl derivative C.H.NPh.NHAc. [114°

PHENYL BUTYL KETONE C.H. CO.CH.Pr. Mol. w. 162. (237°) at 720 mm. Got by boiling propyl-bargoyl-acetic ether with alcoholic potash (Pegkin a. Calman, C. J. 49, 162). Gil. Phenyl isobutyl ketone C.H., CO, CH, Fr.

(228°) at 720 mm. S.G. 175 993. Formed from isopropyl-benzoyl-acetic ether (P. a. C.) and also by distilling a mixture of calcium benzoate and calcium isovalerate (Popoff, A. 162, 153). Liquid. Does not combine with NaHSO. Yields benzoic,

isobutyric, and acetic acids on oxidation.

PHENYL BUTYL RETONE CARBOXYLIC
ACID C.H., CO.CH., CHEL. Co.H. Ethyl-benzoylpropionic acid. [83°]. Formed by heating the
dicarboxylic acid. Small needles.—CaA', aq.

Ethyl ether EtA'. Oil.
Phenyl butyl ketone carboxylic ether C.H. CO.CHPr.CO.Et. Propyl - bensoyl - acetic acid (251° at 300 mm.). Formed from benzovlacetic ether, NaOEt, and PrI at 100° (Perkin a. Calman, C. J. 49, 160). Liquid.

Phenyl isobutyl ketone carboxylic ether C.H. CO.CHPr.CO.Et. (237° at 225 mm.). Formed

in like manner, using isopropyl iodide.

Prenyl butyl ketone dicarboxylic acid

C.H., CO.CH., CEt(CO.H). Benkoyl-ethyl-isosuccinic ether. Got by saponifying its ether, which is formed from sodium-malonic ether and w-brome-scetophenone (Dittrich a. Paal, B. 21, 3463). Organilla mass.—(NH_d)A": amorphous. -KrA": pearly plates, v. sol. water.—CaA" aq.—
Ag.A": plates. Hydrasine salt. [1037].
Phenyl hydraside C.H., N.O., [1227].
PHENYL BUTYL METHYLENE DIRECTORE

C.H. CO.CH. CO.CH. Pr. Valeryl-acetophenone. (184° at 30 mm.). Oil. Got from acetophenone,

isovaleric ether, and NaOEt (Stylos, B. 20, 2181).
PHENYL - BUTYL METHYL KETONE CARBOXYLIC ETHER

CH. CO.CEt(CH.Ph).CO.Et. (c. 297°). Formed from sodium benzyl-acetoacetate and EtI (Conrad, B. 11, 1057).

PHENYL BUTYL OXIDE p. Butyl derivative of PHENOL

PHENYL-ISOBUTYLPHENYL-THIO-UREA C.H.NH.CS.C.H., CH.Pr. [152°]. Formed from C.H., (NH.). CH.Pr. and phenyl-thiocarbimide (Mainzer, B. 18, 2023). Plates, sol. alcohol. DL-PHEFIL-ISORUTYL-QUIFOXALIER

* O.H.(OH.Fr) N:CPh. [144°]. Formed from N:OPh

Bensil and issuitylphenylene-diamine (Gelzer,
B. 20, 8267). Needles, v. sol. alcohol.—B'HCl.
PHENEL-BUTYL-FHIQ-ALLOPHANIC ACID

MIPLOS.N(C,H.).ON. [189°]. Formed from
section systemide, whenyl thiotaxis mide, and isobutyt iedide (Hecht, B. 45, 822). Siender needles, v. al. sol. hot water.

DI-PHENYL-180BUTYL-TRIO-SEMI-CARB-IDE NHPh.CS.NH.NPh(CH.Pr). [140°]. AZIDE NHPh.OS.NH.NPh(Ch. vr). [120].
Formed from phenyl-igobutyl-hydragine and AZIDE phenyl-thiocarbimide (Michaelis a Philips, A. 252, 284). White crystals.

PHENYL-ISOBUTYL-THIO-UREA NHPh.CS.NHC,H, [82°]. Formed from phenylthicoarbimide and isobutylamine (Healt, B. 25, 815). Needles, m. sol. hot water.

PHENYL-BUTYL-THIOHYDANTOIN

CSC NPh.CO (179° uncor.]. Formed by fusing phenyl, thiocarbimide with leucine (Aschan, B. 17, 426). Minute colourless prisms. PHENYL-BUTYRIC ACID C. H. C. i.e. CH.CH.CH.PhCO.H. [42°]. (27°2°). Formed by acconting the nitrile which is made by

by caponifying the nitrile which is made by the action of EtI and solid NaOH on benzyl cyanide (Neure, A. 250, 153). Crystalline Methylether Med. (228°).

Nitrile PhOHEt.ON. (245°).

Phenyl-n-butyric acid

7-range-reserved to the control of t acid by protracted treatment with sodium-amalgam (Jayne, A. 216, 107). Long flat plates

(from water).—CaA',: amorphous mass.

Phenyl-isobutyric acid CH,Ph.CHMe,CO.H. Bensyl-methyl-acetic acid. [87°]. (272°). S. ·81 at 15°.

Formation .- 1. By heating benzyl-methylmalonic acid (Conrad, B. 13, 598).—2. By heating benzyl-methyl-acetoacetic ether with cone. KOHAq.—3. By reduction of the phenylcrotonic acid obtained from benzoic aldehyde. sodium propionate, and propionic anhydride .-4. By reducing phenyl-angelic (methyl-cin-namic) acid with sodium-amalgam (von Miller, B. 23, 1888).

Properties .- Plates. Converted by H.SO, at 150° into oxy-methyl-indonaphthene.

Salt .- AgA'. S. 248 at 20°.

Ethyl ether Eth'. (287°). S.G. 11 Oil (Conrad a. Bischoff, A. 204, 177). Bensyl ether C.H.A'. (820°-528°). S.G. # 1.05.

18 1 046. A product of the action of sodium on benzyl propionate (Conrad a. Hodgkinson, A. 193, 312).

Amide CH.Ph.CHMe.CONH. [100°]. Formed by heating the NH, salt (Edeleano, B. 20, 618). Needles, v. sol. alcohol and ether.

Di-phonyl-butyric acid CH.Ph.OMePh.CO.H. [128°]. Got from its nitrile, which is obtained from a-phenyl-pro-pionitrile and benzyl chloride (Janssen, 4. 250, pionitrie and benzyl chiorine (sanseen, A. 200, 187). Needles, v. sol. ether and alcohol. NaA'7aq: long thin needles,—CaA',—BaA',—CuA'. [78°].—AgA': white insoluble powder. Nitrile O₁H₁₈ON. (887°). Oil.

Isomeride v. Di-Beneyi-Acetic Acid.

References. - Brome, Nitro. Nitro-Amino, and Oxy. Menyi-Butter Acid.

PHENTI-ISORUTTER ACID.

OH, OH(OH,Ph).OHO. (227°). Formed by distilling the corresponding lime salt with calcium formate (Miller a. Rohde, B. 23; 1080). Oil.

PHENYL-BUTYRIC-CARBOXYLIC ACID.

γ-PHENYL-BUTYRIC-o-CARBOXYLIC ACID THE TILE UTTRICE-CARBOXILIO ACID

C1H19O, i.e. C.H4(CO.H).CH.CH.CH.CH.CO.H.

[189]. Formed by heating at 180°-190° the

double-lactone of benzoyl-propionic-o-carboxylic

acid C.H4(CO.O) CCCH2 CH4 with HI

and P (Roser, B. 18, 8118). Small plates.

V. sol. alsohol, sl. sol. cold water.—A"Ba: very

subblem water. soluble in water.

PHENYL-BUTYRO-LACTONE v. Lactone of OXYPHENYL BUTYBIC ACID.

PHENYL-CACODYL v. vol. i. p. 320. PHENYL-CAMPHORAMIC ACID v. CAM-

PHORIC ACID.

PHENYL-CAMPRYL-THIO-URBA *v. CAM-PHYL-THIO-URBA.

PHENYL CARBAMATE NH2. CO.Ph. [148°]. FRIENTL UARBANATFNH, CO, Ph. [148°]. Formed by the action, in ethereal solution, of NH, on ClCO, Ph or of NH, COCl on phenol (Kempt, B. 2, 740; Gattermann, A. 244, 43). Formed also, together with Et, CO,, by heating phenyl ethyl carbonate at 300° (Bender, B. 19, 2268). Needles (from water), sol alcohol and ether. Decomposed by NaOHAq into NH₃, phenol; and Na₂OO, NH₂Aq at 150° forms phenol and uses.

PHENYL-CARBAMIC ACID NHPh.CO₂H.

Carbanilic acid. The ethers of this acid are got by the action of aniline on the chloroformic ethers Cl.CO.OR, and also by the action of phenyl cyanate on alcohols. They are decomposed by potash into CO₂, aniline, and alcohols.

Acetyl derivative NPhAc.CO.H. The Na salt is formed by passing CO₂ over sodium acetanilide in the cold (Seifert, B. 18, 1358). It is decomposed by water into acetanilide and NaHCOs. By heating at 140° under pressure it is converted

into NPhH.CO.CH, CO.Na.

Methyl ether NHPh.CO.OMe. [47°] (Hentschel, B. 18, 978). Prisms. Converted by HNO, (S.G. 1-48) into C,H,(NO₂),NH.CO₂Me [127²] and [6;42:1]C,H,(NO₂),NH.CO₂Me [127²] (Van Romburgh, R. T. C. 10, 185). H₂SO, torms SO₂H,C₂H₂NH.CO₂Me which is converted by horse size of the No. 1985. by bromine into c.H.Br.NH.Co.Me [96:5°] (Hentschel, J. pr. [2] 34, 423). Distillation with lime at 260° gives aniline, methyl-aniline, di-methyl-aniline, and di-phenyl-urea (Nölting, B. 21, 8154).

Ethyl ether NHPh.Co.et. [52°]. (238°) (Wilm a. Wischin, C. J. 21, 192). Formed as above and also by boiling the product of the action of phenyl-urea on aceto-acetic ether with conc. HCl (Behrend, A. 233, 6) and by the action of sodium acetanilide on chloro-formic action of sodium acetanilide on chloro-formic ether (Paal a. Otten, B. 23, 2590). Needles (from water). Not affected by boiling conc. HClAq, but decomposed by HClAq at 150° into CO, aniline, and EtCl. Boiling alcoholic KOH gives aniline and K_cCO_s. Yields a bromoderivative [81°], a di-nitro-derivative [110°], and, a tri-nitro-derivative [144°]. When distilled with NaOPh at 220° it gives phenol and diphenyl-ures [235°] (Hentschel, J. pr. [2] 27, 438). — NKPh-CO_Et. Formed by dissolving phenyl-carbancie ether in alcoholic potash. phenyl-carbagic ether in alcoholic potash. Hygroscopic needles, decomposed by water.

wards with conc. KOH it yields NPh CH CH [124°], which is converted by HClAq at 170° into chloro-ethyl-aniline.

chioro-etnyi-anima.

Ethylene ether C.H.A". [158°]. Formed from ethylene glycol and phenyl cyanate (Snape, B. 18, 2430; C. J. 47, 73). Prisms.

Propyl ether PrA'. [59°]. Slender needles, v. sol. sloopol (Rômer, B. 6, 1101).

v. sol. alcohol (Römer, B. č. 1101).

Isopropyl ether PrA'. [90°] (Gumpert,
J. Jr. [2] 81, 119; 32, 278); [48°] (Spica,
G. 17, 165). Needles (trom dilute alcohol).

Di-chloro-propyl ether (Otto, J. pr. [2]
44, 22) CH.Cl.CH.Cl.CH.A'. [74°]. Prisms.

Isobutyl ether C.H.A'. [80°]. (216°).

Needles, v. sol. alcohol (Mylius, B. 5, 972).

Hepterbyl ether C.H., A'. [85°]. Formed
by the action of phanyl ayanate and he heptenyl
alcohol got by reducing suberone (Markownikoff,
C.R. 110, 466). Prisms (from alcohol).

Giyceryl ether & GIYCERYL-TRI-PHENYL-

Glyceryl ether & GLYCERYL-TRI-PHENYL-

TRI-CARBAMATE.

Phenyl ether NHPh.CO.Ph. [126°]. Formed from phenyl cyanate and phenol (Gumpert; cf. Hofmann, B. 4, 249). Needles (from benzene). With NH Aq it forms phenyl-urea.

Phenylene ethers. Theo [165°], m[164°], and p [207°] compounds are got by heating pyrocatechin, resorcin, and hydroquinone respectively

with phenyl cyanate (Snape, B. 18, 2428).

Phenylphenyl ether C.H., C.H., A'.

[110°]. Formed from p-amido-diphenyl and ClOo_Et_(Zimmermann, B. 18, 1965).

(a)-Naphthyl ether C, H,A'. [178:5°]. Slender needles (Leuchart a. Schmidt, B. 18, 2340; Snape, C. J. 47, 776). Decomposed by [178.50].

 (β) - Naphthyl ether C₁₀H₁A'. [230°].
 (L. a. S.); [155°] (S.). Thick prisms. The tetrahydride C₁₀H₁O.CONPhH [98°5] is formed from (B) naphthol ac-tetrahydride and phenyl cyanatè.

phenyl cyanate.

Di-phenyl-carbamic acid.

Chloride NPh. CGCl. [85]. Formed from COCl. and diphenylamine in CHCl. (Michler, B. 9, 396). White scales (from alcohol).

Ethyl ether NPh. CO.Et. [72]. (above 360°). Formed by heating diphenylamine with ClCO. Et (Merz a. Werth, B. 6, 1511; Hager, B. 18, 2573). Leave prime (from beneze).

Phenyl ether* PhA'. [104*]. Formed from the chloride and KOPh (Lellmann a. Bonhöffer, B. 20, 2122). The compound C,H,(NO2)A [1147], made in like manner from o-nitrophenol, may be reduced to C,H,(NH-)A' [1912]. The mand p-nitrophenyl ethers [90°] and [116°] yield m- and p-amido-phenyl ethers [133°] and [146°] (Lellmann a. Benz, B. 24, 2111).

**PoTolyl-ether C,H,A'. [81°]. (L. B. B.). References.—Amido., Bromo., Dr. Bromo. Nitro., Nitro., Nitro. Mitro., Nitro. Oxy., Oxy., OXY-AMIDO-, and NITRO- PHENYL-CARBANIC ACID

and ETHER.

PHENYL CARBAMINE C.H.NO. Mol. w. 103. (167°). S.V. 121.6 (Lossen, A. 254, 78). Formed by distilling aniline with chloroform and alcoholic potash (Hofmans, A. 144, 117). Stinking liquid, quickly decomposed by acids Chloro-ethyl ether

Chloro-ethyl ether

and alcoholic potash (Hofmans, A. 144, 117).

NHPh.CO.CH.CH.Cl. [51°]. Formed from

aniline and Cl.CO.CO.H.Cl (Nemirowsky, J. pr.

[3] 31, 174; Otto, J. pr. [3] 44, 15). Needles,

sl. sol. hot water. When boiled alone and after
(Weith, B.8, 210). Yieldsphenyl-thiocarbindide

en heating with sulphur. Mixed with propionitude and ether, it yields, by successive treatment with sodium and water, the compound CPh(NH).CHMe.CN [97°] (Von Meyer, J. pr. [2] 89, 189).

Chloride NPh.CCl. (212°). Formed from phenyl-thiocarbimide and Cl (Sell a. Zierold, B. 7, 1228). Pangent liquid, with nasty smell, yielding s-di-phenyl-urea when heated with

water at 100°

PHENYL-CARBAZIC ACID. The or stal-a calt N.H.Ph.CO.ON.H.Rh is formed by the line salt N.H.Ph.CO.ON.H.Rh is formed by the action of CO. on phenyl-hydrazine and water. It is deliquescent, and sl. sol, water and ether (Fischer, A. 190, 124).

Methyl ether NHPh.NH.CO, Me. [117°].

Methyl ether NHPh.NH.CO₂Me. [117°].
Short prisms (Heller, A. 263, 281).

Ethyl other NHPh.NH.CO₂Et. [87°] (F.) ?

[82°] (N.) Formed from phenyl-bydrasine and ClCO₂Et (E. Fischer, B. 22, 1936), or AcC(CO₂Et)₂ (Nef, A. 266, 107). Needles. Ac₂O forms C₄H.N.HAc.CO₂Et [108°] (H.).

PHENYL-semi-CARBAZIDE C.H.N.O i.s.
NHPh.NH.CO.NH. [172°]. Formed from potessium cyanate and phenyl-hydrazine hydrochloride (E. Fischer, A. 190, 113; Freund, B. 21, 2463). Formed also by heating phenyl-hydrazine hydrochloride (1 mol.) with urea (2 mols.) at 160° for 4 hours (Pinner, B. 20, 2358; mols.) at 160° for 4 hours (Pinner, B. 20, 2358; 21, 2329) and by heating di-phenyl-carbazide with urea (Skinner a. Ruhemann, C. J. 53, 550; B. 20, 3378). Prisms, v. sol. hot water. Yields di-oxy-phenyl-triazole [263°] on heating with urea. By heating at 160° it is converted into displenyl-urazine C_{1,}H_{1,}N₁O₂ [264°] and other products. COCl₂ forms C₄H₁N₁O₂ [167°].

Bensoyl derivative NPhBz.NH.CO.NH₄.

[203°]. Formed from benzoyl-phenyl-hydrazine cyanate (Michaelis as Schmidt, A. 252, 317).

Dr-phenyl-semi-carbazide

C.H.NH.CO.N.HPh. [173°]. Formed from phenyl-hydrazine by combination with phenyl phenyl-hydrazine by combination with phenylyanate; and also by heating phenyl-hydrazine
with phenyl-urea (Kühn, B. 17, 2881; Skinner,
C. J. 58, 552). Acedles or plates (from alcohol
or benzene), sl. sol. water. GOCl₂ in benzene
forms C₁₄H₁₁N₂O, [178°] (Freund, B. 21, 2465).
Di-phenyl-carbaside CO(N,H₂Ph), §151°]
(S. a. K.); [164°] (E. Fischer, B. 22, 1930).
Formed by heating phenyl-hydrazine (2 mols.)
with carbamic ether (1 mol.) (Skinner a. Ruhe-

with carbamic ether (1 mol.) (Skinner a. Ruhe mann, C. J. 58, 550; B. 20, 3372). Formed also from phenyl-hydrazine and COCl₂ (Heller, A. 963, 277). Crystalline. Forms with HgCl₂ a crystalline compound B'HgCl, not melted at 136°. Alcoholic potash forms a red solution containing di-phenyl-carbasone N2H2Ph.CO.N:NPh crystallising in orange needles [157°]. Benzene and CSCl, form CS NPh.N C.N; NPh (176°)

(Freund a. Kuh, B. 23, 2833).

PHENYL-CARBIMIDE v. Phenul isocuanate.

vol. ii. p. 815. . DI - PHENYL - DI - CARBINIDO - TETRA - p -AMIDO-TETRA-TOLYL-DI - o-SULPHIDE

PhN:C NH.C.H., S.C.H., NH C:NPh. Di-thiop-tolyl-di-phenyl-di-quanddine. [c. 119°]. Formed by heating di-thiocarbonyl-tetra-amido-tetra-dolyl-di-sulphide with aniline and HgO (Truhlar, B. 20, 674). Amornhous; v. sol. alcohol.

DI-PHENYL-CARBINOL C_{1.}H., O i.e. Ph., CH(OH). Benshydrol. Mol. w. 184. [68°]. Ph. On Oct. 100 p. 100 amalgam (Linnemann, A. 188, 6; Beckmann, B. 22, 915); or by heating bengophenone with zine and alcoholic KOH (Zagumenny, A. 184, 174). Slender silky needles, v. e. sol. alcohol and ether. Converted into bensophenone by oxidation with chromic acid. Bromine forms a dibromo-benzhydrol [163°]. Zn and HOAc form benzpinacone. Zn and HCl in acetic acid Zn and HOAc

tillation contly resolves benzhydrol into water and benzhydrolic efter. P.S. forms C₂,H₂₁(SH)₂ [161°] and oily Ph₂OH(SH) (Engler, H₂, 11, 922). Ethyl derivative C₁₁H₁₁OEt. (288°). S.G. ²⁰ 1·03. From benzhydrol, alcohol, and H₂SO₄, or from Ph₂CHBr and alcoholic KOH (Friedel a. Balsohn, Bl. [2] 33, 389). Liquid.

soletion reduce it to tetra-phenyl-ethane. Dis-

Isoamyl derivative C₁,H₁₁,OC₂H₁₁, (810°).

Chloride Ph.CHCl. [14°]. From benzhydiol and HCl (Engler a. Bethge, B. 7, 1128).

Bromide Ph₂CHBr. [45°]. From di-phenylmethane and bromine at 150° (F. s. B.). Water at 150° decomposes it into benzhydrol and benzhydrolic ether. Conc. NH,Aq forms mono-and di-benzhydryl-amine (Friedel a. Balsohn, Bl. [2] 33, 587).

Acetyl derivative Ph₂CH.OAc. [42°]. (302°). S.G. 22 1·49. Prisms, v. sol. alcohol, acetic acid, and ether (Vincent, Bl. [2] 85, 304). Bensoyl derivative Ph₂CH.OBz. [89°]. Non-volatile. Trimetric, a:b:c=1: 477: 668.

Succinyl derivative

(Ph_CH.O)₂.O₂.O₂.O₂.H., [142°]. Gives, on distillation, succinic acid and benzhydrolene C₁₂H₁₄. [210°].

Anhydride CaH200 i.e. Ph20-CPh2(?)

[111°]. (315°) at 745 mm. From benzhydrol by long boiling with water or by treatment with PCl₂, BzCl, or diluted H₂SO₄. Monoclinic crystals (from benzene). Reduced by zinc and HCl in HOAc to tetra-phenyl-methane (Zagumenny, J. R. 12, 431). Zinck® a. Thorner (B. 11, 1398) obtained this anhydride by heating benzpinacone, $C_{2x}H_{2x}O_{2x}$, and consequently assume the formula $C_{2x}H_{2x}O_{2x}$.

References .- DI-AMIDO-, DI-BROMO-, and OXY-

DI-PHENYL-CARBINOL

Tri-phenyl-carbinel C, H, O i.s. CPh. OH.

Mol. w. 260. [159°]. (above 860°). Formation. — 1. By boiling tri-phenylmethane with chromic acid mixture (Hemilian, B. 7, 1203).-2. From CPh.Br and water.-3. By the action of water on CPh₂Br and water.—8.
By the action of water on CPh₂Cl got from
AlCl₂, benzene, and CCl₃, or CCl₂COCl (Friede
a. Crafts, A. Ch. [6] 1, 499; Hentschel, J. pr.
[2] 86, 311).—4. By heating its dicarbaxylic
acid with baryta (Hemilian, B. 19, 3073).

Properties.—Six cided plates — 11.

Properties.—Six-sided plates, v. sol. alcohol.

Acetyl derivative CPR, OAc. [99°]. Acetyl derivative Prisms (Allen a. Kölliker, A. 227, 116).

Methylether CPh.OMe. [82°]. Lamine. Ethylether CPh.OEt. [72°] (F. s. C.);

[83°] (A. a. K.). Chloride v. Chloro-tri-phenti-methams.

DI-PHENTL-GARRINGL CARBOXYLIC | ACID O. OXY-BENEYL-BENZOIC ACID.

AUD c. ONE-BENEYL-BENZOIC AUD.

Di-phesyl-earbinel dicarboxylic acid

CH(OH)(O,H,&O,H), Formed by heating
benzil di-o-carboxylic (diphthalylic) acid with

KOHAq (50 p.c.) at 180° for 5 minutes (Graebe
a. Juillard, 4. 242, 238). The acid splits up at

the moment of liberation into water and anhy.

dride.—BaA"aq.

Anhydrids C_{1,}H₁₀O₄. [203°]. S. 022 at 23°. Formed as above, and also by reducing benzophenone di-o-carboxylio acid. Monocilinic crystals (from alcohol). On heating, it yields a white sublimate [172°] reconverted by treatment with NaOHAq and HCl into the original anwith Neuthal and stul into the engine an-hydride. Phenyl-hydrazine gives O_2H_1N,O_2 . H_2SO_4 and HNO_2 give $C_2H_4(NO_2)_2O_1$ [c. 275°], which forms EtA' [148°].— $Bg(O_1H_1O_1)_2$ [aq. — OuA'_4 Saq.— AgA'_4 — C_1H_2 MeA'. [155°].— EtA'_4 . [100°].— $C_1H_2O_4(NH_2)_4$. [160°]. Needles. •

Isomeride v. Oxy-BENZYL-ISOPHTRALIC ACID. Di-phenyl-carbinol tri-carboxylic acid

O(OH)(CO,H)(C,H,,CO,H), Anhydrids Cl.H1,Oo. [170°]. Formed by heating benzil dio-carboxylic acid with MaOHAQ (4 p.c.) at 112° for 8 minutes (G. a. J.). Minute crystals, sl. sol. cold water. Gives off CO₂ on oryseas, s., sol. cold water. Gives on CO₂ on heating, yfelding the anhydride of di-phenyl-carbinol dicarboxylic acid.

Ethers of the anhydride Me,A". [148°].

—Et_A". [108°]. Prisms, v. sol. alcohol.

Tri-phenyl-carbinol.o-carboxylic acid *OPh,(OH).C.H..CO.H. The Na salt is formed by heating di-phenyl-phthalide with NaOHAq. but the acid splits up on liberation into water and its anhydride, di-phenyl-phthalide (Baeyer, A. 202, 50).

Tri - phenyl - carbinol m - carboxylic acid. [162°]. Formed by oxidation of di-phenyl-m-tolyl-methane with CrO, and HOAc (Hemilian, B. 16, 2369). Trimetric plates.

Tri-phenyl-carbinol p-carboxylic acid (?). [187°]: Formed by oxidation of CHPh, C.H. CHO (Oppenheim, B. 19, 2028) or of di-phenyl-tolyl-methane (Hemilian, B. 7, 1210). Needles.—
BaA'₂7aq. Needles, v. sl. sol. cold water.
Tri-phenyl-carbinol dicarboxylic acid. An-hydrids CPh. Co.—CO.

Di-phenyl-phthalide carboxylic acid. [246°]. Formed by oxidation of di-phenyl-y-xylyl-methane, di-phenyl-tolyl-methane o-carboxylio acid, di-phenyl-tolyl-carbinol m-carboxylic acid, or di-phenyl-methyl-phthalide (Hemilian, B. 16, 2372). Crystals, v. sol. alcohol and HOAc. Yields benzophenone and terephthalic acid on fusion with potash. Zinc-dust and NaOHAq reduce it to tri-phenyl-methane dicarboxylic acid.

Tri-phenyl-carbinol dicarboxylic acid $C_{\eta,H_1}O_1$, ϵ . $CPh_{\eta}(OH)_{\tau}C_{\eta,H_2}(OO,H)_{\tau}$ [1:3:4]. [180*]. Formed by oxidation of di-phenyl-xylyl-methane with K.Cr.O, and H.SO.Aq (Hemilian, Bs.19, 8072). Needles (from water), v. e. sof. alcohol. On jusion it yields an amorphous anhydride $C_{\eta,H_1}O_{\tau}$. On fusion with $B_{\eta}(OH)_{\tau}$ it forms tri-phenyl-carbinol.—Ag.A": pp. Tri-phenyl-carbinol dicarboxylic soid $CPh_{\tau}(OH)_{\tau}CH_{\tau}(OH)_{\tau}$. [12:24]. Anhydride Tri-phenyl-carbinol dicarboxylic acid

QPh_(OH, O,H,(OO,H), [1:2:4]. Anhydride C_nH,O. Di-phonyi-phthalide carboxylic acid. [228]. Formed by oxidation of the correspond-

ing di-phenyl-xylyl-methane (H.). Tables (coning di-phenyi-xylyi-methane (m.). Issues tout-taining EtOH)....Cah', 3aq....Agh': needles. DI-PHENYI-CARBINYLAMINE C13H12N i.e.

OHPh, NH. Benshydrylamins. Exo-amido-di-phenyl-methane. (289°). Formed, together with tetra-phenyl-di-cathinyl-amine, by leaving benzhydryl bromide, CHPh.Br. with conc. NH.Aq for 48 hours (Friedel a Balsohn, Bl. [2] 33, 587). Got also by reducing benzophenone oxim in alcoholic solution by sodium-amalgam and accetic acid (Goldschmidt, B. 19, 3233).

Properties.—Albaline liquid, absorbing CO. from the air.

Salts.—B'Hcl: [270°]; long needles, sl. sol.

Salts.—B'HCl: [270°]; long needics, si. soi. cold water.—B',H,PlCl, 2aq: lancet-like needles (L. a. B.); B'H,PtCl, aq (G).—*B',H,CO, [91°]. Formyl derivative Ph,CH,H,CHO. [182°]. (860°). Formed, almost quantitatively, by heating benzophenone with ammonium formate at 200°–220° (Leuchart a. Bach, B. 19, 2129).

Urea Ph,CH,NH,CO,NH, [143°] (J. a. B.).

Tatra_nhanvl_di_cashinvl_amina(Ph,CH),NH.

Tetra-phenyl-di-carbinyl-amine (Ph.CH),NH. [136°]. Prepared as above, crystallises from alcohol in slender needles, not affected by MeI or AcCl at 100° (F. a. B.).

Tri-phenyl-carbinyl-amine CPh, NH, [103°] TTI-phenyl-carbinyl-amine CPh, NH, [103°]. Torned by passing dry NH, through a solution of CPh, Br in benzene (Hemilian a. Silberstein, Bl. [2], 43, 118; B. 17, 741; cf. Nauen, B. 17, 442). Needles, sl. sol. cold alcohol. Yields B'HCl, B'H.PtCl, 7|aq, CPh,NHWE [73°], CPh,NHCH,Ph [110°], and the acetyl derivative CPh, NHAo [208°]. Forms a crystalline oxalate [253°] (Elbs, B. 17, 701). and the compounds C. H. NRE, R'I. and 701), and the compounds C1.H1, NBr2, B'I2, and B',I,

PHENYL-CARBINYL CHLORIDE v. CHLORO-TRI-PHENYL-METHANE.

TRI-PHENYL - CARBINYL - MAIONIC TRI-PHENYL - CARBINYL - MAIONIC THER CPh., CH(CO_Ett_ [33859]. Gof from sodium malonio ether and CPh., Br (Henderson, B. 20, 1014). Needles (from alcohol).

TRI-PHENYL CARBINYL SUTPHOCYANIDE CPh., NCS. [1379]. Formed from CPh., Br and ammonium sulphocyanide Elles, B. 17, 700).

TRI-PHENYL - CARBINYL - TOLUIDINE CPh., NHO, H., The o [1429] and p [1779] compounds are formed from CPh. Br and o and p

pounds are formed from CPh,Br and o and p toluidine respectively (Elbs, B. 17, 706). The p- compound yields a crystalline nitrosamine [1450_1480].

PHENYL-CARBIZINE. Formyl derivative C.H.N (N.CHO). [72°]. (256°). Formed by the action of COCl, in benzene on the phenyl-hydrazide of formic aldehyde (Freund, B. 21, 1240, 2458). Needles (from CS.), ... sol. alcohol and ether. Decomposed by boiling Na CQ.Aq into CO, and the phenyl-hydrazide of formic aldehyde.

Acetyl derivative CO (280°). Formed in like manner from acetic aldehyde. Monoclinic prisms; a:b:c=1.210:1:1:557; $\beta=73^{\circ}23'$.

Propionyl derivative. [68°]. Needles. Bensoyl derivative CO NPh. [114°]. Meedles (from alcohol) or plates (from HOAc), PHENYL CARBONATES.

Phenyl-sarbonic acid *6.H.O.CO.H.

Boldium sail PhO.CO.Na. Prepared by treating dry sodium phenylate in the cold for a mouth with CO, until it has taken up the calculated quantity of the gas. The product is a very hygroscopic powder.

hygroscopic power.

Reactions.—1. With water it gives off half its CO_2 in gaseous form: $2\text{PhO.CO.Na} + \text{H.O} = \text{PhONa} + \text{PhOH} + \text{NaHOO.} + CO_2 - 2$. At 12^{10} ts splits up into CO_2 and PhONa = 3. Heated rapidly to $180^{-2}.200^{\circ}$ it gives off smaller quantities of CO, together with phenol, the regidue being sodium salicylate. -4. In a sealed sube at 120°-180° for several hours it changes completely to sodium salicylars: C₄H₂O.CO₂N₀ = C₃H₄(OH)CO₂N₀ (R. Schmilt, J. pr. [2] 31,

108).
Di-phenyl carbonate C₁₂H₁₀O₂ i.e. CO(OPh)₂.
78°] (Kenpf. J. pr. [2] 1,404; Hentschel, J. pr. [2] 27,41; 36, 315); [88°] (Richter, J. pr. [2] 27,41). (303°). Formed by passing COCl₂ into in aqueous solution of NaOPh, or into phenol ontaining AlCl₂. Formed also from ClCO₂CCl₂, henol, and AlCl₂. Needles (from alcohol)* (leoholic potash forms phenol and K.CO₂. VaSEt gives NaSPh and (EtS)₂CO (Seiffert, J. pr. [2] 31, 464).

References.—Di-Bromo-*and Nitro-*phenyl.**

• References. - DI-BROMO and NITRO PHENYL CARBONATE.

DIPHENYL o-CARBOXYLIC ACID C₁₁H₁₀O₂
i.e. C₄H₃,C₄H₄,CO₃H [1:2]. Phenyl-benzoic acid.
Mol. w. 198. [111²]. Formed by potash-fusion from diphenylene ketone (Fittig a. Ostermaier, B. 5, 933; A. 166, 374; Schmitz, A. 193, 115). Formed also, together with diphenylene ketone oxide, by distilling sodium salicylate with triphenyl phosphate (R. Richter, J. pr. [2] 28, 305). Small needles (from hot alcohol), m. sol. hot

Small needles (from hot sleohol), m. sol. hot water.—KA'aq.—BaA',aq.—CaA',2aq.—AgA'.

Ethyl ether Eth'. (300°-305°).

Teorahydrida C.H.,C.H.,e.Co.H. Phenylhexamethylene carboxylk acid. [405°]. Formed
by heating the corresponding dicarboxylic acid,
and by the higdrolysis of phenylhexamethylenyl
methyl ketone carboxylic ether (Kipping a.
W. H. Perkin, inc. C. J. 57, 319). Rosettes of
crystals (from ligroin).—AgA': amorphous pp.

Bibhenyl m. sarboxylic acid.

Diphenyl m carboxylic acid C.H., C.H., (Co.H. [161°]. Formed by exidation by chromic acid and HOAc from [1:3] C.H.Ph., from C.H.PhMe, and from C.H.Ph.CH.Br (Schmidt a. Schultz, A. 203, 132; Adam, A. Ch. [6] 15, 243). It is also a product of the fusion of benzoic acid with potash (Barth a. Schreder, M. 8, 808). Leaflets (from alcohol), sl. sol. water. Yields isophthalic acid on oxidation.— NaA', 2aq.—CaA', 3aq.—BaA', 3aaq: needles.—

Bad', 43aq.

Ethyl ether EtA'. (above 360°). Oil.

Diphenyl p-carboxylic acid C.H., C.H., CO.H., [219]. Formed by saponification of its nitrile, which is got by heating potassium diphenyl sulphonate with KCy in a current of dry CO. (Doebner, A. 172, 109). Formed also by oxidation of [13] C.H.Ph. or [1:4] C.H.PhMe (Schultz, A. 274, 213; Carnelley, C. J. 87, 713). It is also a product of the fusion of benzoic said with potent. Tafts of needles (from alcohol), r. al. sol. hot water. May be sublimed. Yields

terephthalic acid on oxidation—Bah',—Cah', Mthyl ther Eth'. [46°]. Prisms. Mitrile CisH., ON. [85°]. Crystajs.

Anilide G. H., CO.NHPh. [224°]. Got by heating C. H., CONOH. C. H., with HOAc, Ac, O, and dry HOl at 100° (Koller, M. 12, 503).

Diphenyl dio-carboxylic acid C. H., O, i.e. [2:1]CO.H.O.H., C.H., CO.H.[12]. Diphenic acid. Mol. w. 242. [228°]. Formed by the oxidation of phenanthraquinone or phenanthrene (Fittig a. Ostermayer, A. 166, 361; Schmitz, A. 198. 116). It is also produced when phenanthra-quinome is boiled with conc. alcoholic potash (Anschutz a. Schultz, A. 196, 50 208, 97). Plates or prisms, m. sol. hot water. May be sublimed. By exhaustive chlorination with SbCl. it rields perchloro-diphenyl, together with a small quantity of perchloro-benzene (Mers a. Weith, B. 16, 2872). Distillation over with red-hot CaO yields diphenylene ketone; distillation with Ca(OH)₂ gives diphenyl.

Salts.—BaA"aq: v. sol. water.—CaA" 2;aq.

-MgA'4aq.—AgA'': bulky white pp.

•Methyleethers Me₂A''. [73:5°].—MeHA''.

[110°]. Plates, m. sol. water. Got by boiling the anhydride with McOH.

Ethyl ethers Et, A". [42°]. Crystals, insol. A. (Hummel, A. 193, 128).—EtHA". [88°]. Anhydride C.H.CO O. [213°]

Formed by boiling the acid with AcCl or Ac.O Assolutz, B. 10, 1884; 13, 1802: Graebe, B. 20, 848; A. 247, 261). Needles, insol. water, sol. alcohol. Decomposed by heat into CO₂ and diphenylene ketone. H.SO, at 100° forms diphenylene ketone carboxylic acid [217°]. Phenyl-hydrazine forms the crystalline compound CO₂H.C₂H₄.C₄H₄.CO₂N₂H₄Ph [174° cor.] which at 250° yields C₄H₄.CO₂N.NHPh [150°]. Benzene and AlCl, form an acid [148°].

Chloride C_{1.}H_e(COCl)₂. [98°]. Formed from the anhydride and PCl₃. Yields di-oxyphenanthrene on reduction.

dmide C₁₂H_a(CO.NH₂)₂. [212°]. Formed

by warming the imide with cone. NH₂Aq.

Amic acid C₁₂H₂(CO₂H)(CONH₂). [193°].

Got by boiling the anhydride with NH₂Aq.

Plates (from alcohol). Converted by heat into the imide.

Imide C.H. CO NH. [2202]. Formed as above, and also by the action of conc. HClAq on the mono-oxim of phenanthraquinons (Wegerhoff, A. 252, 18). Needles (from alcohol), Yields an acetyl derivative sl. sol. hot water. [92°], and forms C14H.O2(NNa), C14H.O2(NAg),

and C_{1.}H₂O₂(NMe).

Diphenyl om-dicarboxylic acid [2:1]CO,H.C,H.,CO,H.[1:3]. Isodiphents. acid. [216°]. Formed by fusing diphenylene ketone carboxylic acid with potash (Fittig a. Lieppmann, B. 12, 163; A. 198, 155; 200, 9). Reedles (from hot water). Yields diphenylene Isodiphenia. ketone on heating with lime. Gives isophthalic

ketone on heating with lime. Gives isophthalic acid on oxidation with CrO₂.—BaA" 6aq. Crystalline.—CaA" 2aq.—Ag,A": pp., al. sol. hot wateg. Mathy l either Me,A". [69-50]. Ethy l either Et,A". Thick bil. Diphenyl op-di-carboxylic acid [2:1] CO,H.O,H.,C,H.,CO,H.[1:4]. [252°]. Formed by saponification of its nitrile [158°] which is got by Sandmeyer's reaction from op-di-amido-diphenyl (Reuland, B. 22, 8018).

Bishenyldi-m-earboxyfic seid. [above 840°]. | forms (C.H.,SO,C.H.),NH.—7. Alcoholic KHS rmed by the action of nitrous acid on di-p-ido-diphenyl dicarboxylic acid (Griess, B. | Phenyl chloro-ethyl anlphone Formed by the action of nitrous acid on di-p-amido-diphenyl dicarboxylic acid (Griess, B.

amido-diphenyl dicarboxylic acid (Griess, B. 21, 982). Small needles, almost insol. cold water.—Bah" Baq ; crystalline aggregates.

Diphenyl di-p-earboxylic acid
[4:1] CO,H.O,H.,C.H.,CO,H.[1:4]. Formed by saponification of its nitrile, and also by oxidation of p-ditolyl (Doebner, B. 9, 129, 272; A. 172, 109). Amorphous powder, nearly-insol. most solvents.—Cah"; insoluble pp.—Bah".—Ar,A'", white np.

Ag₂A": white pp.

Ethyl ether Et,A". [112°]. Prisms.

Nitrile C,H,(CN). [234°]. Formed by heating potassium diphenyl diswiphonate with KCy. Needles (from alcohol)

Diphenyl dicarboxylic acid a C₄H₄,C₆E₄(C₀,H₄), [1:3:5]. [c. 310°]. Formed by heating benzoic aldehyde with CH₂,CO.CO₂H and baryta-water (Doebner, B. 23, 2381 • 24, 1750) 'Orwatals v. al. sol. cold HeAc. Yields 1750). Crystals, v. sl. sol. cold HOAc. Yields diphenyl on distillation with lime.—BaA"4}aq: needles.-CsA".-CuA".

Diphenyl tricarboxylic acid C_{1.}H₁₀O₆ i.e. CO₂H.C₂H₁,C₆H₁(CO₂H)₂. Formed by fusing diphenylene ketone dicarboxylic acid with KOH (Bamberger a. Hooker, B. 18, 1035; A, 229, 169). White crystalline powder, v. sol. alcohol and ether, sl. sol. hot water.—Pb,A'''2: insoluble crystalline pp.—Ag, A", white pp.

References.—Amido-, Bromo-, Iodo-, Nitro-,

and Oxy- DIPHENIC and DIPHENYL CARBOXYLIC ACIDS.

PHENYL-CETYL-AMINE v. CETYL-ANILINE. PHENYL-CHELIDAMIC ACID v. CHELI-

DONIC ACID PHENYL-CHLORO-ACETIC ACID v. CHLORO-

PHENYL-ACETIC ACID PHENYL CHLORO-BENZYL KETONE

C.H.,CO.OHCI.C.H., [65°]. (Curtius, J. pr. [2] 44, 547). Formed by reducing phenyl dichlorobenzyl ketone with iron and acetic acid (Lashovitch, B. 17, 1163). V. sol. alcohol.

Phenyl di-chloro-bensyl ketone C.H., CO.CCl., C.H., [71°]. (Zinin, A. 119, 177); [61°] (L.). Formed from benzil and PCl., Prisms (from ether). Reduced by zinc and HCl to phenyl benzyl ketone.

PHENYL CHLORO-BENZYL SULPHONE CH.CO.CHCI.O.H. Formed by heating benzylidene obloride with C.H., SO.Na and alcohol at 150° (Otto, J. pr. [2] 40, 517). Needles (from HOAc), sl. sol. hot alcohol.

PHENYL-CHLORO-ETHANE v. CHLOBO-

ETHYL-BENZENE. PHENYL CHLORO-ETHYL OXIDE

**Chloro-thyl derivative of Phenon.

PHENYL CHLORO-ETHYL SULPHONE
C.H., SO., CH., Chl. (56°). Formed by the action of PCl, or HCl on phenyl oxy-ethyl sulphone (Otto, J. pr. [2] 30, 197). Six-sided tablets (from benzene), sl. sol. water.

Reactions.—1. Boiling with alcohol and Ag₂O

converted it into O.H., SO., C.H., OH. — 2. By heating with Q.H., SO., C.H., — B. Sodium-dradgam reduces it, in alcoholic solution, to benzene sulphinic acid.—4. Alcoholic NaOEt forms O.H., SO., C.H., OEt. — 5. Converted by P.H. SO., C.H., OET. — 6. Ammonia column (C.H., SO., C.H.,)2. — 6. Ammonia

CH.SO. CHCI.CH. [52°]. Formed by heating aqueous CH. CCI.CO.Na (1 mol.) with sodium benzene sulphinate (2 mols.) at 100° (Otto, J. pr. [2] 40, 532). Crystals (from alcohol). PHENYL-CHLORO-IMERAMN v. ISATIN. PHENYL CHLORO-METHENYL DI-ETHYL

TRI-SULDHONE CCI(SO2Ph)(SO2Et)2. [130°]. Got by chlorinating CH(SO,Ph)(SO,Et), (Laves,

B. 65, 863). Plates, sl. sol. hot water.
TRI-PHENYL CHLOROMETHENYL TRI-SULPHONE CC(SO,Ph), [260°]. Got by chlorinating CH(SO,Ph), (Laves, B. 25, 350).

PHENYL CHLORO-METHYL KETONE v. Got by

CHLORO-ACETOPHENONE

PHENYL CHLORO-METHYL SULPHONE

C₄H.,SO₂.CH.Cl. 753°]. Formed by boiling an
aqueous solution of C₄H₃SO₂Na (2 mols.) with the theoretical quantity (Otto, J. pr. [2] 40, 527; 32, 21, 656). Formed also from C.H., 80, Na and CH,Cl2

Phenyl di-chloro-methyl sulphone C.H.SO.CHCl. [59°]. Formed by treatment of C.H.SO.CH.CO.H with Cl in diffused days light (Otto, J. pr. [2] 40, 511). Monocl prismatic tables, v. sol. hot alcohol.

PHENYL-CHLORO-NAPHTHYL-AMINE. Monoclinia

Bensoylderivative C₆H,NBz.C₆H₆Cl. [152°]. Formed from NPhBz.C₁₆H, and PCl. (Claus a. Richter, B. 17, 1590). Needles, sol. alcohol. PHENYL-GHLORO - NITRO - PHENYL-HY-

DRAZINE C.H., N2H2.C.H3Cl(NO2) [1:4:6]. [140°].

DRAZINE C₂H., N₂H₂C.,H.,Cl(NO₂) [1:4:6]. [140]. Formed from phenyl-hydrazine and C₄H.,Cl(NO₂). in the cold (Willgerodt, J. pr. [2] 37, 355). Red prisms (from alcohol and ether).

PHENYL TRI. CHLORO OXY PROPYL

KETONE C₂H.,COCH.,CH(OH).CH., [64°] and [77°]. Got from acetophenone, chloral, and HOAc (Koenigs, B. 25, 795). V. sl. sol. water. Converted by H.,SO, into C₆H.,CGCH:CH.CCl, 1103°]. [102°]

PHENYL CHLORO PHENYL HYDRAZINE C₂H₂,N₂H₂,C₃H₄,D₄D₅ Formed by reducing C₄H₂,N₂,C₄H₄Cl with alcoholic ammonium sulphide (Heumann a. Mentha, B. 19, 1688).
PHENYL CHLORO-PHENYL RETONE

CHLORO-BENZOPHENONE

PHENYL-CHLORO-PROPIONIC ACID CHLORO-PHENYL-PROPIONIC ACID

PHENYL &-CHLORO-p-TOLYL RETONE
C.H., CO.C., H., CH., Cl. Benzoylbenzyl chloride. ketone at 110° (Thorner, A. 189, 89). Silky needles (from dilute alcohol). May be sublimed. On further chlorination at 135° it yields phe On ruther chiormation at 135° It yields phenyl dichlorotolyl ketone or benzoyl benzylidene chloride C₂H₄.CO.C₂H₄.CHCl₂ [95°] and, at 155°, phenyl tri-chloro-tolyl ketone or benzoyl-benzo-trichloride C₂H₄.CO.C₂H₄.CCl₄ [111°], which is converted by PCl₄ into C₄H₄.CCl₄.CH₄.CCl₄ [80°] crystallising in thin plates.

PHENYL-CHRYSYL-THIO-URBA

CHANGO NUC. 1 (186°) Formed to the children of the converted to the converted to the children of the childr

C.H.NH.CS.NH.C.,H.1. [186°]. Formed from phenyl-thiocarbimide and chrysylamine and from chrysyl-thiocarbimide and aniline in benz-

ene solution (Abegg, B. 24, 957). Crystals.
PHENYL-GINGHONIC ACID v. PHENYL

PHENYL-CINCHONIDINE FHENYL-CINCHONIDINE C₁₀H₂₁PhN₂O. Formed in two modifications (an oil, sol. ether, and an amorphous powder, insol. ether) by heating cinchonidine with aniline (Claus a. Bätcke, B. 18, 2194). Both give B"H2PtCl, 2aq.

PHENYL-CINNAMIC ACID C₁₈H₁₂O₂ i.e.

C.H. CH:CPh.CO.H. [170°]. Formed by saponifying the nitrile or heating sodium phenylacetate with banzoic aldehyde and Ac.O at 150° (Oglialoro, G. 9, 429). Needles, sol. alcohol and ether, v. sl. sol. cold water. Reduced by sodium-

ether, v. sl. sol. cold water. Reduced by sodium-amalgam to $\alpha \beta$ -di-phenyl-propionic acid.— BAA_24aq: micaceous plates. Methyl ether MeA'. [78°] (Cabella, G. 14, 114). Needles (from dilute alcohol). Nitrile C.H.CH.CH.CN. Phenyl-styryl cyanide. [87°]. (360° cor.). Formed by the action of benzyl cyanide on henzoic aldehyde on benzylidene chloride in presence of NaOEt or solid NaOH (Rossolymo, B. 22, 1235; Meyer, A. 250. 124: Janssen. A. 250. 129: Nebre. A. A. 250, 124; Janssen, J. 250, 129; Neure, A. 250, 155; Frost, A. 250, 157). White plates (from alcohol). Yields CHPhBr.CPhBr.CN [130*] and CHPhCl.CPhCl.CN. [168°].

e-Carboxylic acid. Imide

C.H. CO NH. [174°]. Formed by heating the imide of carboxy-phenyl-acetic acid (vol. i. p. 706) with benzoic aldehyde (Gabriel, \hat{B} . 20, Needles.

References .- NITRO- and OXY- PHENYL-CIN-NAMIC ACID.

PHENYL-CINNAMYL-HYDRAZINE CHPh:CH.CH, NPh.NH, [54°]. Formed from sodium phenyl-hydrazine and cinnamyl bromide (Michaelis, B. 22, 2233). Crystals.

PHENYL-CINNAMYL KÉTONE v. PHENYL STYRYL KETONE.

PHENYL-p-COUMARIC ACID [1:4]

 $C_6H_4(OH)$.CH.CH.CO.H. [219°]. Formed by heating p-oxy-benzoic aldehyde with Λc .O and sodium phenyl-acetate and boiling the resulting acetyl derivative with baryta-water (Oglialoro, (J. 13, 173). --AgA': nearly insol. water. Acetyl derivative. [170°]. Methyl ether MeA'. [170°].

Ethyl ether HeA'. [170]. Methyl deriver Eth'. [152].

Ethyl ether Eth. [152]. Vol.iii.p. 738.

Methyl derivative. [489]. Vol.iii.p. 738.

PHENYL-COUMARIN C₁₅H₁₀O₂. [140].

Formed, together with C₂H₄(OAc).CH:CPh.CO₂H, by heating salicylic aldehyde with sodium phenyl-acetate and Ac₂O for 8 hours at 150° (Oglialoro, G. 9, 428). Prisms, sol. ether.

Mono-sulphonic acid C12H2O2(SO3H) 212q. [263]. White needles (Curatolo, G. 14, 257).

—BaA'₂.—PbA'₂4aq: needles, m. sol. hot water.

Disulphonic acid C₁₃H₂O₂(SO₃H), 6aq. [89°]. Deliquescent crystals.—BaA', 4aq: white prisms.—PbA', 5aq: needles, v. sol. water. PHENYL-CROTONIC ACID C₁₆H₁₆O₂ i.e.

C.H. CH: CMe.CO.H. Phenyl-methacrylic acid. (a)-Methyl-cinnamic acid. [82°]. Formed by heating benzoig aldehyde with propionic anhydride and sodium propionate (Perkin, C. J. 31, 391; 32, 661). Formed also by heating benzoic aldehyde with Ac.O and sodium methyl-malonate; and by heating benzois aldehyde with sodium propionate and HOAc or Ac,O (Stuart, C. J. 48, 404; Slocum, 4 227,57). Obtained also by oxidation of the corresponding aldehyde (Miller a. Kin-kein, B. 19, 526). It is also a product of the action of Na on benzyl propionate (Conrad a. Hodgkinson, A. 193, 814).

Transparent plates (from alcohol), sl. sol, hot water. When prepared by Perkin's method it ap pears to be accompanied by an isomeride [740] crystallising in needles, which is converted into the crystallising in needles, when is converted into the acid [82°] by frequent recrystallisation (Raikoff, B. 20, 3396). Yields methrohol (q, v.) when, heated with dilute H₂SO₄. Bromine forms CHPBR₂CMeBr.CO₂H[137°] (Körner, B. 21, 276).

Balt's—Bal', aq: very minute, plates.—
Bal', 4aq: small white crystals, got by slow cooling.—AgA'. S. 374. Needles.

Methylether MeA'. [30°]. (254°).

Amige 128°] [Edeleano, B. 20, 619).

Phenyl-isocretonic acid.

C₄H₅.CH:CH.CH₂.CQ.H. [86°] (J.); [88°] (B. s. D.). (302°). Formed by heating ben2oic aldehyde with succinic anhydride and sodium succinate (Perkin), the yield being 2 p.c. (Jayne, A. 216, 100). • Formed also by heating phenyltrimethylene tricarboxylic acid C.H.Ph(CO.H). in a current of Co at 190° (Buchner a. Dessauer, B. 25, 1155). Prepared by heating benzoic aldehyde with sodium succinate and Ac.O at 125°, and separated from phenyl-paraconic soid by solution in CS₂. Long thin needles (from water) or prisms (from CS₂). When heated with H₂SO₄ (4 pts.) and water (4 pts.) it changes to the isomeric phenyl butyrolactone and an acid [179°] (Erdmann, A. 227, 257). Yields γ -phenyl-nbutyrio acid [49°] on reduction. Boiling NaOHAq converts it into the isomeric C.H.,CH.,CH.;CH.CO.,H [55°]. Split up by long boiling into water and (a)-naphthol. Alkaline KMnO, at 0° forms di-oxy-phenyl-butyric lactone (Fittig a. Obermüller, A. 268, 44).—BaA', 3aq.—

CaA', 3aq. — AgA': bulky pp.
a-Phenyl-crotonic acid CH, CH: CPh.CO, H. Methylatropic acid. [185°]. Formed by heating sodium phenyl-acetate with paraldehyde and Ac₂O (Oglialoro, G. 15, 514). Minute prisms (from water), sol. alcohol and ether.—AgA': m. sol. hot water.

Phenyl-crotonic acid CaH, CH:C(CH,Ph).CO,H. [158°]. Formed from sodium phenyl-propionate, benzoic aldehyde, and Ac.O at 160° (Oglialoro, G. 20, 162). Needles (from alcohol).

Reference. -- OXY-PHENYL-GROTONIC ACID. PHENYL-CROTONIC ALDEHYDE v. PHENYL-METHACRYLIC ALDEHYDE

PHENYL-CUMAZONIC ACID

 $C_{17}H_{15}NO_{2}$ i.e. $C_{6}H_{2}(CO_{2}H) < \frac{CMe_{2}O_{2}}{N}$ [220°]. Formed by heating (3,4,1)-amido-oxypropyl-benzoic acid with BzCl at 100°-120° (Wid-

pyl-benzoic acid with B2Cl at 100°-120° (Wid-mann, B. 16, 2585). White crystals. Sol. alcohol, insol. water.—HA'H,SO, 2aq: thin plates. PHENYL-CUMINYL-AMINE C_{i.H.i.N} i.e. C_{s.H.i.N}II.CH_{.C.i.H.}Pr. [41°]. Formed by re-ducing C_{s.H.i.N}I.CH.C.H.Pr (Uebel, A. 245, 289).

PHENYL-CUMINYL-THIO-UREA
PHENYL-CUMINYL-THIO-UREA
PHENYL-CUMINYL-THIO-UREA
PHENYL-CUMINYL-THIO-UREA
PHENYL-CUMINYL-THIO-UREA [100°-106°]. C.H.Pr.CH2.NH.CS.NHPh. Formed from cuminylamine and phenyl-thio-

romed from cummytamine and phenyr-more carbimide (Goldschmidt a. Gessner, B. 20, 2416)
PHENYL-CUMINYL-UREA C₁,H₂N₁O i.e.
C₁H₁NH.CO.NHC₁eH₁₁. [144°]. Formed from cuminyl cyanate and aniline (Baab, B. 8, 1151)

NPh:C(NH.C.H.(C.H.)[1:4]). Formed from dicumyl-thio-ures and aniline (Francksen, B. 17, 1226). · Resin. ·

PHENT. 4-CUMYL KETONE C., H. O. i.e.

O.H., CO.C.H.Me, [1:2:4:5]. (329°). From
BzCl, 4-cumene, CS, and ACl, (Elbs, J. pr. [2]
35, 491; C. Claus, B. 19, 2891); the yield is
65 p.c. of the calculated.

Reactions .- 1. Boiling produces small quantities of needles [180°], probably (B. 2,8)- di methyl-anthraquinone.—2. Conc. or furning H.SO, st 100° forms benzoic acid and d-cumene sulphonic acid C.H.Me.(SO.H.) [1:2:4:5].—8. Funning HNO, mixed with H.SO, gives two isomeric trinitro-derivatives; one [185°] is v. al. sol. alcohol, the other [155°] is m. sol. v. at soil atcolor, the other [100] is in soil.

alcohol.—4. Dilute nitric acid forms bensayltrimellitic acid. C.H..CO.C.H..(CQ.H), and
C.H..CO.C.H..Mc(CO.H).
Phenyl cumyl ketone C.H..CO.C.,H.Pr.
(348°) at 788 mm. Formed from curringly

chloride, benzene, and AlCl, (Smith). • Yields two oxims [106°] and [132°], the latter of which forms an acetyl derivative [90°].

Phenylen-cumyl ketone. C.H., CO.C.H.Pr. (845° at 716 mm.). Formed from n-cumene, BsCl, and AlCl, (Smith, B. 24, 4033). Yields two oxims [180°] and [104°], which yield acetyl derivatives, melting at 116 and 60°.

PHENYL-4-CUMYL-METHANE CAR3OXY.

LIO ACID [1:2:4] C.H.M., C.H., C.H., CO.H. [1:2] [1869]. Got by reducing C.H., Mc.CO.C. H., CO.H with Zn and NH, Aq (Gresly, A. 234, 238).
DI-PHENYL-W-CUMYL-METAPYRAZOLE

TETRAHYDRIDE C. H.N. i.e.

C,H,,,CH<NPh>C,H,. [125°]. Formed from

p-cuminio aldehyde and di-phenyl-ethylene-di-amine at 100° (Moos, B. 20, 738). Silky needles. PHENYL-UCUMYL-UREA C₁₀H₁₁N₁O i.e. NHPh.CO.NHC,H₂Me₁ [211°]. Formed from w-cumidine and phenyl oyanate (Goldschmidt a. Bardach, B. 25, 1361). White needles. PHENYL-UYANAMIDE v. vol. ii. p. 316. Di-phenyl-oyanamide C₄H₁₀N₂ t.e. C(NPh)₂. Carbodiphenyl-bride. Mol. w. 194. (631° cor.).

Formed by warming a solution of s-di-phenylrormed by warming a solution of the Arrival Rev. 10, 1803; 9, 810). Syrup, drying up to a vitreous mass. Changes spontaneously into an opaque polymeride [170°] resembling porcelain.

Reactions.—1. Boiling dilute alcohol con-

verts it into s-di-phenyl-urea.—2. Aniline yields (a)-tri-phenyl-guanidine.—3. H₂S passed into its solution in benzene forms CS(NHPh)₂.—4. s-Diphenyl-thio-urea at 150° forms phenyl-thiocarb-imide and (a)-tri-phenyl-guanidine. — 5. Di-phenyl-urea at 150° acts in like manner, forming phenyl-wree at 150° acts in like manner, forming phenyl cyanate and tri-phenyl-guanidine.—6. Phenyl-hydrasine at 120° forms the compound C.H.N.:C(NHPh), [204°] which gives the salts B'HCl, B'zH.PcOl., and B'H.SO,, and is converted, by heating with phenyl-hydrazine at 185°, into C.zH.,N. [200°], which gives the salts B'zH.Cl, and B'zH.PCl.. The compound PhN.:C(NHPh), is converted by heating with phenyl-thiocarbimide at 190° into C.zH.,N.S [176°], and by heating with di-p-tolyl-dyanamide

and from phenyl cyanate and cuminylamine into C.H.N. [128°] which gives the salts (Goldschmidt, B. 20, 2415). Small needles.

BHENYL-DI-OPMYL-GUANIDINE

HCV passed into its solution in benzelle forms (C.H.), N. crystalliging from alcohol in prisms [1379]. A little of its solution in H.SO, mixed with water is coloured deep blue by NaOH (Laubenheimer, B. 13, 2155).—8. Tolyleneodiamine at 135° forms C.H., N. [1619] which yields B',H,Cl, [174°] (Dahm a Gasiorowski, B. 19, 3057).

Salt .- B'HCl. Needles (from benzene).

Tri-phenyl-di-eyan-di-amide C₂₀H₁₆N₄.
Formed from NHPh.CS.NH.C(NPh).NHPh, alcohol, and HgO, and also by heating di-phenylconol, and ngo, and also by nearing at pressing guanidine at 175° (Bathke a. Oppenheim, B. 23, 1673). Yellow needles (containing EtOH) (from alcohol).—B'HCl. Needles, insol. water.

—B',H,PtCl, 2aq.—B',H,SO,2aq.

—B',H,SO,2aq.

Reference.—OXY-PHENYL-CYANAMIBE.

PHENYL CYANATE v. vol. ii. p. 315.

PHENYL-CYANIC ACID v. CYANIC ACID.
PHENYL CYANIDE v. BENZONITRILE and PHENYL-CARBAMINE.

Di-phenyl dicyanide C, H, N, i.e.

PhC≪N>CPh? [152°]. Formed from benzamidine and benzoic aldohyde (Pinner, B. 22, 1610; 23, 2925). Prisms. Changes at 200°-270° into cyaphenine.

PHENYL-CYANUEIC ACID v. Cyanuric

acid in the article on Cyanic acid.

PHENYL-p-CYMYL-CARBINOL C₀H₃,CH₂(OH),C₂H₃(C₃H₂) [1:2:5]. (327° uncor.). Formed by reduction of phenyl p-cymyl ketone (Claus a. Elbs, B. 18, 1798; J. pr. [2]

35, 497). Thick colourless oil. PHENYL .-CYMYL ECTONE C.,H,,O i.e. C,H,,CO.C.,H,MePr[1:2:5]. (224° at 40 mm.); (340°) at 760 mm.

Formation.—1. From cymene by heating with benzoic acid and P₂O₃ (Kollarits a. Merz, B. 6, 546, -2. From cyanene, BzCl, and zino (Grucarevic a. Merz, B. 6, 546, 1246). -3. From cymene, BzCl, CS_x and AlCl, (Elbs, J. pr. [2] 25, 4041 35, 494].

35, 494].

Properties.—Yellowish oil, v. sol. alcohol and ether, m. sol. HOAc. Very slightly volatile with steam.

Reactions .- 1. Bromine and iron powder at 140° give benzoic acid and bromo-cymene, C_sH₃BrMePr [1:2:5] [232°]. — 2. Conc. H SO₄ and KNO, give an amorphous di-nitro-deriva-tive.-4. Dilute PNO, gives benzoyl-terephthalic acid .- 5. Concentrated H2SO, at 100° gives benzoic acid and cymene sulphonic acid.

C.H.,MePr(SO.H) [1:4:2]. PHENYL-CYSTEINE C.H., NSO. i.e. PHENYL-USELEMB U.H. INCO. 1-6.
CH., C(SPh)(NH.). CO.H. Formed by boiling phenyl-mercapturic acid with dilute H.SO. (Baumann a. Preusse, H. 5, 337). Plates (from NH.AQ) or six-sided tables (from water), v. sol. acids and alkalis, sl. sol. cold water. Yields phenyl mercaptan on boiling with NaOHAq.

Reference. BROMO-PHENYL-CYSTRING. PHENYL-DECOIC ACID. Nitrile C.H.,OH(C.H.,),ON. (328°). Formed from benzyl cyanide, octyl iodida, and NaOH (Rossolymo, B. 32, 1337). Yellow oil.

PHENYL-DURYL-GARBINOL

[6:4:8:2:1] C₄HMe, CH(OH).O₄H₄. (above 860°)e Formed by seduction of phenyl iso-duryl ketone

Essuer a. Gossin, Bl. [2] 42, 172). Liquid. fields an acetyl derivative boiling above 160° inda bensoyl derivative [75°].

DI PHENYL DURYLENE DIRETONE
J.H.O. i.e. (C.H.CO),C.Me. [270]. (above
180°). Formed from derene, BzCl, and AlCl, Friedel a. Crafts, A. Ch. [6] 1, 512). Prisms.

PHENYL DURYL KETONE C,, H,O i.e. leH.CO.C.HMe. [119°]. (343°) at 725 mm. for from durene, BzCl, and AlCl, (Friedel a. rafts, A. Ch. [6] 1,511). Acioular prisms, v. sol. rarm alcohol. Reduced by HI and P to C., H., 50.59 (310° at 716 mm.). Brooms C., H., Br., O 225°] and other products.

Phenyl isoduryl ketone. [63°]. (300°). ormed by the action of BzCl and AlCl, on the isodurene derived from toluene (Essner a. Gossin, Bl. [29, 42, 170). Suggessive treatment with HCy and alcoholic potash gives the said C.HMe..CPh(OH).CO.H, sol. water and alcohol.

PHENYLENE. The Padicle C.H. PHENYLENE-ACETAMIDINE

C_eH₄<NH>C.CH₂. [170°] (H.); [175°] (L.). Formed by boiling phenylene-o-diamine with HOAc, or by reducing C₄H₄(NO₂)(NHAc) with tin and HCl (Ladenburg, B. 8, 677; Hübner, A. 209, 353). Needles.—B'HCl.—B'₂H₂PtCl₈ aq.— B'HNO₃.—B'H₂SO₄.

Phenylene - di - acetamidine C10H14N4 [1:4] C_oH₁(CH₂C(NH),NH₂). [182°]. Formed by the action of alcoholic NH₃, followed by NaOHAq, upon the hydrochloride of phenylenedi-acetimido-ether (Glock, B. 21, 2660). Plates.

o-PHENYLENE-DI-ACETIC ACID $C_{10}H_{10}O_4$ e.e. [1:2] $C_aH_4(CH_2\cdot CO_2H)_2$. Mol. w. 194. [150°]. Formed by saponification of its nitrile by boiling with dilute H.SO, (Baeyer a. Pape, B. 17, 44%. Slender needles, v. sol. alcohol, m.

sol. cold water.—Ag.A". insoluble pp.

Nitrile C.H.(CH.CH.). [60°]. Form
by the action of KCy on di-ω-bromo-o-xylene.

m-Phenylene-di-acetic acid C.H. (CH2.CO2H)2.

m-Phenylene-di-acetic acid C_sH₁(CH₂·CO₂H)₂.

[170³]. Formed by-boiling its nitrile with alcoholic potash (Kipping, C. J. 53, 42; B. 21, 42).

Needles, v. sol. water.—Ag₅A'': white pp.

Nitrile C₂H₁(CH₂CN)₂.

[29³]. (308° at 300 mm.). From [1:3] G₂H₁(CH₂Br)₂ and gCy.

p-Phenylene-di-acetic acid C₃H₁(CH₂CO₂H)₂.

[241³]. Got from its nitrile (Biedermann, B. 5, 703; Klippert, B. 9, 1766; Kipping, C. J. 53, 44). Needles, m. sol. water.—CaA''2aq.—

[taA''Rag.—RaA''2iag: needles, v. sol. water.

44). Needles, m. sol. water.—CaA" 2aq.—CaA" 8aq.—BaA" 2½ aq: needles, v. sol. water.—ZnA".—CaA".—Ag.A": white amorphous pp. Ethers.—Me.A". [57°].—Et.A". [58°]. Chloride. Oil (Klippert).

Amide. [above 290°]. Plates and needles. Nitrile C.H.(CH.CN)... [96°]. Formed by the action of KCy on C.H.(CH.Br), or C.H.(CH.Cl)... Three-sided prisms (from other). Alcoholic ammonium sulbhide at 100° converts Alcoholic ammonium sulphide at 100° converts it into C₆H₄(CH₂CS.NH₂)₂ [206°] which crystallises from HCAc.

Di-phenylene-acetic acid C.H. CH.CO.H. [222°]. Formed by heating C_{1.}H₁:C(OH).CO_.H with HI and P at 140° (Friedländer, B. 10, 538). Small crystals (from alcohol). Decomposed by heating with soda-lime into CO₅ and fluorens.— AgAb: unstable pp.

Ethul ether Etk'. [165°]. Reference .-- OXY-DIPHENTLENE-ACETIC ACID. Reference.—UXY-DEPHENYLENE ACETIC ACID.
p-PHENYLENE DI-ACETTRIDO-ETHER
C.H.(CH.-C(NH)-OEt). The hadrochloride
B"2HCl [above 240°] formed by the action of
alcohol and HCl on C.H.(CH.-CN), crystallises
in needles (Glock, B. 21, 2660). It is insol, ether.

o-PHENYLENE-DI-ACRYLIC ACID C.H.(CH.CO.H)₂. [above 300°]. Formed by boiling C.H.(CH.;CCI(CO.Et)₂)₂ with also holic potash (Perkin, C. J. 53, 14; B. 19, 435). Sl. sol. water, v. sl. sol. alcohol.—Ag.A": pp.

p-Phenylene di-acrylic acid p-Phenylene di-acrylic acid C.H.(CH:CH.CO.H), [310°]. Obtained by saponitying the mono-ethylether HEtA* [200°] which is got by heating p-aldehydo-cinnamic ether with NaGAc and Ao.O (Low, A. 231, 377). Got also by boiling C,H.(CH.,CBr(CQ.Et)), with alcoholic potash (Kipping, C. J. 53, 41). Yields a tetrabromide crystallising in needles.—Ag.A.".

PHENYLENE - DI - ALLYL - DI - THIO - DI -UREA C.H.(NH.CS.NHC,H.)2. The o- [159°], m- [105°], and p- 200°] compounds are formed by heating the corresponding phenylene-diamines with algohol and allyl-thiocarbimide (oil of mustard) at 100° (Lellmann a. Würthner, A. 228, 201). The o- and p- compounds decompose when heated. They are all sol. HOAc.

o-PHENYLENE - DI - AMIDO - DI - ACETIC ACID [1:2] C.H. (NH.CH., CO., H). The ether Et. A'' [135°] is got from o-phenylene diamine and ClCO Et (Zimmermann a. Knyrim, B. 16, 515).

m-Phenylene-di-amido-di-acetic acid m-Phenylene-di-amido-ai-acetic acia [1:3] C_sH_s(NH.CH_sCO_sH)_s. The ethyl ether Et.A" [78°] is got by heating m-phenylene-diamine with OH_sCl.CO_sEt (Zimmermann B. 15, 518; 16, 514). It is converted by conc. HClAq into crystalline HA"H_sCl_s v. sol. water. p-Phenylene-di-amido-di-acetic acid. The

ethyl ether Et.A" [83°] and the hydrochloride. H2A"H2Cl2 are formed in like manner from p-phonylene-diamine.

o-PHENYLEME-DIAMINE [1:2] C₆H₄(NH₂)₂ Mol. w. 108. [104°]. (252°). Prepared by reducing o-nitro-aniline with tin and HCl (Zincke Sintenis, B. 6, 123; Vignon, Bl. [3] 2, 675; Sandmeyer, B. 19, 2654). Formed also by heating the corresponding di-amido-benzoic acids with baryta (Griess, J. pp. [2] 8, 148; Salkowski, A. 173, 58) and by the action of tin and HCl on bromo-o-nitro-aniline (Wurster, A. 171, 63; Hübner, A. 209, 360) and on o-di-nitro benzene (Zincke, B. 7, 1874). Plates (from water) or tables (from chloroform), v. e.

sol. hot water, sloohol, and ether.

Reactions.—1. FoCl, added to a solution of the hydrochloride forms di-amido-phenazine hydrohydrochloride forms di-amido-phenazine hydrochloride, which crystallises in ruby-red needles C₁.H₁.N₄.HCl (Fischer, B. 22, 355).—2. Pyrocatechin at 200° forms phenazine C₂.H₄.N₃.C₄.H₄. S. (B)-Naphthoquinone forms naphthophenazine C₁.H₄.N₄.C₄.H₄.—4. Cyanogen gas forms C.H₄.N₄ a yellow crystalline powder [c. 280°], sl. sol. water, forming B'.H.PtCl, 3aq and B'.H.PtCl, aq. By heating with HCl it is converted into C.H.N₄.O [280°] and di-oxy-quinoxaline (Bladin, Bl. [2]42, 104; B. 18, 672).—5. The sulphocyanide is converted by heat into a mixture of phenylengverted by heat into a mixture of phenylenethio-urea and thio-urea (Lellmann, A. 221, 8).-6. KNO, added to a very dilute solution of the sulphate forms 'amidoszophenylene' C.H.N.

meedles [98-6] (Ladenburg, B. 9, 219).—7. ICy forms C_{1,H},N_c, which yields the salts B"H_{cl}, b" ACI 2\(\) aq, B" 2HNO, 2\(\) aq, and B"H_c, N_c, Q_c thin y intro us següin to C_{1,H}, N_c, Q_c thin by prictors again to C_{1,H}, N_c, Q_c thin by prictors again to C_{1,H}, N_c, Q_c thin be converted by benzoic aldehyde into dibenzylidene amplene diamine (C_{1,H}, (N.C) Hh)_c, 134 C₁; yieldigh B'_c H_cPtCl_c. B'HNO_c B'H_cSO_c. B''H_cNO_c B'H_cSO_c. B''H_cSO_c. B''

benzenyl-pnenylene-diamine (q. v.).

Dibenzoyl derivative C.H.(NHBz).

[c. 300°]. Thin prisms (from HOAc) (Bistrzycki).

Di-p-toluyl derivative
C.H.(NH.CO.C.H.Me). [228°]. Got, logother with tolenyl-benzamidine C.H.(N.H.CO.H.Me [268°], by the action of p-toluyl chloride on o-phenylene-diamine dissolved in benzene (Hübner, A. 210, 828). Colourless needles, sl. sol. alcohol.

m-Phenylene - diamine C_aH₁(NH₂)₂. [63°]. (277° i.V.). Prepared by reduction of m-dinitro-benzene or m-nitro-aniline (Hofmann, Pr. 11, 518; 12, 639; Zincke, B. 5, 792). Formed also by heating s-di-amido-benzole acid with baryta (Wurster, B. 7, 214; Hübner, A. 222, 86), and by the action of tin and HCl on (4,2,1)-di-nitro-benzole acid (Wurster, B. 7, 149) and on (1,2,4)-bromo-di-nitro-benzene (Z.). Got also by heating resorein (1 pt.) with ammoniacal CaCl, (4 pts. containing 35 p.c. NH₃) for eight hours at 275° (Seyewitz, C. R. 109, 814). Crystalline, m. sol. water, v. sol. alcohol and ether. Its solutions are alkaline in reaction. KNO2 added to a solution of a salt of m-phenylene-diamine forms a brown pp. containing C₄H₃(NH₂)₂N₂C₆H₁NH₂. A solution in dilute H₂SO₄ is coloured yellow by a trace of nitrous acid. Aldehyde added to an alcoholic solution of m-phenylene-diamine hydrochloride forms an orange-red colour, with a green fluorescence. orange-red colour, with a green hoursescence. From this liquid NH_{*}Aq ppts. di-methyl-phenanthroline tetrahydride $O_{i_1}H_{i_2}N_{i_3}$ (Girard a. Roques, C. R. 107, 1158; Schiff, A. 253, 328). Benzoic aldehyde in alcohol forms with the hydrochloration of the colour of the colou The hydroide the base CHPh(C₆H₄(NH₂)₂)₂. chloride of m-phenylene-diamine gives a crimson colour when boiled with oxygenated water (Deniges); in presence of ammonia the liquid becomes blue, but is turned red by NaOHAq. Hydrogen peroxide gives a bluish-green tina (Cazeneuve, Bl. [3] 5, 855) PbO₂ and dilute HOAc give a brown colour (Lauth, C. R. 111, 975). Alkaline NaOBr gives a maroon-red pp. (Deniges, 6. R. 107, 662). CS, in alcohol at 35° forms

yellow monochnic prisms of C.H. NH CS and several other bodies (Gucci, G. 17, 523, 2657). The sulphocyanide is converted by heat into added to a solution of the hydrochloride forms $C_cH_c(NH_cCS,NH_c)_c$ (Lellmann, A. 221, 8).

The sulphocyanide is converted by heat into added to a solution of the hydrochloride forms $C_cH_c(NH_cCI)N_cCI$, and in presence of a large excess of HCI it forms $C_cH_c(N_cCI)_p$.—6. Mixed

C,H,(NHAc)2.4

m-Amido-bensoyl derivat\$vs $C_sH_4(NH_2)(NH.Co.C_sH_NH_2)$. [129°]. Needles (from dilute alcohol) (Hugh, B. 7, 1268).

o-Oxy-benzoy) derivative C_sH₁(NH_s).NH.CO.O_sH_sOH. [143°]. Orystals (Bell, C. J. 28, 1201).

• p-Phenylene-diamine C.H.(NH.).

Formation .- 1. By reduction of Formation.—1. By reduction of p-nitro-aniline and of p-di-nitro-benzene (Hofmann, Pr. 11, 518; 12, 639; Zincke, B. 7, 871).—2. By reduction of C_uH₁, N₁, C_uH₁, NH₁ (Martius a. Griess, Z. 1866, 136).—3. By distilling (5,2,1)-di-amido-benzoia acid (Griess, B. 5, 201).—4. In the pre-paration of induline by heating C_uH₁, N₁, C_uH₁, NH₁ with aniline hydrochloride (Witt; Fischer a. Happ. B. 23, 2920. Hepp, B. 23, 839).
Prenaration.—From acelanilide by nitration

Preparation.—From acetanil and reduction with tin and HCl.

and reduction with tin and HCl.

Properties.—Plates (by sulfilmation) or
monoclinic crystals (from waker) changing in
the solution to trimetric plates. Mosol. water,
v. sol. alcohol and ether. Forms a hydrate
C,H,N,2 aq [80°]. With PbO₂ and aqueous HO₂
it gives a bright bluish-green colour (Lauth,
C.R. 111, 975). p-Phenylong-diamine is very
poisonous (Vignon, C. R. 107, 533). A mery
race of a mixture of m and p- phenylene-diamine gives on warming with HOAo and K,Cr.,
hlue colour changing on boiling to red [W].

amine gives on warming with HOAc and K.Cr.O. a blue colour, changing on boiling to red (Witt, O. J. 35, 356; Meldola, C. J. 51, 105).

Reactions.—1. Ornitised to quinone by H.SO., and MnO.. Quinone is also formed together with NH, by oxidation of the sulphate with K.Cr.O., (Meldola a. Evans, C. J. Proc. 5, 115).—2. When exposed to air, O. H.O., or K.FeCy, p. phenylene-diamine and its salts are oxidised to C.H.N., a feeble red base with green lustre [2307] yielding C.H.AcN, [2947] (Bandrowski, M. 10, 126).—3. Chlorine passed into a solution in HOAc forms tetra-chroro-quinone,—4. FeCl. added to a solution of the hydro-4. FeCl, added to a solution of the hydrochloride saturated with H.S ppts. Lauth's violet, which is v. sol. pure water, but ppd by salts (Lauth, C. R. 82, 1441).—5. Potassium nitrite

with aniline (2 mols.) and oxidised by K,Cr,O, it yields pheno-safranine .- 7. The sulphocyanide is sometised by heat into $C_sH_s(NH.CS.NH_s)_s$ (Leilmann, A. 221, 8).—8. Bleaching-powder solution added to a solution in HClAq ppts. yellowish-white quinone di-chloro-di-imide which detonates at 124° (Krauso, B. 12, 47). -9. Aceto-acetic ether at 170 forms C, H, N, O, [176°] which is probably C₂H₄(NH.CO.CH₂.CO.CH₃)₂ (Knorr, B. 17, 545; 19, 3303).

Salts.—B"H₂Cl₂. Triclinic tables, v₂ sol. water, almost insol. HClAq.—B"H₂PtCl₂.— B'H.Sn.cl. (Hübner, A. 203 366).—B"H.Br., B'H₂S₂O₃ (Bernthsen, A. 251, 62).—B''H₂S₂O₃.

Micaceous plates, sl. sol. water (Vignon, Bl. [2] 50, 152).—B''H₂C₂O₄. S. 15 at 15°.

Di-formyl derivative C.H.(NH.CHO)...
[204]. Amgrphous mass (Wundt, B. 11, 828).
Mono-acceyl derivative

MONO-actery aervoutives.

C.H.(NH.)(NHAC). [161°]. Formed by reduction of C.H.(NO₂).NHAc with iron and acetic acid (Nietzki, B. 17, 343). Needles, sl. sol. cold water.—B'_2H_PtCl₂.

Di-actery l derivative C₂H₁(NHAc).

[above 295°]. Formed by boiling the base with HOAc (Biedermann a. Ledoux, B. 7, €531). Small octahedra, sol. HOAc.

Behzoyl derivative C₀H₄(NH₂) (NHBz). [128°]. Formed by reducing benzoyl-p-nitro-aniline (Hübner, A. 208, 295). Plates, sl. Sol. water.—B'HCl.—B'₂H₂SO₄. Needles.

Di-benzoyl derivative C₄H₄(NHBz)₂.

[above 300°]. Formed from the base, BzCl, and NaOHAq (Hinsberg, A. 254, 254). Plates. Yields a nitro- product [251°].

o-Oxy-benzoyl derivative

C,H,(NH.)(NH.CO.C,H,OH). [158°]. Glittering

needles (Bell).

Hexahydride C.H.10(NH2)2. Di-amido-hexamethylene. Formed by reducing the di-Di-amidooxim of quinone tetrahydride in alcohol with Na (Baeyer a. Noyes, B. 22, 2172). Liquid, with faint atmoniacal odour, forming crystalline salts and an acetyl derivative melting above 310°

References.—BROMO-, BROMO-NITHO-, CHLORO-, NITRO-, and OXY- PHENYLENE-DIAMINE.

PHENYLENE-DIAMINE SULPHONIC ACID v. DI-AMIDO-BENZENE SULPHONIC ACID.

PHENYLENE-DI-AMYL-DIAMINE

[1:4] C_eH₄(NH.C₅H₁₁)₂. [49°]. Colourless crystals (Baeyer a. Noyes, B. 22, 2173).

DIPHENYLENE-AZONE C_0H_1 , N. [156°]. Formed, together with C12HN2O2 [240°] and $C_{12}H_1N_2O$ [152°] by boiling di-o-nitro-diphenyl with alcohol and zinc-dust (Täuber, B. 24, 3081, 3883). Greenish-yellow needles by sublimation, not volatile with steam. Almost ensol. water, v. sol. sleohol, m. sol. ether, v. e. sol. HOAc. Reduced by tin and HCl to $C_{12}H_{10}N$, HCl, which crystallises in white needles, rapidly reoxidised by ar to diphenylene-azone.

Salts.—B'HCl. Flat bronzed prisms.—
B'HAuCl₄.—B'₂H₄PtCl₅: yellow needles.—
B'H₂CrO₄.—B'C₆H₁N₄O₇. [194°]. Brown needles.

PHENYLENE-BENZALDEHYDINE v. vol. i.

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PHENYEENE-BENZAMIDINE v. BENZENYL-PTENTLENE-DIAMINE. Vol. IV.

PHENYLENE-DI-BENZIDENE-DIAMINE v. DI-BENZYLIDENE-PHENYLENE-DIAMINE

PHENYLENE-BENZYL-m-DIAMINE

CaH. (NH2).NHC, H,. Formed by reducing benzyl. m-nitro-aniline (Meldola a. Coste, C. J. 55, 597). Oil. -B"2HCl: hexagonal tablets. FeCl, colours its solution red and gives a white pp. on heating.

Di-bensoyl derivative C.H. (NHBz).NBz.C.H., [178°]. Sol. Tohol. Phenylene-bensyl-p-diamine. [80°]. Got by reducing benzyl-p-nitro-aniline (Meldola a. Coste, C. J. 55, 590) or p-nitroso-benzyl-aniline Costef C. J. 55, 590) or p-nitroso-benzyl-aniline (Boeddinghaus, A. 263, 302). Wax-like mass of crystals, turning red in air. When mixed with the m-isomeride it yields di-benzyl-amido-indamine on oxidation.—B'2HCl. White plates, v. sol. water. FeCl. colours its aqueous solution green, changing to red. After saturation with H.S it gives a blue pp. with FeCl.—Diagraphy desiration. [1179] Primes

Pi-acetyl derivative. [117°]. Prisms. Di-beneoyl derivative. [124°]. Needles. Phenylene-di-benzyl-diamine v. vol. i. p.

Phenylene-tetra-benzyl-m-diamine

C.H.(N/C.H.),2, [81°]. Formed by heating phonylene-m-diamine with NaOHAq and benzyl chloride. Amorphous powder, sol. IIOAc.

Phenylene-tetra-benzyl p-diamine. [149%] White crystalline powder. HOAc and CrO, form a blue-violet colouring matter.

PHENYLENE - BENZYLIDENE - DI -METHYL-DIAMINE C₁₆H₁₆N₂ i.e. C₆H₄,CH:N.C₆H₄,NMe_{...} [93³] (Calm, B. 17, 2940); [101°] (Köhler, A. 241, 361). Formed from phenylene-di-methyl-p-diamine and benzoic

aldehyde. -B"2HCl.

PHENYLENE - BENZYL - DI - METHYL -DIAMINE C.H.CH.NH.C.H.NMe. [48]. Formed by reducing the preceding body in alcohol with sodium-amalgam (Köhler, A. 241, Plates. Yields a nitrosamine [128'].

PHENYLENE-BLUE or Lauth's violet v. Amido-imido-di-phenyl-sulphide.

PHENYLENE - BROMO - ACETYLENE -KETONE v. BROMO-OXY-INDONAPHTHENE.

CH, CH.CH, DI-PHENYLENE-BUTANE Diphensuccindene. [100°]. Formed by heating (β)-di-phenyl-succinic anhydride with H1 and P and 180° (Roser, A. 247, 156). White needles.

PHENYLENE-ISOBUTYL-p-DIAMINE C.H.,NH.C.H.,NH. [39°]. Formed by reduction of p-nitroso-isobutyl-aniline (Wacker, A. 243, 299). Plates (from benzone-ligroin).

PHENYLENE - BUTYLIDENE - o - DIAMINE $C_{_{0}}H_{_{1}} < \stackrel{NH}{\sim} CHPr.$

[233°]. Formed from phenylene-o-diamino and isobutyric aldehyde (Lassar-Cohn, B. 22, 2724). Needles (by sub-limation). – B'HCl. [184°]. -B'₂H,PtCl_s.

The isomeric compound from phenylene-mdiamine melts at 216°, while that from phenylene-p-diamine is oily, and yields B',H,PtCl

DI - PHENYLENE - ISOBUTYL - QUINOX -ALINE C₆H₄,C:N>C₆H₂,CH₂Pr. [\$47°]. Formed from phenanthraquinone in HOAc and isobutylphenylene-diamine in alcohol (Gelzer, B. 20, 3256). Yellowish needles.—B'HCl: needles.

o-PHENYLENE-DICARBAMIC ETHER C.H.(NH.CO,Et)2. [88°]. Formed by heating

o-phenylene-diamine with OlCO, Et (Snape, C. J. 49, 259). Needles (from alcohol).

m-Phenylene-dicarbamic ether. [145°]. p-Phenylene dicarbamic ether. [193°]. Got by heating p-phenylene dicyanate with alcohol (Gattermann a. Wrampelmeyer, B. 18, 2605). Di-phenylene-dicarbamic acid. Eth

ether CO_Et.NH.Q.H., C.H., NH.CO_Et. [230⁵]. Formed from benzidine and ClCO_Et or by boiling diphenylene dicyanate with alcohol (Snape,

C. J. 49, 256; Schiff a. Vanni, A. 258, 369). Di-phenyl ether. [c. 240°]. Matte by heating diphonylene dicyanate with phenol at

140° (Snape). Tables, sl. sol. alcohol.
DI-BHENYLENE CARBINOL C. II. 00 i.e. С.Н.>СН.ОН. Fluorene® alcohol. Formed by reducing diphenylene ketone with sodium-amalgam (Barbier, A. Ch. [5] 7, 504). Hexagonal plates (from benzene). Oxidised by CrO, to diphenylene ketone. And at 190° forms an acetyl derivative [75°]. When heated

rorms an acetyl derivative [75]. When heated above its melting-point, diplemylene carbinol yields C₂₂H₁₈O [290°], a nearly colourless resin.

o-PHENYLENE CARBONATE CALLOGO.

[118°]. (225°-230°). Formed from sodium pyrocatechin and ClCO₂Et (Wallach, A. 226, 84). Four-sided prisms (from alcohol-benzene).

 $C_6H_4 < 0 > CO.$ m-Phonylene carbonate Formed by heating resorcin with cyanuric acid and ZnCl₂, and also by the action of COCl₂ on resorcin (Birnbaum, B. 14, 1753). Amorphous

solid, sol. HOAc. m:-PHENYLENE DICARBONIC ETHER C₂H₁(O.CO₂Et)₂. (298°-302°). Formed from sodium resorcin and ClCO₂Et in ether (Wallach, A. 226, 84). The p-isomeride, [100°], (310°), is got in like manner from hydroquinone (Bender, B. 13.697

PHENYLENE-CHLORO-OXY-ACETYLENE RETONE v. CHLORO-DI-OXY-INDONAPHTHENE. PHENYLENE - CINNAMYLIDENE -

METHYL DI AMINE C_{1,H in}N, i.e. C_{1,H in}CH::OH::OH::OH::N.O₅H₁,NMo₂. [141°]. Formed from cinnamic aldehyde and phenylene-dimethyl-p-diamine (Nuth, B. 18, 575). Needles.

methyl-p-diamine (Num, p. A., 515). Assausa PHÉNYLENE - CUMINYLIDENE - DI -METHYL-DIAMINE C, H, N, i.e. C,H,C,H,CH:N.C,H,NMe₂. [100°]. Formed

from cuminol and phenylene-di-methyl-diamine (Nuth, B. 18, 575; Uebel, A. 245, 299). Needles. 202-PHENYLENE DICYANATE CoH4(N:CO).

[51°]. Got by distilling m phenylene-dicarbamic

[91], Got by assitting m-phenylene-distribution cher (Bender, Bn. 3, 897). Crystals.

p-PHENYLENE DI-CYANATE C.II. (N:C:O)...
[91]. (231° at 745 mm. i.V.). V.D. 5.79 (for 5-54). Prepared by passing a stream of carbonyl chloride COCl. through p-phenylene-diamine hydrochloride heated to 200°-250° (Gatter-mann a. Wrampolmagar R. 18, 2604). mann a. Wrampelmeyer, B. 18, 2604). Coloure less modles less needles. Sublimable. Pungent vapour. Reacts like phenyl-cyanate, forming di-ureas with amines, and di-carbamic ethers with alcohols.

PHENYLPNE DI-CYANIDE v. Nitrile of PHTHALIC ACU

PHENYLENE ETHYL-ACETAMIDINE

 $C_eH_i < NE_N^{NE_i} > C.CH_i$. [180°]. Formed by the action of Ac.O on phenylene-ethyl-o diamine [C.H.(SO.),C.H., Formed by heating ethylen (Hompel, J. pr. [2] 39, 200; 41, 166). Plates.

PHENYLENE-ETHYL-O-BIAMINE C.H.(NH.)(NHEt). (249°). Formed by reducing o-nitro-ethylaniline with tin and MCl (Hempel, J. pr. [2] 39, 199; 41, 164). Oil,

turning red in air and light.

Acetyl derivative C.H.N.EtAc. [104°]. Phenylene ethyl-m-diamine

C, H, (NH,)(NHEt). (276° uncor.). Oil, formed in like manner (Nölting a. Stricker, B. 19, 546). B"H_Cl,: white powder.

Ehenylene ethyl-p-diamine. (270°). Oil, sol. bonzene (Nölting a. Collin, B. 17, 267; Schweizer, B. 19 149; Facher a. Hepp, B. 19, 2994; Bernthsen a. Goske, B. 20, 930).-B"II,SO,: needles or prisms.—B"H,Cl2. Plates,

v. sol. water.—B"H₂PtCl₈.
Phenylene-di-ethyl-m-diamine

C.H.(NH.) (NEt.). (277°). Formed by reducing m-nitro-di-ethyl-atfiline (N. a. Se; Groll, B. 19, 200). Gil.

Phenylene-di-ethyl-p-diamine. (261° un-cor.). Formed by reducing nitroso-diethyl aniline or C₆H₄(NEt.).N₂.C₆H₄.NEt₂ (Lippmann a. Fleissner, B. 16, 1424). Oil.—B'H.I.Cl.PtCl₄. Red crystals.—B"ZnCl, 2aq. Converted by treatment in aqueous solution with alaminium sulphate, Na₂S₁O₃, and K₂Cr₂O₇, into NEt₂.C₈H₃(NH₂).S.SO_.H [229°], whence by diazotisation $C_0H_3(NEt_2) < \frac{N_2}{S^2}$ [107°] may be got

(Bernthsen, A. 251, 1). Phenylene-s-di-ethyl-p-diamine.

Nitrosamine C,H,(NEt.NO)2. [90°]. Formed from p phenylene-diamine by successive treatment with EtBr and HNO. (Nietzki, B. 16, 465). Yellowish plates (from benzene-ligroin).

Phenylene-tetra-ethyl-p-diamine C,H₄(NEt.)₂. [52°]. (280° uncor.). Got by heating phenylene-di-ethyl-diamine or N₂(C₆H₄.NEt.)₂, with Etl (Lippmann a. Fleissner, B. 16.1427; M. 4, 301. Manoclinic plates (from dilute alcohol), a:bcc = 99:1:1-833; β = 90-30′.—B″ILPtCl.—B″ILHg.Cl. Monoclinic prischs.—B″_L:black prisus.—B″HI.—B″HI.—PHENYLENE-ETHYL BENZAMIDINE

 $C_sH_i < NE_N^{NE} > CPh.$ [81°]. Got by ethylation of phenylene-benzamidine (Howe, Am. 5, 421).— B'HCl 3aq.—B'.H.PtCl.,—B'HNO, aq. [155°].— B'EtOH [136°].—B'EtI aq.—B'EtCl 2aq.— B',Et,PtCl... B'EtHSO, aq.

PHENYLENE-ETHYLENE-o-DIAMINE

C_sH_s
 NH.CH₂ Quinoxaline tetrahydride.

 [97°]. (290°). V.D. 4.44 (calc. 4.64). Formed

by heating pyrocatechin with ethylene-diamine hydrate at 200°-210° (Merz a. Ris, B. 20, 1191). Formed also by reducing quinoxaline with alcohol and Na. Plates (from water). FeCl, colours its dilute aqueous solutions blue or violet. Alkaline K_LFeCy, oxidises it to quinoxaline.—B",3HCl. [above 150°]. Scales.—B"₂H₂C₂O₂. [184°].—B"₂2C₂H₂N₃O₂. [above 120°]. Yellow crystal.

line.pp., sl. sol. ether.

Acetyl derivative C.H.:N.Ac.:C.H...
[144°]. [350° uncor.). Granules, sl. sol. cold water Di-phenylene-ethylene-tetramine wol, ii.

p. 491. PHENYLENE-ETHYLENE-DISULPHONE bromide with potassium benzene m-disulphinate

(Otto, J. pr. [2] 36, 450). White plates, m. sol. conc. HNO...

PHENYLENE DI-ETHYL DIKETONE

C_sH₄(CO.C₂H₅)₂. [220°). Formed from terephthalic chloride and ZnEt₂ in ether (Münchmeyer, B. 19, 1850). Needles (from ether).

PHENYLENE DI-ETHYL DISULPHONE C₆H₄(SO₂Et)₂ [142°]. Obtained by heating C₆H₄(SO₂K)₂ [1:8] with EtBr at 100° (Otto, J. pr. [2] 36, 449). Colourless plates.

PHENYLENE-FURFURALDEHYDINE .v. vol. i. p. 109. .

PHENYLENE-DIGLYCOLIAC ACID v. Oxy-DIPHENYLENE-ACETIC ACID.

DIPHENTLENE-DIHYDRAZINE C12H14N4 t.e. N.H., C.H., C.H., N.H., [167°]. Formed from benzidine hydrochloride by diazotisation and reduction by Na.SO, or SnCl. (Arheidt, A. 239, 206). Small white plates, sol. hot water. Aqueous potassium cyanate forms the semicarbazide $C_{11}H_{16}N_{\circ}O_{2}$ [307°]. Nitrous acid forms a dinitrosamine $C_{12}H_{13}N_{\circ}O_{2}$ [112°]. Pyruvicacid forms $C_{11}H_{14}N_{\circ}O_{2}$ [197°]. Acetone yields $C_{11}H_{13}N_{\circ}O_{2}$ [198°], whence fusion with ZnCl. yields diphenyl-di-methyl-indole $C_{11}H_{16}N_{\circ}$ [270°]. Reference. - DI-OXY-DI-PHENYLENE DIHYDRAZ-

INE.

DIPHENYLENE-IMIDE v. CARBAZOLE. DIPHENYLENE KETONE

[83°]. (above 300°).

Formation. -1. By distilling phenanthraquinone or diphenyl di-o-carboxylic acid with CaO (Fittig a. Ostermayer, A. 166, 373; Anschutz a. Schultz, B. 9, 1400).—2. By heatoing anthraquinone with lime (Anschütz, B. 11, 1213). - 3. By dry distillation of the Ag salt of 1213.—5. By any distination of the Ag Sant of its dicarboxylic acid. (Bamberger a. Hooker, B. 18, 4034; Ar 229, 156).—4. By passing a mixture of phenol and CS₂ over hot copper (Carnelley a. Dunn, C. J. Proc. 4, 53; B. 21, 2005, who regard the product thus obtained as incompatible). isomeride).

Properties.—Yellow needles or plates (from alcohol). Yields phenyl-benzoic acid by potashfusion. Distillation over zinc-dust gives diphenylene-methane [113°] (Fittig, B. 6, 187). Forms a nitro derivative [220°] and a di-nitro-distinction [200°] (Fittig, B. 6) 202. [104]. derivative [290°] (Schultz, A. 203, 104). Alkaline KMnO, oxidises it to phthalic acid (Anschütz a. Japp, B. 11, 213). H.SO, forms at 260° a disulphonic acid, whence CaA" (Schmidt a. Schultz, A. 207, 345).

Oxim. [192°] (Spiegler, M. 5, 195).

References .- BROMO-, DI-CHLORO-, NITRO-, and

OXY, DIPHENYLENE KETONE.
DIPHENYLENE KETONE CARBOXYLIC **ACID** [1:2] $C_sH_s < \frac{CO}{2} > C_sH_s$. $CO_sH \begin{bmatrix} 1 \\ 2 \end{bmatrix}$. [192°]. Formed by oxidation of fluoranthene by chromic acid mixture (Fittig, A. 193, 149; 200, 6).

Orange-red needles (from dilute alcohol).

Reactions.—1. Potash-fusion gives diphenylom-dicarboxylic acid.—2. Yields diphenylom ketone on distillation.—3. Distillation with zincdust gives diphenylene-methane (fluorene).

Salts. - BaA', 4aq. - CaA', 2aq. - AgA'. Diphenylane ketone carboxylic acid. [above 275 . Formed by heating the dicarboxylic acid (Bamberger a. Hooker, B. 18, 1034; A. 229, 158). Pale yellow needles, sl. sol. alcohol. May be sublimed.—BaA'₂.—AgA': yellow pp. Diphenylene ketone carboxylic acid

[1:2] $C_{e}H_{e} < {}^{CO} > C_{e}H_{e}$. $CO_{e}H \left[{}^{1}_{2} 5 \right]$. [227° cor.].

Formation (Graebe, B. 13, 1303; B. 20 845; A. 247, 275).—1. From diphenyl di oozo; A. 24', 275).—1. From diphenyl dio-carboxylic acid by heating with H₂SO₄ at 120° or with POCl, or ZnCl₂.—2. By heating di-phenylene dicarboxylic acid with H₂SO₄ for 10 minutes at 150°.

Properties.—Yellow needles, v. sol. hot al-cohol. Conc. H₂SO₄ forms a red solution.

Receives.—1 Patch freque with dishard.

Reactions.—1. Potash-fusion yields diphenyl di-o-carbonylis acid.—2. PCl. (1 mol.) forms C.H. (COCI) CO [128°], which may be crystalelised from ligroin.—3. PCl_s (2 pts.) at 160° yields C₆H₄(COCl) CCl₂ [95°], which yields fluorene carbexylic acid on reduction with zincdust and dilute acetic acid. 4. Zinc-dust and ammonia reduce it to C₈H₃(CO₂H)>CH(OH).— 5. HI and P give fluorene. 6. Phenol and SnCl₄ at 120° give $C_{0}^{0}H_{1}(CO_{0}H)$ $C(C_{0}H_{1}OH)_{2}$ $C(C_{0}H_{1}OH)_{2}$ $C(C_{0}H_{1}OH)_{2}$ $C(C_{0}H_{2}OH)_{3}$ $C(C_{0}H_{2}OH)_{3$ C.H.-C₀H₂(CO₂H)>C(C₀H₂(OH)₂)₂, a yellowish-brown powder which exhibits green fluorescence in alkaline solutions.

alkaline solutions.

Salts. — NH₄A' aq. — NaA' 6aq: yellow needles, v. sol. hot water.—AgA': yellow pp.

Methyl ether MeA'. [132°]. Needles.

Ethyl ether EtA'. [103°]. Needles.

Chioride C₁₄H,ClO₂. [128°].

Amide C₁₄H,(NH₂)O₂. [225°]. Silky yellow needles (containing hOEt). Formed from the chloride, and also by heating phenanthraquinone monopoxim with H₂SO₄ at 100° (Wegerhoff, B. 21. 2357). 21, 2357).

Oxim C₁₄H,(CO₂H)(C:NOH). [263°].

Phenyl-hydrazide C₁₄H₂(CO₂H)(C:N₂HPh). [205°]. yellow prisms, m. sol. alcohol.

Diphenylene ketone dicarboxylic acid C_eH_s CO $C_eH_c(CO_2H)_z$ $\begin{bmatrix} 1\\23:6 \end{bmatrix}$. Formed by oxidation of retene-quinone and of oxyisopropyldiphenylene-ketone carboxylic acid (Bamberger a. Hooker, B. 18, 1033; A. 229, 151). Yellow needles (from HOAc). Not melted at 270°, but loses CO, at a higher temperature. Yields diphenyl on heating with CaO. Potash-fusion forms diphenyl tricarboxylic acid.—BaA".—

Ag.A": yellow pp. Methyl ether Me,A". needles.

Ethyl ether EtA". [115°]. Needles. Oxim C12Ha(CO2H)2:C(NOH). Yellow pp., not melted at 250°

DIPHENYLENE KETONE OXIDE

 $CO < \stackrel{C_uH_1}{C_uH_1} > 0$. Xanthone. [174°]. (350°) at 730 mm. (Graebe, A. 254, 280). S. (alcohol) .7 in the cold; 8.5 at 78°.

Formation .- 1. Obtained by oxidation of $CH_{2}C_{2}H_{4}>0$ with CrO_{3} and HOAc (Me z a.

Weith, B. 14, 192) .- 2. By the dry distillation of salicylide; the yield being 35 p.c. of the theoretical (Perkin, B. 16, 339). -3. By distilling phenyl phosphate with sodium m- or p-oxybenzoate (Richter),—4. By the action of POCI, on potassium-salicylate of ethyl.—5. By distilling neutral or basic sodium salicylate with P₂O₅.—6. In small quantities, when salicylic acid is distilled.—7. By strongly heating sodium o-chlorobenzoate.—8. From sodium o-phenyl-benzoate and POCl₂.—9. To the amount of 12 p.c. of the theoretical quantity, by the action of o-chlorobenzoyl chloride on basic sodium salicylchlorobenzoyl chloride on basic socium sancyinate.—10. By the action of cone. H_SQ, on 11:2] QH_QOPh_CO_H (Graebe, Z. 21, 563).—11. By distilling phenyle salicylate (Seiffert, J. pr. [2] 31, 479).—12. By heating salicylic acid (1 mol.) with PCl, (1 mol.), then adding phenol and distilling (Klepl, J. pr. [2] 28, 217.—13. By distilling calcium p-oxy-benzoate Gold-sheriet M A 1981—14 A mothet of the elecschmidt, M. 4, 128).-14. A product of the electrolysis of a solution of phenol in KOHAq at 200° (Bamberger a, Berlé, B. 24, 3212).

Preparation.—1. Phenyl phosphate (20 g.) and sodic salicylate (20 g.) are distilled together; a violent action ensues; when it is over the residue is distilled over at 400°, best in a current of air. The crude product is shaken with solu-tion of NaOH and distilled with steam. The residue is extracted with alcohol, from which, on cooling the ketone crystallises (R. Richter, J. pr. [2] 28, 276).—2. By distilling salicylic acid with Ac₄O, the salicylide which is first formed splitting off CO2 when the temperature rises (Perkin, C. J. 43, 35). In this process there is formed a by-product $C_{14}H_{\pi}O_{3}$ [192°] which is converted by boiling alcoholic potash into an acid C14H,O4 [275°] (A. G. Perkin, C. J. 43, 187).

Properties.—Long white needles, grouped concentrically. M. sol. ether, alcohol and benzoline, more sol. benzene and chloroform, insol. water. The solution in conc. H.SO shows blue fluorescence (Graebe, B. 15, 1679). Does not react with hydroxylamine or phenyl-hydrazine (Spiegler, B. 17, 808).

Reactions.—1. Reduced by zinc-dust or by HI to CH₂ C_cH₄ O [100.5°] but no further.—

2. Potash-fusion converts it into salicylic acid and phenol.—3. If the fusion be stopped when the mass is pasty (at about 200°), dissolved in water and ppd. by HCl, di-oxy-benzophenone is obtained, CO(C_aH₁OII)₂—4. Sodium-amalgam reduces the di-phenylene-ketone oxide (in dilute alcoholic solution) to C₂.H₁₈O₃ [200°]. This body crystallises from CHCl₃ in prisms. It is split up by chromic acid into di-phenyleneketone oxide and diphenylene methane oxide, so that it is perhaps a molecular compound of these two bodies. - 5. Bromine at 200° forms a fibromo- derivative [212°]. — 6. Furning H.SO. gives a disulphonic acid which forms BaA" aq,

A product of the action of POCl, on sodium salicylate (Richter, J. 2r. 12). 28, 294). Formed selective Richter, J. 2r. [2] 28, 294). Formed selective Richter, J. 2r. [2] 28, 294). Formed selective Richter, J. 2r. [2] 28, 294). also by heating the sulphate of o-diazobenzoic o acid with phenol (Griess, B. 21, 981). Needles, .v. e. sol. ether. Yields diphenyl on distillation | Needles, sl. sol. cold alcohol, v. e. sol. CHel.

with zinc-dust. Br gives C, H, BrO, [1980]. H.SO, yields a disulphonic acid, which gives BaA"aq crystallising in needles.

Dixanthone • C₆H₄ < O_{CO} > C₆H₂ < O_{CO} > C₆H₄.

[256°]. Occurs in the product of the action of salicylic acid on resorcin (Kostanecki a. Seidmann, B. 25, 1654). It crystallises from HOAc in groups of needles, and its solution in H.SO. shows greenish fluorescence.

eReferences. - DI-AMIDO-, NITRO-, and Oxv-

DI THENYLENE RETONE OXIDE.

PHENYLENE MERCAPTAN v. DI-THIOBESORCIN BUILD DI-THIO-HYDROQUINONE.

Diphenylene mercaptan C.H.(SH).C.H.(SH). [176°]. Formed by diazotising benzidine, and treating the product with potassium xanthate and alcoholic petash successively (Leuckart, J. pr. [2] 41, 212; cf. Gabriel, B. 13, 390). White plates (from alcohol).

Di-methyl ether $\text{Me}_2\text{A''}$. [184°]. Plates. Di-ethyl ether $\text{Et}_2\text{A''}$. [135°]. Plates. 00-DIPHENYLENE-METHANE v. FLUOR-ENE.

(9) - Diphenylene - methane CH₂ C₀H₁.

Methylene-diphenyl. [118°]. (295° uncol.). V.D. 84 (calc. 83). Occurs, together with the (8)immeride, among the products of the passage of a mixture of benzene and toluene through a red-hot tube (Carnelley, C. J. 37, 708). Pearly plates (from alcohol), sl. sol. cold alcohol, v. sol. ether. . Its alcoholic solution shows faint blue fluorescence. CrO₃ and HOAc oxidise it to $C_{13}H_{\gamma}O_{2}$ [281° cor.]. Bromine in ether gives $C_{13}H_{\gamma}B_{T_{2}}$ [162°]. Pieric acid forms a compound $C_{13}H_{\gamma}G_{2}H_{\gamma}N_{2}O_{\gamma}$ crystallising in blood-red needles relief

(3)-Diphonylene-methane $C_{13}H_{10}$ [205°]. (320°). V.D. 86.2 (cala 83). Formed as above. Pearly plates (from alcohol). Oxidised by CrO3 in HOAc to C12H3O2 [2889 cor.] which sublimes in white needles.

DIPHENYLENE-METHANE OXIDE

 $\text{CH}_2 < \frac{\text{C}_8 \text{H}_4}{\text{C}_8 \text{H}_4} > \text{O}$ [100°]. (315° cor.). Formed, to the amount of 2 p.c., in the preparation of Ph.O by heating phenol with AlCl, (Merz a. Weith, B. 14, 191). Formed also from di-Wetti, B. 12, 121). Formed also from diphenylenc ketone oxide by heating with fuming HIAq at 160° or by distilling with zinc-dust (R. Richter, J. pr. [2] 28, 280; Graebe, A. 254, 282); and by distilling envanthone over heated zinc-dust (Wichelinaus a. Salzmann, B. 10, 1399; Graebe a. Ebrard, B. 15, 1678). White plates (from alcohol).

plates (110m alconol).

Reactions.—1. Oxidised by CrO₂ or dilute
HNO₃ to diphenylene ketone oxide.—2. PCl₁
'forfis HCl and a product whence water at 0°
produces C₁₁H₂O.PO(OH), [255°-260°] an acid
forming Ag,A" and (NH₁),A".—3. Br forms
C₁₂H₂Br₂O and C₁₃H₃Br₂O [136°].

DIPHENYLENE - METHANE SULPHIDE CH, C, H, S. [128°]. (342°). Formed by reducing CO $\stackrel{\text{C}_{\circ}H}{\stackrel{\text{C}_{\circ}H}{\stackrel{\text{N}}{\sim}}}$ S with HI and $\stackrel{\text{P}}{\text{P}}$ at 170°; and also by passing phenyltolyl sulphide through a red-hot tube (Graebe a. Schultess, A. 263, 12).

DIPHENYLENE - METHANE SULPHONE CH CH SOr [170°]. Formed by heating CO C.H. SO, with HI and P at 170° (Graebe a. Schultess, A. 263, 15). Needles, v. sol. hot

PHENYLENE-METHENYL-AMIDINE

 $C_{\bullet}H_{\bullet} < NH > CH$. [167°]. (above 360°). Formed by boiling phenylene-o-diamine with formic acid (Wundt, B. 11, 826; Fischer, B. 22, 645). Trimetric crystals (from alcahol).-B'HCl aq. Yields on methylation C,H,N, [33°] (278° at 730 mm.).

Carboxyfic acid $CO_2H.C_eH_3 < NH > CH.$ Formed by reducing the formyl derivative of (2.1.4)-nitro-amado-benzoic field (Zehra, B. 23, 3634). White needles, blackening without fusion when heated.—HA 'HCI: white needles.

***m - PHENYLENE - METHYL - DIAMINE**

[1:3] C.H. (NH2).NHMe. . Methyl - phenylene diamine. •Amido-methyl-aniline (265°-270° uncor.). Formed by reduction of m-nitromethyl-aniline (Nölting a. Stricker, B. 19-548). Oil. Gives a methyl-chrysoïdine with diazo-benzene chloride.

p-Phenylene-methyl-diamine

[1:4] C,H,(NH,2)(NHMe). (258° uncor.). Formed by reduction of p-nitroso-methyl-aniline (Fischer, B. 19, 2992) or of C₆H₄(NHMe).N₂.C₆H₄.SO₃H₄ (Bernthsen a. Goske, B. 20, 929). Oil, v. sol. water. FcCl, gives a red colour, which on successive treatment with HCl and H.S becomes blue (dimethylthionine). - B'2H2SO4: white needles (from water).

m-Phenylene-di-methyl-diamine

[1:3] C_aH₁(NH_a)(NM_{e.}), (269°) at 740 mm. S.G. ²³ 995 (Groll, B. 19, 200); (258°) (Staede a. Bauer, B. 19, 1945). Formed by reduction of m-nitro-di-methyl-aniline. Oil. With nitrous acid it yields a colouring-matter closely resembling Bismarck brown. With diazobenzene effloride it yields a di-methyl-chrysoïdine which dies a somewhat redder shade than chrysoïdine. PbO₂ and aqueous HOAc gives a yellowish-brown colour (Lauth, C. R. 11, 975).—B'HCl. Acetyl derivative C₈H₄(NMe₂)(NHAc).

p-Phenylene-di-methyl-diamine [1:4] C₆H₄(NH₂)(NMe₂). [41°]. (257° i.V.). 11:19 U_nH₁(NM_c) [41"]. (257° i.V.). Prepared by reduction of nitroso-di-methyl aniline and of (C₀H₁NM_c)₂N₂O by tin and HCl (Schraube, B. 8, 616; Wurster, B. 12, 522; Weber, B. 10, 760). Prepared also by reduction of C₀H₁(NM_c)₂N₂O₂H₄(SO₂H₄(E. Fischer, B. 16, 235.6) 2255). Formed also together with di-chloro-pphenylene-diamine and di-chloro-p-phenylene-di-methyl diamine by boiling nitroso-di-methyluniline with HCl (S.G. 1.2) (Möhlau, B. 19, 2010).

Properties.—Long white needles or short prisms, v. sol. water, alcohol, and ether. PbO₂ and aqueous GOAc give a magenta-red solution changing to violet-black (Lauth, C. R. 111, 975).

colours wood, and paper made from wood, erimson (Wurster, B. 20, 808).

Reactions.—1. Yields quinone on oxidation with MnO and H.SO,—2. Bromins in HOAc forms C,H11N2Br, which crystallises from its red

alcoholic solution in green scales [146] (Wurster a. Sendtner, B. 12, 1803).-3. H₂S and an oxidising agent (e.g. FeCl.) gives methylene-blue (v. vol. ifi. p. 265). Methylenered S₂ $\stackrel{C_aH_3}{N}$ NMe₂CP is a by-product (Bernthsen, A. 230, 137; 251, 1).—4. Na₂S₂O₃ and CrO, give C.H. (NMe.) (NH.) S.SO.H, which yields methylene-blue on further oxidation. 5. Aldehydes and ketones form products of condonsation, e.g. C.H. (NNc.), N:CHPh (937) (Calm, B. 17, 2939), C.H. (NNe.), N:CH.C.H. (0H [1:2] [1342], and C.H. (NNe.), N:CH.C.H. (OMe [1:4] [134°], and C_aH₄(NMe₂).N:CH₄C₃H₄OMe [1:4] [148°] (Nuth, B. 18, 574; Steinhart, A. 241, 344). Benzil and alcoholic KOH form CPhBz:N.C_aH₄NMe₂ [139°]; benzoyl-acetone forms in like manner CH₄Bz,CMe:N.C_aH₄NMe₂ (136°] (Vogtherr, B. 25, 635). Benzoin gives CHPh(OH).CPh:N.C_aH₄Ne₂ [127°] on heating, while deoxybenzoin forms C₂₇H₂₂N₂ [139°].— 6.0Cxalic coher forms, on heating, the ether C_aH₄(NMe₂),NH.CO.CO₂Et [117°] which yields California (192°) and amide [259°] (Sendther, B. 12, 530).
Salts.—B"2HCl. Very deliquescent plates.
—B"H_SnCl. Cubes.—B"H_PtCl.,
Actyl derivative CaH_(NMe_)(NHAc).

[130°]. (855°). Small leaflets or needles.

p-Phenylene-tri-methyl-diamine [1:4] C₆H₄(NMe₂)(NMeH). (265°). Obtained by reduction of its nitrosamine, which is formed by the action of nitrous acid on p-phenylene-tetramethyl-diamine (Wurster a. Schobig, B. 12, 1809). Oil.

Acetyl derivative. [95°]. Prisms. Nitrosamine CoH4(NMe2)(NMe.NO). [99°]. Leaflets or tables, sl. sol. cold water.

m-Phenylene-tetra-methyl-diamine [1:3] C_aH₄(NMc₃)₂. [-2°]. (266° i.V.). S.G. ¹²
992. Prepared by heating phenylenc-m-diamine with methyl alcohol and HCl at 190° (Wurster a. Morley, B. 12, 1814). Purified by distilling with Ac₂O (Romburgh, R. T. C. 7, 2). Oil, sl. with Ac₂U (Romburgh, R. T. C., 1, 2). OII, si. sol. water. HOAc and nitric acid give C₈H(NO₂),N₂Me₄NO [132°]. s-Tri-nitro-benzene forms B"C₈H₄(NO₂), [121°] m.Di-nitro-benzene gives B"C₈H₄(NO₂), [158°] crystallising in needles. Bromine forms oily C₈H₄(NO)(NMe₂), which forms a hydrochloride B'HCl, crystallising in Jeck red needles (Witt R 18 R77) dark-red needles (Witt, B. 18, 877).

Salts.—B"H,Cl, 2aq: hygroscopic crystals. B"H,FeCy, aq. Pearly plates (Wurster a. -B"H, FeCy, aq. Roser, B. 12, 1826).

Methyliodide B"Mel. [192°]. Crystals. v. sol. water .- B"MeHI2.

Di-methylo-di-iodid B"Mc,I, Plates, v. sol. water (Hofmann, Pr. 12, 639).

p-Phenylene-tetra-methyl-diamine [1:4] C₀H₄(NMe₂)₂. [51°]. (260° i.V.). Prepared by heating p-phenylene-di-methyl-diamine with MeOH and HClAq at 200° (Wurster, B. 12, 526, 1803, 1827). White leaflets, sl. sol. cold water, v. sol. alcohol. Its aqueous solution becomes violet-blue on exposure to air ar addition of oxidising agents. The blue substance appears only to exist as a salt, e.g. C.H. NMe, Cl NMe, Cl NMe - CH, (Wurster, B. 19, 3195; 20, 256; 21, 921). It becomes colourless on further oxidation.

Reactions .- 1. Bromine in HOAc forms a

blue colouring matter C, H, N, which forms blue solutions in water and alcohol.—2. K, FeCy, added to a solution of the sulphate forms C₁₆H₁₄N₂2H₄FeCy₆ crystallising in lustrous blue needles. — 3. Sodium nitrite and hydrochloric needles. — 5. South series and hydrodanacid give C.H. (NMs.) (NMe.) (N EMO.) [98°] at C.H. (NO.) (NMs.) NMe.NO [87°].

Salts.—B"2HCl; crystals.—B"H_2PtCls.

B"2H_5O..—B"H_FeCys: white needles. [98°] and

Methylo-iodides B"Mel. [above 270°]. Leaflets (W.).—B"Me₂L. Plates (Hofmann). Reference. - NITRO-PHENYLENE-DI-METHYL-DI-AMINE.

PHENYLENE - DI - METHYL - DI - AMINE SULPHONIC ACID C,H,(NH,)(NMe,).SO,H. Got by reduction of p-nith-di-methyl-amido-benzene sulphonic acid (Michler a. Walder, B. 14, 2176). Large rhombohedra, v. sol. water. BaA' - CaA' : plates.

-PHENYLENE-DI-METHYL-DI-ETMYL-DIAMINE C.H. (NMe.) (NEt.). (2672). Formed from [1:4] C.H. (NEt.) (NH.). McOH, and HCIAq at 200° (Lippmann a. Fleissner, M. 4, 791). Liquid. Coloured blue by oxidising agents.

Methylo-iodide B"2Mel. [218°]• Yields B"Me₂PtCl_e, B"Me₂AuC B"Me₂(C₄H₂N₃O₇)₂ [235°]. B"Me2AuCl, B"Me2CdI,

o-PHENYLENE - METHYL - ETHYLENE -DIAMINE C.H. NII C.H. v-Methyl-quin-

exaline tetrahydride. (274°). Formed by heating phenylene-ethylene-diamine with MeI at 110° (Ris, B. 21, 381). Liquid. Its aqueous solution is coloured blue by FeCla.

Methylo-iodide B'MeI. [above 200°]. Crystals.—B',Me,PtCl. Yellow needles.

DIPHENYLENE - METHYL - FURFURANE C.H..C.O.CMe. Got by reducing C.H., C(OH).CH, Ac (Japp a. Klingemann, B. 21, 2932).

PHENYLENE - DI - METHYL - DI - MALONIC **ACIDS** C.H. $(CH_1,CH(CO_1H)_2)_T$ The ethers of these acids are formed by the action of zincdust on the acids $C_4H_1(CH_2,CCl(CO_2Et)_2)_2$ which are formed from sodium chloro-malonic ether and a-di-bromo-xylenes (Perkin a. Kipping, C. J. 53, 16; B. 19, 437; 21, 36). The o- and methers are oily, the p- ether is crystalline [51°]. The ethers form deliquescent sodium derivatives Na₂C₂₂H₂₂O₂, and the o-compound of this formula is converted by iodine into the tetrahydride of naphthalene tetracarboxylic ether. The macid is a liquid v. sol. water, the p-acid is crystalline [1959]. The p-acid forms Ag,A", and when heated splits up into CO, and C,H,(CH,CH,CO,H), [223°].

PHENYLENE - METHYL - METHENYL -AMIDINE C.H. $\langle N_N^{Me} \rangle$ CH. [33°]. (278°) at Formed from phenylene-methenylamidine, Mel, and McOH at 100° (O. Fischer, B. 22, 644). Prisms.—B'HAuCl., Needles.

DIPHENYLENE-METHYL-PYRAZINE C_4H_1 C.N:CMe C_4H_4 C.N:CH . [128°]. Formed from phenanthraquinone and propylene-diamine (Strache, B. 21, 2362). White needles.—B'_*H_PtCl_*.

p-p-DIPMENYLENE. TETRA. METHYL. DI. PYRROLE Ca.H. N. i.e. CH:CMe N.C.H.C.H.N CMe:CH •[150°]. Got by heating an alcoholic solution of acetonylacetone (2 mols.) and henzidine (1 mol.) (Paal a. Schneider, B. 19, 3158). Colourless tables. Sol. alcohol, ether, benzene, and ligroin.

DIPHENYLENE-METHYL-QUINOXALINE $C_{2i}H_{1i}N_{2}$ i.e. $C_{o}H_{1}Me < \stackrel{N:C.C_{o}H}{N:C.C_{o}H}$. [213°]. Formed from (1,3,4)-tolylene-diamine and phenanthraquinone in HOAc Hinsberg, B. 17, 323). Yellow hair-like crystals, v. sol. benzene.

DIPHENYLENE - NAPHTHOQUINOXAL . INE $C_{io}H_{\bullet} < \stackrel{N:C.C_oH_{\bullet}}{N:C.C_oH_{\bullet}}$. [273°]. Formed by boiling an alcoholic solution of (1,2)-naphthylene diamine with phenanthraquinone in HOAc (Lawson, B. 18, 2426). Small yellow crystals.

The sulphonic acid, got by mixing a hot

aqueous solution of naphthylene-o-diamine sulphonic acid with phonanthraquinone dissolved in NaHSO, Aq with addition of NaOAc, forms a yellow crystalline Na salt, sol. hot water, but ppd. By alkalis (Witt, B. 19, 1719, 2701). When fused with KOH it yields the insoluble eurhodol $C_{12}H_s < N > C_{10}H_s(OH) \begin{bmatrix} 1 \\ 2 \end{bmatrix}$, which forms a scarlet hydrochloride.

m - PHENYLENE - DI - (β) - NAPHTHYL -DIAMINE C.H.(NHC,,H), [126]. Formed by heating m-phenylene-diamine with (8)-naphthol (Ruhemann, B. 14, 2651). Felted needles, sol. alcohol and ether.

needles, sol. alcohol and collection.

p.Phenylene-di-(β)-naphthyl-diamine
C_sH_s(NHC₁₀H_s)... [235°]. (over 400° in vacuo). Collection of the collect plates, almost insol. boiling alcohol, v. sol. nitro-benzene. KNO₂ added to its solution in conc. H., SO, gives a egreenish wickt colour, changing to blue, B'2C, H., N,O. [c. 217].

Acetyl derivative C, H., (NAc. C, eH.), [210]. Plates (from benzene).

0°]. Plates (from benzede).

Benzoyl derivative C₂₂H₁₄Bz₂N₂. [220°]. Reference. - NITRO-PHENYLENE-NAPHTHYL-DI-

AMINE. PHENYLENE - NAPHTHYLENE - AMINE

C₁₈H₁₁N i.e. [1:2] C₈ H₁ NH. Phenyl-naphthyl-carbazole. [3:3] C₁₉H₂ NH. Phenyl-naphthyl-(35) S. (alcoh.l.) 25 at 78°; S. (toluene) ·5 at 111° (Bechi, B. 12, 1978). Occurs in crude anthracene, from which it may be got from the residues after sublimation of the anthracene (Graebe a. Knecht, B. 12, 341, 2242; A. 202, 1). Formed by passing phenyl- (β) -naphthyl-amine through a red-hot tube. Colourless plates, v. sl. sol. HOAc. Its solutions show blue fluorescence. Oxidation by K2Cr2O, and H2SO, forms the Oxidation by $n_{\rm cons}$ NH [307°] which crystallises from HOAc in reddish-yellow needles, and is accompanied by $C_{\rm is}H_{\rm io} > 0$ which crystallises from benzene in red prisms. 0

Moetzeld derivative C₁₈H₁₂NO. [121°]. Nitrosamine C₁₈H₁₈N₂O. [210°]. Tetrahydride C₁₈H₁₈N. Formed Formed by reduction with HIAq and P at 210°. Syrup. B'HI. Long needles.

Theaylene-naphthylene-amine

[1:2] C, H NH. [225°]. Formed by heating SCO H NH with reduced copper at 240° (Kym, B. 23, 2465). Greenish-yellow plates, sl. sol. cold benzene, v. sol. hot alcohol.

PHENYLENE - NAPHTHYLENE - RETONE

oxide CO CoH O. [155°]. Formed by boiling (a)-naphthy salicylate (Graebe a. Feer, B. 19, 2612). Formed also by heating (a)-naphthol with salicylic acid and HOAc; and by distilling (1,2)-(α)-naphthol carboxylic acid with salicylic acid (Kostanecki, B. 25, 1643). Crystals, sl. sol. cold alcohol. Its solution in H2SO4 shows green. Converted by potash-fusion into fluorescence. Converted by potash-fusion into o-(α)-di-oxy-phenyl-naphthyl-ketone (Phomina,

A. 257, 92) Isomeride. [140°]. Formed in like manner from (β)-naphthyl salicylate; and by heating (2.1)-(8)-naththol carboxylic acid with salicylic Needles. Reduced by zinc-dust acid.

CH. C. H. O. [80°].

p. PHENYLENE-DI (3) - NAPHTHYL - DI -METHYL DIAMINE C₄H₁(NMe.C₁₀H₁)... [180°]. Formed from C₄H₄(NHC₁₀H₁)... MeI, and Me⊕li at 140° (Rueff, B. 22, 1080). Plates.

PHENYLENE - NAPHTHYLENE C, H, O. [178°]. Formed by distilling a mixture of phenol and (a)-naphthol with PbO (Arx, B. 13, 1726; A. 209, 141). Yellow needles, sl. sol. alcohol. H.SO, forms a tetrasulphonic acid which gives Ba₂C₁₆H₄S₂O₁₇4aq. CrO₃ and HOAc form C₁₆H₄O₂ [140°].—C₁₆H₄O₂C₂H₄N₃O_. [165°].

Isomeride C₁₆H₁₉O. [296°] (A.); [300°] (G. a. K.). Formed in tike manner from (β)-

naphthol (A). Got also by distilling the compound C₁₀H₂O₃ (from phenylene-naphthylene-amine) with zmc-dust (Graebe a. Knecht, A. 202, 15). Plates x. sol. toluene.

References.—DI-BROMO-, DI-GRIGORO-, and DI-

NITRO- PHENYLENE-NAPHTHYLENE OXIDE.

PHENYLENE OXIDE C.H.O? [103°]. A product of the distillation of o-oxy-benzoic acid (Märker, A. 124, 249). Silky needles (from alcohol). HNO, yields the nitro-compound C₆H₃(NO₂)O [150°].

Diphenylene oxide $C_{12}H_{0}O$ i.e. $C_{0}H_{4}>0$. [87°]. (283°) (Galewsky, A. 264, 188).

Formation.—1. By distilling Ph.PO, over lime, MgO, or PbO (Lesimple, A. 138, 375; Hoffmeister, Z. [2] 7, 24; A. 159, 211; Kreysler, B. 18, 1720).—2. By distilling phenol (2 pts.) with PbO (3 pts.) (Behr a. Dorp, B. 7, 398; Graebe, A. 174, 190).—3. By distilling Ca(OPh), (Niederhäusern, B. 15, 1120).-4. By the action of red-hot lime on di-phenylene-ketone oxide.— 5. One of the products of the action of HCl on mucic acid at 150°

Properties.—White plates (from accohol).

Converted by AscCl into CH₂.CO.C.H. O [81°], which yields an oxim [146°] and a phenyl-hydraxide [133°]. H₂SO₄ forms a deliquescent disciphonic soid, which yields BaC₁₂H₂S₂O₇ aq.

Picric soid compound C,H,OC,H,N,O, [24°]. Yellow crystals (Goldschmiedt a. Schmidt, M. 2, 14).

References.—Amido-, Brono-, Tevra-chloro-, Di-todo, Dinitro- Phenylene oxides.
o-PHENYLENE - OXY - BENZAMIDINE

 $C_{\bullet}H_{\bullet} < \stackrel{NH}{N} > C.C_{\bullet}H_{\bullet}.OH.$ [223°]. Formed by reducing salicyl-o-nitro-aniline with tin and HCl (Mensching, A. 210, 345). Needles.—B'HCl ad-B'H, SO, 4aq. Needles, sl. sol. Aq. o-PHENYLENE-PHENYL-DIAMINE. The

sulphonic acid which gives the barium salt sutphonic acta which gives the parium sate BaA', 2aq may be got from its amiliale [12:4] C_a[0.5,NHPh](NH₂).SO₂NHPh [157°] which is got by reduction of C_aH (NHPh)(NO₂).SO₂NHPh, and yields B'HCl [182°] (Fischer, B. 24, 3794).

p-Phenylene-phenyl-diamine
C_aH (NHPh).NH₂. Amido-diphenylamine. [67°]

and [75°]. (354°). - 1. By reduction of nitrodiphenylaraine (Nietzki a. Witt, B. 12, 1401). From p-nitreso-diphenylamine by boiling with alcoholic potash, by reduction with tin and HCl (Ikuta, A. 243, 279), or by treatment with phenyl-hydrazine in ether (O. Fischer, B. 21, 2615). 3. Together with azophenine, by heating p-nitroso-diphenylamine with aniline and aniline hydrochloride (O. Fischer a. Hepp, B. 20, 2480). 4. By reducing C₆H₄(NHPh)N₂C₆H₄SO₂Na (Hess a. Bernthsen, B. 18, 692).

Properties.—Plates or needles, sl. sol. water, v. sol. alcohol. Melts at 75° after crystallisation from ligroin. FeCl, added to a solution of its salts gives a red colour, turned green by excess. Yields quinone on oxidation.

Sult.—B'.H.SO. Plates.
Nitrosamine C,H.H.N.O. [c. 130°].
Acetyl derivative C,H.N.O. [158°].
Bensoyl derivative (Lellmann, B. 15,

Sulphonic acid.
[1:£2]C_aH_a(NHPh)(NH_a).SO₃H. Formed by reducing C_aH_a(NHPh)(NO_a).SO₃H (Fischer, B. 24, 3800). Yields Bah', aq and an anilide [171°], which gives B'HCl [215°].

m-Phenylene-di-phenyl-diamine C_oH₁(NHPh)₂. [95°]. Formed by heating resorcin (2 mols.) with aniline (2 mols.), CaCl₂ (8 mols.) and NnCl₂ (1 mol.) for 35 hours at 210° (Calm, B. 16, 2702). Flat needles, v. sol. ether. Oxidising agents give a green colour passing to bluish violet. Amyl nitrite and alcohol HCl form the p-nitroso-derivative C₁₈H₁₈N₂O, crystallising in brown-red prisms and yielding B"2HCl (Fischer a. Hepp, A. 255, 145). B"2HCl: needles decomposed by water.

Acetyl derivative C₄H₄(NPhAc)₂. [163°]. Benzoyl derivative C₄H₄(NPhBz)₂. [184"].

Nitrosamine C.H.(NPh.NO). Yellow needles, forming a violet solution in

H.SO., p.Phenylene-di-phenyl-diamine C_sH.(NHPh)_p. [132°] (Bandrowgki, M. 8, 475); [141°] (Limpricht, B. 22, 2910); [145°] (O. Fischer, B. 21, 2615); [152°] (Calm, B. 16, 2803). Formed by heating hydroquinone (5 pts.) with aniline (17 pts.), CaCl, (20 g.), and ZnCl, (5 g.) for 18 hours at 210°. Formed also by the action of phenyl-hydrazine on nitroso-diphenylamine in alcohol, and from the hydrochloride ! of amido-salicylic acid and aniline. Plates, v. sol. hot benzene. . HNO, added to its solution in H.SO, gives a blue liquid, changing to red.— B"2HCl: needles, decomposed by water.

Acetyl derivative C.H. (NPhAc). [192°]. Bensoul derivative C.H. (NPhBz).

Nitrosamine C18H14N4O2. [c. 120°].

Phenylene-di-phenyl-diamine C,H,(NH₂),NPh₂. Formed by reducing nitro-tri-phenyl-amine (Herz, B. 23, 2537). Crystalline. -B'HCl: silvery needles.

Acetyl derivative CoH4(NHAc).NPh2.

o-Phenylene-Phenyl-guanidine

C,H, NH>C:NPh. [1903]. (440°-450°).

Formed by heating phenylene o-diamine with di-phenyl-cyanamide at 215° (Keller, B 24, 2499). White needles (from benzese) or prisms (from alcohol). Phenyl-cyanate forms the compound NPh CO N2(CNPh) CH4. [266°]. B'HCl.—B'2H.PtCl.—B'H.SO4: long needles.

Mono-acetyl derivative. [160].

Di-benzoyl derivative. [171]. Needles. PHENYLENE - DI - PHENYL DIHYDRAZ. Rexahydride C6H16(NH.NHPh), Formed by reducing the di-phenyl-dihydrazide of quinone with sodium and alcohol (Baeyer a. Noyes, B. 22, 2175). Crystalline, sl. sol. alcohol.—B'H₂C₂O₁ aq.
m-PHENYLENE DI-PHENYL DIKETONE

C₆H₄(CO.C₆H₅)₂. Isophthalophenone. [95°] (M.); [100°] (A.). (above 360°). Formed from isophthalyl chloride, benzene, and AlCl₃ (Ador, Bl. [2] 33, 56; B. 13, 320; Münchmeyer, B. 19, 1848). Plates (from alcohol). Yields a monooxim [201°] (Nölting a. Kohn, B. 19, 146), a dioxim [70°-75°], and two di-nitro-derivatives [260°] and [c. 100°

p-Phenylene diphenyl diketone C_aH₄(CO.C_aH₄)₂. [160°]. Formed from terephthalic chloride, benzene, and AlCl₄ (M.). Yields a dioxim [235°].

Diphenylene di-phenyl diketone C₁₂H₈(CO.C₆H₅)₂. [218°]. Got from diphenyl, BzCl, and AlOi₃ (Wolf, B. 14, 2031). Crystals.

DIPHENYLENE-PHENYL-METHANE

 $C_{19}H_{14}$ i.e. $C_{C_8}H_{1}$ CHPh. [145.5°]. Formed by the action of P.O. or AlCl. on a mixture of benzene and diphenylene-carbinol; and also by heating CPh,Cl at 200° (Hemilian, B. 11, 202, 837; Bl. [2] 34, 325). Formed also in small quantity in the distillation of calcium benzoate or phthalate (Kekulé, B. 5, 910; Miller, B. 12, 1489). Needles, sl. sol. ether. Yields o-benzoylbenzoic acid on oxidation.

Reference.—DI-BROMO-DI-PHENYLENE-PHENYLE METHANE.

ν - m - PHENYLENE - DI - PHENYL - DI -METHYL-DI-PYRROLE DI. CARBOXYLIC-

FTHER C₂,H₂,O₄N₂ i.e.

CO₂Et.C:CMe

N.C₂H₁,N

CMe:C.CO₂Et

CPh;CH

Obtained by mixing together in acetic acid solution acotophenone-aceto-acetic ether (2 mols.) and m-phenylene diamine (1 mol.), and allowing the mixture to stand a long time (Paal a. Schneider, B. 19, 8161). Slender white

pyrrole di-carboxylic-ether C₄₀H₄₂O₄N₂ i.e. CO_Et.C:CMe N.C.H C.H C.H C.CO_Et HC:CPh N.C.H C.H C.H C.H.

[179]. Obtained by mixing together in acetic acid solution acetophenone-aceto-acetic, ether (2 mols.) and benzidine (1 mol.), and allowing the mixture to stand for a long time (P. a. S.). Hais like needles. Sol. alcohol and acetic acid,

v. sol. ether, chloroform, and petroleum-spirit.

p-PHENYLETE-TETRA-PHENYL-DI. PYRROLE DICARBOXYLIC ACID

CO₂H.C:CPh N.C₆H₄.N CPh:C.CQ₂H [above 300°]. Formed by saponification of its ether [250°] which is got from phenocyl-benzoylaccic ether and phenylene p diamine (Paal a. Braikoff, B. 22, 3095). Small grains.

m-PHENYLENE IN-PHENYL SULPHONE C₆H₁(SO₂Ph)₂. [191°]. Formed by heating benzene with P₂O₃ and benzene madisulphonic acid or di-phenyl sulphone m-sulphonic acid (Otto B. 19, 2421; 20, 185). Minute needles (from HOAc). Alcoholic potash at 170° forms O(C,H,SO,Ph), [70°] and C,H,SO,K.

Di-phenylene di-phenyl trisulphone $S\odot_2(C_aH_a,SO_2C_aH_a)_2$. [193°]. Formed from $SO_2(C_aH_a,SO_3H)_2$, benzene, and P_2O_a at 200° (Otto a. Rössing, B. 19, 3127).

PHENYLENE-DI-PHENYL-DI-THIO-DI-UREA C.H.(NH.CS.NHPh) alcohol (Lellman a. Würthner, A. 221, 28; 228, 200). The o- and p- compounds are decomposed by heat into di-phenyl-thio-ures and phenylene-thio-urea; the on- compound melts at 161°, and the o- isomeride at about 290°s. They are insol. ether.

m-PHENYLENE-DI-PHENYL-UREA C.H.(NH.CO.NHPh), Formed from m-phenylene-diamine and phenyl cyanate (Kühn, B. 18, 1478). Amorphous.

PHENYLENE-PROPENYL-DIAMINE

 $C_sH_s < NII > CEt.$ [169°]. (above 360°). Got by boiling o-phenylene-diamine with propionic acid (Wundt, B. 11, 829), and by reducing propionyl-o-nitro-aniline with tin and HOAc (Smith. Am. 6, 172). Plates (from water).—B'HCl.— B'HgCl₂.—B'₂H₂PtCl₈ 2aq.—B'₂H₂Cr₂O₇.

PHENYLENE-DI-PROPIONIC ACIDS C.H. (CH., CH., CO, H), Formed by heating C.H. (CH., CH. (CO, H), (Perkin a. Kipping, C. J. 53, 8, 32; B. 21, 27, 40). The o-acid [162°] forms Ag.A". The m-acid [147°] forms Me.A" [61°] and Et.A" (250° at 60 mm.). The p- acid [224°] forms Ag₂A" and Me₂A" [115°].

p.PHENYLENE-PROPYL-DIAMINE C.H.(NH.)(NIIPr). (281°). Got by reducing p-nitroso-propyl-aniline with SnCf. (Wacker, A. 243, 294). Plates.—B"2HCl. Plates, v. e. sol. Aq. o-PHENYLENE-PROPYLENE-DIAMINE

C_sH₄<NH>C₅H₆. [72°]. (28%). Formed by beating pyrocatechin with propyleng-diamine at 200° (Ris, B. 21, 382). Plates (from ligroin).

—B'_3HICl.—B'_2C_H_3N_O. Thin needles.

DIPHENYLENE-PYRAZINE. Dihydride C₁₆H₁₂N₂ i.e. C₆H₁,C.N.CH₂ Formed phenanthraquinone phenanthraquinone and ethylene-(Mason, B. 19, 112; 20, 267),—B',H.,PCl. ethylene-diamine (a)-PHENYLENE-BERIDYL-KETONE

C.H. CO.C.CH:CH. [141°]. Formed by dis-

tilling the dicarboxylic acid $C.H.O < \stackrel{().C(CO.H):CH}{C.N} > \stackrel{().C(CO.H):CH}{C.O.H} > [284°]$, which is formed by oxidising (a) styryl-(β)-naphthoquin-oline carboxylic acid (Doebber a. Peters, B. 23, 1241). Yields a picric acid compound [1972]. The dicarboxylic acid yields Ag₂A''. 1241).

[197°]. The dicarboxylic acid yields Ag,A".

(8) Phenylene-pyridyl-ketone

C₆H, CO,C. N. CH

CH, CO,C. N. manner from the corresponding dicarboxylic acid [264°] which is got by oxidising (a)-styryl-(a)-naphthoquinoline garboxylic acid with KMnO, Needles. Yields B'.H.PtCl, 2a_I. The dicarboxylic acid forms Ag,A' as a p.p. arboxylic acid forms Ag.A" as a pp.

PHENTLENE - QUINOLYLENE KETONE

OXIDE $C_{16}H_{9}NO_{2}$ i.e. $O< \stackrel{C_{6}H_{4}}{C_{9}H_{5}N}> CO$. Pheno-• quinoxanthone. [188°]. Formed by distilling p-oxy-quinoline with salicylic acid. (from alcohol).—B'HCl: needles. Needles

DIPHENYLENE QUINOXALINE C20H12N2 i.e. C₆H₁,C.N C₆H₄, [217°]. Got from phenylene-

o-diamine and phenanthraquinone (Hinsberg, A. V. sl. sol. alcohol. 237, 340),

DIPHENYLENE-STYRYL-OXAZOLE

C.H. C.N C.CH:CHPh. [172°]. Formed from phenanthraquinone, cinnamic aldehyde, and alcoholic NH₃ at 100° (Wadsworth, C. J. 57,

11). •Yellow needles.

p-PHENYLENE •DISULPHIDE C.H.S.. p-rheat least distinct of the solution of the solution of the solution (Lenckart, f. pr. [2] 41, 206). Chars without melting at 300°, incole ordinary solvents. Is reduced by former with could be solvents.

fusing with potash to dithiohydroquinone.

Diphenylene sulphide C.H. S. [97°]. (333°
î.V.). Formed by passing Ph₂S through a redhot tube (Stenhouse, A. 156, 332; Graebe, A.
174, 185). Needles, m. sol. alcohol. Yields on oxidation the sulphone C₁₂H₈SO₂ [230°].

Diphenylene - disulphide $C_sH_4 < S > C_sH_4$ [154°]. (366°). A product of the distillation of sodium benzene sulphonate (Stenhouse, Pr. 17, 62; A. 149, 252). Formed also by heating phenol with P.S. (Graebe, A. 174, 185; 179, 178), by heating benzene with S and AlCl., at 80° (Friedel a. Crafts, A. Ch. [6] 1, 550; 14, 439), and by heating C.H. (No. 1) N (Jacobson a. Elley R. 22, 210). Prisms (from CS.). Conc. Elley, B. 29, 910). Prisms (from CS₂). Conc. H₂SO₄ forms a purple solution. CrO₂ in HOAc gives the Sulphone C₁₂H₁₈S₂O₄ [325°] and the sulphoxide C₁₂H₁₈S₂O₄ [241°], sl. sol. cold benzene. Br forms C₁₂H₁₈S₂D₄ erystallising from CS₂ in a coll block witness

alcohol at 100° (Gabriel, B. 10, 184). Needles. v. e. sol. hot alcohol. Yields a nitro- compound

C.H.(NO.)(SCN), [150].
DIPHENYLENE SULPHONE v. DIPHENYL-ENE SULPHIDE.

DI-PHENYLENE SULPHONE KETONE

 $C_oH_i < SO_2 > C_oH_i$. [185°]. Formed by heating benzophenone with fuming H.SO, (Beckmann, B. 6, 1112; 8, 992), and by oxidising C.H. CO. C.H. (Graebe a. Schultess, A. 268,

Yellowish needles, v. sol. alcohol.
PHENYLENE DITHIOCARBAMIC ETHERS

o- compound [56°], m- compound [58°] (250°), and p- compound [130°] all crystallise in needles.

m-PHENYLENE - DI - THIO - DIGLYCOLLIC
ACID C.H.(SCH.,CO,H), [127°]. Formed from di-thio-resorein and ClCH,CO,H (Gabriel B. 12, 1639). Microcrystalline powder. Diphenylene-di-thic-di-glycollic koid

 $C_{12}H_8(S.CH_2.CO_2H)_2$. [252°]. Formed from $C_{12}H_8(SH)_2$. NaOHAq, and chloro-acetic acid (Gabriel, B. 13, 390).

o-PHENYLENE-THIO-URBA

 $C_sH_s{\stackrel{
m NH}{\sim}}CS$. [298°]. Formed by heating o-phenylene-diamine hydrochloride with am monium sulphocyanide and water at 180 (Lellmann, B. 15, 2146; A. 221, 9). Formed also from o-phenylene-diamine and CSCl. (Billeter a. Steiner, B. 20, 231). Plates (from dilute alcohol, sl. sol. water). The crystalline m-isomeride is got by heating m-phenylene-di amine with CS, and some alcohol at 150° (Gucci G. 17, 524). The p-isomeride melts at 271°. Phenylene-di-thio-di-ureas

C.H.(NH.CS.NH2)2. C_sH₄(NH.CS.NH₂)₂, m. [215°]. p. [220°] Formed by heating phenylene-diamine hydro chloride with ammonium sulphocyanide (Lell mann, A. 221, 11; B. 15, 28409. The p-compound is also formed from p-phenylene dithiocarbimide and alcoholic NH, (Billeter a. Steiner, B. 20, 230).

C.H.NH>CS. Diphenylene - thio - urea [238°]. Formed by heating di-op-amido-diphenyl with alcohol and CS2 (Reuland, C. J. 58, 167; B. 22, 3014)

o-PHENYLENE-TOLENYL-AMIDINE

 $C_eH_4Me.C \leqslant_N^{NH} \gt C_eH_4$. [268°]. Formed from o-phenylene-diamine and p-toluic chloride, and also by reduction of p-toluyl-o-nitro-aniline (Hübner, A. 210, 328; of. Brückner, A. 205, 115).

Hudner, A. 210, 528; cf. Bruckner, A. 200, 115).

Prisms (from alcohol).—B'H.Cl.—B',H.PtCl.—B'HNO,.—B',H.SO,: slender needles.

PHENYLENE-DI.-p.TOLYL.-n.-DIAMINE

C.,H.SN, i.e. C.,H.(NH.C.,H.Me).. [187°].

Formed by heating resorcin with p-toluidine,

ZnCl., and CaCl. (Hatschek a. Zega, J. pr. [2]

33, 218). Needles. Yields a di-nitrosamine

C. H. N.O. (c. 15°). a discatal derivative. CS, in small black prisms.

m-PHENYLENE SULPHOCYANIDE

C.H.(SCN), [54]. Formed by heating the lead salt of di-thio resoroin with ICy and C., H₁, N₁O₂ [c. 150°], a di-acetyl derivative C.H.,Ac.N., [1760], and a di-benzoyl derivative

Carlaber, [165], and a di-benzyl derivative Carlaber, [152].—B"2HCl; crystalline powder, decomposed by water.

Flemylene-di-o-tolyi-p-diamine [135]. (420°). Formed by heating hydroquinone with o-toluidine and CaClast 290° (Philip, J. pr. [2] 34, 65). Plates (from HOAc). Yields a di-benzylene [140°] Yields C. H. R. N. [235°]. [4] 64, 69. Plates from HOAC. Fields & dinitrosamine [140°]. Yields C₂₀H₁₆Bz₂N₂ [235°] and C₂₀H₁₆Ac₂N₂ [189°].—B"2HCl: needles. Phonylene-di-p-tolyl-p-diamine. [182°].

Formed by heating hydroquinone or phenyl-pamido-phenol with p-toluidine and ZnCl₂ at 220° (H. a. Z.); Calm, B. 16, 2810). Plates. Yields a di-nitrosamine [152°], a di-acetyl derivative [178°], and a di-benzoyl derivative [222°].—B"2HCl.

PHENYLENE-TOLYLENE-KETONE OXIDE

C.H. CO C.H.Me. Methyl-xanthone. [105°]. Formed by boiling p-tolyl salicylate (Graek a. Feer, B. 19, 2612; of. Scilert, J. pr $\P[2]$ 31, 479).

Isomeride $C_0H_4 \subset {}^{\circ}O_0$ $C_0H_0M_0$ $\begin{bmatrix} 3\\4 \end{bmatrix}$, $\begin{bmatrix} 16\\6 \end{bmatrix}$, $\begin{bmatrix} 16\\6 \end{bmatrix}$

Made by heating C₀H₃Me(OH)CO₂Ph [49°] (Weber, B. 25, 1745). Crystals (from algohol). o-PHENYLENE-p-TOLYL-GUANIDINE

C.H. C:N.C.H.Me. [209°]. Formed by heating o-phenylene-diamine with di-p-tolyl-cyanamide at 210° (Keller, B. 24, 2509). Tables. Yields a mono-acetyl derivative [152°], a dibenzoyl derivative [191°], and a nitrosamine $C_{14}H_{12}(NO)N_3$ [150°-160°]. Phenyl cyanate forms, C₆H₆N < CO N₂(C₆H₄):C:NC₆H₄Me [254°] crystallising from benzene in small needles. Di-p-tolyl-cyanamide at 210° forms the compound (NHC,H,)₂C:N₂(C₆H₄):C:N.C₆H₄Me [188°]. Salts.—B'HCl.—B'₂H₂PtCl₆.—B'₂H₂SO₄

DIPHENYLENE-TOLYL-METHANE C.OH16 i.e. C.H. CH.C.H.Me. [128°]. Formed by the action of P2Os on a mixture of diphenylenecarbinol and toluene, or of AlCl, on diphenylenecarbinyl chloride dissolved in toluene (Hemilian, B. 11, 203; Bl. [2] 34, 325). Silky needles.

PHENYLENE-DI-p-TOLYL-DI-METHYL-m-DIAMINE C₈H₄NMe.C₈H₄Me)₂. (c. 400°). Got by heating phenylene-di-p-tolyl-m-diamine with MeI and KOH at 150° (Hatschok a. Zega, J. pr. [2] 33, 223). Liquid smelling like geraniums.

The isomeric phenylene di-o-tolyl-di-methyl-p-diamine (385°-390°) and phenylene-di-p-tolyl-di-methyl-diamine [153°] may be prepared in like manner (Philip, J. pr. [2] 34, 57; H. a. Z.).

o-PHENYLENE-UREA C_eH₄<NH>CO.

[308°]. Formed by heating o-amido-phenyl-carbamic ether at 90° (Rudolph, B. 12, 1296), by Würthner, A. 228, 220), by heating its ethyl derivative with HCl (Sandmeyer, B. 19, 2654), and by the action of COCl2 in toluene on a solution of o-phenylene-diamine hydrochloride at 100° (Hartmann, B. 23, 1046). Leaflets, sl. sol. water.—B'HCl. Decomposed by water.

Ethyl derivative C.H. NH C.OEt. [160°]. Formed from o-phenylene-diamine and NH:C(OEt). Plates.

m-Phenylene-ures. Spore 500'l. Formed by similar methods (Michler a Zimmermann, B. 14, 2177; L. a. W.). Insoluble powder, ^Q
p. Phenylene-urea. [above 320°]. Got by

heating p-amido-di-phenyl-urea (L. a. W.). Isomeride. [130°]. Got by boiling an alcoholic solution of oxy-phenyl-thio-ures with HgO

(Bendix, B. 11, 2264). Tables, sol. water. Phenylene - di - ureas C₀H₄(NH.CO.NH₂)₂[290°]. · m- [above 300°]. Formed from phenylene-diamine hydrochloride and potassium cyanate in cold aqueous solutions (Warder, B. 8, 1180; Lellman, A. 221, 13; B. 16, 592). The p-compound can be heated to carbonisa tion without melting.

References .- AMIDO- and NITRO- PHENYLENE-

PHENYL-ENNOIC ACID.

G_aH₁₀C₃N₃Ph₂. [c. 38°]. (c. 293° at 15 mm.). Formed from decoic chloride, benzonitrile, and AlCl, (Krafft a. Koenig, B. 23, 2384).

PHENYL-ENNYL-THIO-UREAC, H. N. St.e. NHPh.CS.NHC, H19. [60°]. Formed from ennylthiocarbimide and aniline (Freund a. Schönfeld,

B. 24, 3359). Tables, v. sol. alcohol and ligroin.

PHENYL-ENNYL-UREA C₁₆H₁₂CN₂O i.e.

NHPh.CO.NHC₆H₁₈. [63°]. Formed from NHPh.CO.NHC₉H₁₉. [63°]. Formed from phenyl cyanate and aniline in alcohol (Freund a. Schönfeld, B. 24, 3358). Long prisms. s-DI-PHENYL-ETHANE CHH i.e.

CH_Ph.CH_Ph. Dibenzyl. Mol. w. 182. [53°]. (277°). S.V.S. 174·2 (Schiff, A. 223, 261). H.F. - 31,200. H.C.v. 1,828,300. H.C.p. 1,830,200 (Berthelot a. Vieille, Bl. [2] 47, 866).

Formation .- 1. By the action of Na on benzyl ehloride (Cannizzaro a. Rossi, At 121, 250; Fittig, A. 137, 257).—2. From ethylene chloride, benzene, and AlCl₂ (Silva, C. R. 89, 606; A. Ph. S. 18, 345).—3. From CHBr:CHBr, benzene, and AlCle (Anschütz, A. 235, 155). 4. From acctylene, benzene, and AlCl. Varet a. Vienne, Bl. [2] 47, 919).—5. By heating benzyl chloride with copper powder (Onurovitch, B. 17, 833).—6. A product of the action of Na on o-bromo-benzyl-bromide (Jackson a. White, Am. 2, 390). -- 7. By adding sodium (70 g.) to an alcoholic solution of phenyl-cinnamonitrile (Freund Remse, B. 23, 2859).

Properties.-Lung colourless needles, sol. alcohol, ether, and CS,

Reactions .- 1. Yields toluene and di-phenylethylene when passed through a red-hot tube (Otto, Z. [2] 6, 22; A. 154, 176; Barbier, C. R. 78, 1769).—2. Chlorine passed into fused s-diphenyl-ethane forms first CHPh:CHPh and then C.H.CI.CH:CH.CH.CH. (Rade, J. pr. [2] 19, 466). C.H.(C.CH.CH.C.H.(C. (Rade, J. pr. 12) 19, 400).
In presence of I, chlorine forms p-di-chloro-diphenyl-ethane in the cold. Exhaustive chlorization yields C.Cl. and C.Cl. (Merz & Weith, B.
16, 2877).—3. H.SO, forms a disulphonic acid
C.H.(SO,H), 5aq, which 'yields K.A'' 2aq,
BaA'' åaq, and PbA'' aq (Kade, B. 6, 958). A
tetra-sulphonic acid, C.H.(SO,H), 3aq, is also
formed. formed.

u-Di-phenyl-ethane CH₈.CHPh₂. (270°) (0.); (286°) (H.). Formation.-1. From CCl, CHPh, alcohol, and Na (Goldschmiedt, B. 6, 1501) .-- 2. From CH.Ph.CH.Br, benzene, and zinc-dust (Radzis-zewski, B. 7, 140).—8. From paraldehyde, benzene, and H.SO. (Bacyer, B. 7, 1190).—4. Together with ethyl-benzene and di-methyl-anthracene dihydride by heasing ethylidene chloride with benzene and AlCl. (Silva, Bl. [2] 41, 418; Anschütz, B. 17, 160).—5. By distilling its dicarboxylic acid (Haiss, B. 15, 1481).

Properties.—Oil, with blue fluorescence.

Solidities in a freezing mixture. Yields benzo-phenone on oxidation. Fuming HNO, added to pnenone on oxidation. Furning HNO, added to its solution in ROAc folius benzophenone, CPh_(OH), CH_2O.NO₂ [107°], di-phenyl-vinyl nitrite [87°], and a body [148°] which yields diphenyl-acetenitrile on reduction (Anschütz a.

Romig, A. 233, 329).

Tri-fhonyl-ethane CH.Ph.CHPh. (above 360°). Formed from CH.Cl.CHCl.OEt, benzene, and AlCl. (Waas, B. 15, 1128). Liquid, with violet fluorescence. Insol. cold alcohol.

s-Tetra-phenyl-ethane C₀₂H₂, i.e. CHPh₂-CHPh₂, Mol. w. 334. [210°]. S. (benzene) 14 at 80°. S. (95 p.c. alcohol) '8 on boil-

Formation.-1. By distilling benzoyl- and * succinyl- di-phenyl-carbinol and by distilling diphenyl-carbinol with succinic acid (Linnemann, 1. 133, 24).—2. By distilling benzophenone with zinc-dust (Staedel, B. 6, 1401).—3. By reducing benzpinacone CPh₂(OH).CPh₂(OII) with HI and P (Graebe, B. 8, 1055).—4. From di.phenyl-carbinol, glacial HOAc, conc. HClAq, and zinc (Zagumenny, A. 184, 176; BL [2] 34, 329).—5. By reducing (β)-benzpinacolin CPh₃.CO.C₆H₃ with HI and P (Zincke a. Thörner, B. 11, 67).— 6. By boiling (CHPh₂)₂S₂ with alcohol and copper powder (Engler, B. 11, 926).—7. By reducing CPh2:CPh2 (Friedel a. Balsohn, Bl. [2] 33, 388).—8. From CHIPI, Cl and Na (Engler).
9. By the action of benzene and AlCl, on CBr, CH, Br, on CHBr, CHBr, on CPhHBr, CHBr, on CPhBr. CPhBr., and on CHPhBr.CHPhBr, the yield in the last case being excellent (An-schütz, A. 225, 196).—10. By distilling CPh, HCl (Anschütz, A. 235, 220).

Properties .- Needles (by sublimation), sl. sol. alcohol. Crystallises from benzene with C.H. Yields a crystalline tetra-nitro-derivative, a crystalline tetra-sulphonic acid, which gives

Ba₂A¹ and C₂₅H₁₈(OH), [248°].

u-Tetra-phenyl-ethane CPh, CH, Ph. [140°]. Formed from CPh, K and benzyl chloride (Hanriot, C. R. 108, 1119).

References .- AMIDO-, BROMO-, BROMO-AMIDO-, DI-BROMO-DI-NITRO-, CHLORO-, PENTA-CHLORO-DI-MTRO-, NITRO-, and OXY-, PHENYL-ETHANES.

PHENYL-ETHANE DICARBOXYLIC ACID v. CARBOXY-PHENYL-PROPIONIC ACID and Prienyl-BUCCINIC ACID.

Phenyl-ethane tricarboxylic acid CHPh(CO,H).CH(CO,H),. [171°]. Got by sa ponifying its ether, which is made by the action ponitying its etner, which is made by the action of a-chloro-or a-bromo- phenyl-actic ether on sodium malonic ether (Spiegel, A. 219, 31; Alexander, A. 258, 71). Small tablets, v. sol. hot water. Decomposed on fusion into CO₂ and phenyl-succinic acid. Salts.—Ca₂A''', 10aq. Ga₂A''', 5aq. ppd. from aqueous solution by alcohol—Ag₂A'''; erystalline pp.

Ethyl ether Et.A". [46°]. (202° at 10 mm.). Needles (from dilute alcohol).

Di-phenyl-ethane o-carboxylic acid C_{la}H₁,O₂
i.e. C.H.,CH.,C.H.,CO.H. [131]. Formed
by the action of HI and P & 200° on isobenzylidene-phthalide, and on deoxybenzoin
carboxylic acid (Gabriel, B. 11, 1019; 18, 2440). Tablets (from dilute alcohol) .- AgA': pp.

Isomerides v. DI-PHENYL-PROPIONIC ACID. Di-phenyl-ethane di-o-carboxylic acid C₁₈H₁₁O₂• i.e. CO₂H.C₂H₄.CH₂.CH₂.C₄H₄.CO₂H. [186°] (H.) • [229°] (D.).

Formation.—1. By heating diphthalyl with HI and P (Grache, B. 8, 1055).—2. By the action of HI and phosphorus on the acid CO Co. CH. CH.CH.C.H.(CO.H. (Wislicenus, B. 17, 2181; Hasselbach, A. 243, 254), and on

diphthalylic acid (Dobreff, A. 239, 66).

Properties.—Small needles, v. sol. alcohol and dilute WOAc. KMnO, in alkaline solution forms diphthalylic acid [263°]. Distillation over soda-lime forms s-di-phenyl-ethylene.

Salts.—(NH₁),A" (dried at 100°),—CaA' (at *100°),—BaA".— Cu₂A"O.—Pb₂A"O.—Zn²A"O.—AgHA".

Methyl ether Me₂A'. [101°].

**Ethyl ether Et₂A''. [71°]. Converted by alcoholic NH, into the amic ether C₂H₄(C₆H₄,CO₂Et)(C₆H₄,CONH₂) [0. 67°].

Di-phenyl-ethane dicarboxylic acid C₄H₂CH₂CH₃CO₂H₃CO₂H₄ [1:2]. [154°]. (above 300°). Formed by heating the nitrile with conc. HCl at 220° (Eichelbaum, B. 21, 2082). Small prisms, sol. alcohol, insol. ether.

Nitrile C.H. CH. CH(CN).C.H. CN. [110°]. (above 300°). Formed from benzyl chloride and [1:2] C.H. (CN). CH. CN. Plates, insol.

water, alkalis, and acids. Amide. [221°]. Formed by the action of conc. H.SO, on the nitrile. Converted by conc. HC (S.G. 1.19) at 100° into the imide

 $C_uH_4<_{CO-NII}^{CH(C_1H_1)}>_{CO}[176^\circ]$ (above 300°).

Di-phenyl-ethane di-carboxylic acid CH₃CH(C₆H₁,CO₂H)₂. [275°]. Got by heating the tri-carboxylic acid (Haiss, B. 15, 1481). Long needles. May be sublimed.—CaA".

Isomeride v. DI-PHENYL-SUCCINIC ACID. Di-phenyl-ethane tri-carboxylic acid

CO.H.CMc(C₆H,CO₂H).. [255°]. Formed by oxidation of di-a-tolyl-propionic acid with KMnO₄ (Haïss, B. 15, 1479). Sol. alcohol and ether.—Ag₂HA'".—Ag₃A'".

Di-phenyl-ethae tri-carboxylic acid
C₁,H₁,O₂ i.e. CHPh(CO,H).CPh(CO,H).
A mide CHPh(CO,H).CPh(CO,H).CONH.

[190°]. Got from CHPh(CO,Et) CPh(CN).CO,Et [105°] which is got by heating a-chloro-phenylacetic ether with alcoholic KCy on a water-bath (Poppe, B. 23, 114).

Mono-nitrile CO.H.CHPh.CPh(CN).CO.H. The ethers Me.A" [101'] and Et. " (v. supra) are got from a [101] and Et. " (v. supra) are got from a-chloro-phenyl-acetic acid and KÖy in MeOH or EtOH. Conc. H.SO, converts Et. A" into CO Et. CHPh. CPh (CO. Et). CONH 1 [157] crystallising in aggregates of needles.

References.—Nitho- and Oxx- Di-Phen't-

PHENYL-ETHENYL-AMIDINE v. PHENYL-

PHENYL - ETHENYL - AMIDO - PHENYL -MERCAPTAN C., H, NS i.e.

 $C_*H_* <_S^N > C.CH_*Ph.$ Formed by heating phenyl-acetic chloride with o-amido-phenyl mercaptan (Hofmann, B. 13, 1234). Oil, sol. alcohol and ether. On fusion with potash it yields phenyl-acetic acid and amido-phenyl mercaptan B'HCl.—B',H.PtCl, 5aq: heedles, PHENYL-ETHENYL-AMIDOXIM C,H, N,O

i.e. C₆H₂CH₂C(NOH).NH₂. Phenyl-acetamid-oxim. [67°]. Got by heating phenyl-acetooverm. [07]. Got by heating phenyl-aceto-nitrile with a solution of hydroxylamine, in dilete alcohol (Knudson, B. 18, 1968, 2482). Thin prisms, v. sol. water. Converted by phenyl cyanate into C.H., C.H., C.(NH.CO.NHPh):NOH-[123°].—B'HOI. [155°]. White prisms. Acetyl derivative. [124°]. Plates.

Benzoyl derivative C,H,C(NOBz).NH2. [144]. Prisms, v. sol. alcohol.

[58°].

Ethyl other C,H,C(NOEt).NH₂.

Converted by potassium cyanate CH_Ph.C(NOEt).NH.CO.NHPh [148°]. into Bensyl ether. [55°]. Prisms.

Phenyl-ethenyl-amidoxim CH₃.C(NOH).NHPh. [121°]. Formed by heat-thioacetic anilide with hydroxylamine solution at 100° (Müller, B. 22, 2408; cf. Nordmann, B. 17, 2746). Satiny plates, v. sol. alcohol. FeCl, gives a violet colour, changing to olive green and, on heating, to red.—B'HCl: needles. -B'-H.PtCl.: vellow needles.

Bensoyl derivative C.H.,(NOBz).NHPh.
0°]. White needles (from dilute alcohol).
PHENYL-ETHENYL-AZOXIM V. AZOXIMS.
PHENYL-ETHENYL-DI-ETHYL-TRI-SUL-

PHONE CH. C(SO₂Et)₂(SO₂Ph). [109°]. Got by oxidation of CH₂.C(SPh)(SO₂Et)₂ (Laves, B. 25, 364). Needles, v. sol. alcohol.
TRI-PHENYL ETHENYL TRISULPHQNE

CH.,C(SO,Ph), [182]. Formed by the action of alcoholic NaOH, and MoI on CH(SO,Ph), Got also by oxidation of CH₂,C(SPh), by KMnO₄ (Laves, B. 25, 352). Needles, v. sol. CHCl₃.

DI-PHENYL-ETHENYL-DI-UREA

NHPh.CO.N:CMe.NH.CO.NHPh. [169°]. Formed by adding aqueous NaOH (2 mols.) to an aqueous solution of acetamidine hydrochloride (2 mols.) shaken with phenyl cyanate (1 mol.) (Pinner, B. 23, 2923). Needles, m. sol. alcohol. Converted by boiling dilute (50 p.c.) acetic acid Converted by boiling didde (so p.o., access doing into accety-phenyl-urea [189°].

PHENYL ETHER v. Dr.-PHENYL OXIDE.

C-PHENYL-ETHYL ALCOHOL C.H.10 i.e.

OH, CHPh.OH. Mol. w. 122. (203°). S.G. 1-013. Formed from CH, CHBr.C. H, by successive treatment with AgOAc and NaOH (Radziszewski, B. 7, 141; Berthelot, Z. 1868, 589). Got also by reducing acetophenone with sodiumamalgam (Emmerling a. Engler, B. 6, 1005). Yields an acetyl derivative C₈H₉OAc (217°-220°) which yields styrene on treatment with alcoholic potash.

Ethylether C.H.OEt. (186°). S.G. 22 931. Formed from CH, CHBr.C.H, and alcoholic NH, at 100° (Thorpe, Z. 1871, 131).

B-Phenyl - ethyl alcohol CH_Ph.CH_OH.

Bensyl-carbinol. (212°). S.G. 21 1034. Formed
by reducing phenyl-acetic aldehyde with sodiumforms the corresponding C2H_Ph_NH.CS NHPh

amalgam (Radziszewski, B. 9, 373). Oil. As.O at 150° converts it into an acetyl derivative C_sH₂OAc, (224°), S.G. 1·029. PHENYL-ETHYL-ALLOPHANIC ETHER

C₁₂H₁₆N₂O₃ i.e. C₈H₉.NH.CO.NH.CO₂Et. [106° Formed from phenyl-ethyl-urea and ClCO.Et (Neubert, B. 19, 1825). Needles (from water). PHENYL-ETHYL-ALLYL-GUANIDINE

PHENYL-ETHYL-ALLYL-GUANDINK CL2H., N. i.e. CN3,H_PhEt(C,H_). Formed by boiling ethyl-allyl-thio-urea with NHPh.HgCl and shoohol (Forster, A. 175, 41).—B'HgCl, aq. BHENYL-ETHYL-ALLYL-THIO-UBEA NH(C,H_).CS.NPhJ. [c. 26°]. Formed from allyl-thiocarbinide and ethyl-aniline (Gebhardt, B. 17, 180-180). B. 17, 3037). Colourless very soluble crystals. PHENYL-ETHYL-ω-AMIDO-ACETOPHEN-

ONE C16H17NO i.e. C6H3.CO.CH2.NPhEt. [95°]. Formed from ω -bromo-acetophenone and diethylaniline (Weller, B. 16, 26). Needles, PHENYL ETHYLAMIDO - ETHYL SUL-

PHONE C.H., SO., C.H., NHEL Formed from C.H.(SO, C.H.), and ethylamine at 85° (Otto, 7. pr. [2] 30, 337).—B'HCl. [130°]. Needles. PHENYL-ETHYL-AMIDO (a) NAPHTHO

QUINONE C₁₀H₃(NPhet)O₂ [155°]. Formed by heating (a)-naphthoquinone (2 pts.) with ethyl-aniline (3 pts.) and HOAc (5 pts.) (Els-bach, B. 15, 1810). Violet needles (from alcobach, B. 15, 1810). Violet needles (from alcohol,—19 HCl. [c. 230°]. Yellow needles, decomposed by water.

Phenyl - ethyl - amido - (β) - naphthoquinone. [165°]. Formed by heating (β)-naphthoquinone with ethyl-aniline and alcohol (Elsbach, B. 15, 691). Dark-red needles (from ether). Decomposed by boiling HClAq into ethyl-aniline and oxy-naphthoquinone.

PHENYL-ETHYL-AMIDO-PHENOL. Ethyl ether CushioNO i.e. NPhEt.CaH .OEt. (319"). Formed by heating phenyl-p-amido-phenol with alcoholic potash and Eti (Philip a. Calm, B. 17, 2434). Oil.

a.PHENYL-ETHYL-AMINE C.H., N i.e., CH., CHPh.NH., (187.5° i.V.). S. 4'166 at 20°. Formed by reducing the phenyl-hydrazide or the oxim of accophenone in alcoholic solution with HOAc and godium amalgam (Tatel, B. 19, 1999; 22, 1856; Kraft, B. 23, 2783). Formed also from acetophenone and sodium formate (Leuckart a. Janssen, B. 22, 1413). Liquid, miscible with alcohol and ether.—B'HCI, [158°]. -B'₂H₂PtCl_a.-B'₂H₂SO₄. [170°].-B'₂H₂CO₄. [238°]. Prisms, almost insol. alcohol.—B'H₂C₂O₄. Plates, m. sol. boiling alcohol.

Isomerides : - AMIDO-PHENYL-ETHANE ETHYL-ANILINE.

Di-phenyl-ethyl-amine C₁H₁N i.e. NPh_.Et,
Ethyl diphenylamine. (296°) (Girard, Bl. [2]
23, 3); (286°) (Lippmann a. Fleissner, M. 4,
727). Got by heating diphenylamine with
alcohol and HClAq. Oil.
Di-phenyl-ethyl-amine CHPh₂CH₂NH₂.

Formed by reducing di-phenyl-acetonitrile in alcohol with Na (Freund a. Immerwahr, B. 23, 2845). Oil.—B'HCl. [255°], V. sol. water. Di-phenyl-ethyl-amine CH.Ph.CHPh.NH. (310°) at 737 mm. Formed by heating deoxybenzoin (1 pt.) with ammonium dormate (2 pts.) at 225° (Leuckhart a. Janssen, B. 22, 1409). [170°]; while phenyl cyanate gives the com-

[170]; while pienyl cyanate gives an compound C.H.Ph.,NH.CO.NHPh [120].—B'H.Cl.,—B'H.NO,: needles.—B'H.SO,.

**Actyl derivative. [148°]. Needles.

**Benzoyl derivative. [178°]. Needles.

**Diphenyl-di-ethyl_mine NH(CH_CH_Ph),.

[336° at 603 mm.). Formed, together with NH_CH_CH_Ph and N(CH_CH_Ph), by the exting of give and HCHaq on paryl agenticities. action of zinc and HClAq on phenyl-acetonitrile (Spica, G. 9, 567). Formed also by distilling CH_Ph.CH_NH_Cl (Fileti a. Piccini, G. 9, 294). Liquid, sl. sol. water.—B'HCl. [270°]. Pearly scales.—B',H,PtCl, m. sol. water.
Tri-phenyl-ethyl-amine CPh,.CH,.NII,.

phenyl-acetonitrile (Spica, G. 9, 567). Oil.— b'HCl. [138°]. Needles, sl. sol. water. PHENYL-ETHYL-ARSINE v. vol. i. p. 321. PHENYLETHYL-TRIAZOLE CARBOXYLIC

ACID N.NPh C.CO.H. [145°]. saponifying its nitrile (Bladin, B. 18, 1548; 25, 176). Melts at 123° when crystallise from water or alcohol, but at 145° when crystallised from benzene.—B'HCl: plates.—CuA'₂ 33aq.— AgA': crystalline pp.

Methyl ether MeA'. [41°].

Ethyl ether EtA'. Oil.

Nitrile C₁₁H₁₀N₄. [38°]. Formed by the action of propionic anhydride on phenyl-hydrazine dicyanide. Converted by alcoholic NH, and H,S into C,N,PhEt.CS.NH, [150°] which crystallises in yellow prisms.

C,N,PhEt.CO.NH, Amide Formed from the nitrile, alcoholic potash, and

H.O., Small prisms, sl. sol. water.

De PHENYL-DI-ETHYL-DITRIAZYL

C. H. S. C. No. C. Formed by boiling phenyl-hydrazine dicyanide with propionic anhydride (Badin, B. 22, 3115). Groups of prisms.—B"2HCl: minute prisms, decomposed by water.

PHENYL ETHYL CARBAMIC CHLORIDE NPhEt.COCl. [c. 52°]. Formed from ethylaniline and CO₂ (Michler, B. 9, 396). Needles. PHENYL-ETHYL-SEMICARBAZIDE

C,H13N3O i.e. NHPh.CO.NH.NHEt. Formed from ethyl-hydrazine and phenyl cyanate (E. Fischer, A. 199, 295). Thin plates, m. sol. hot water. Yields a crystalline nitrosamine.

Phenyl-ethyl-semicarbazide

NHEt.CO.NH.NHPh. [151°]. Formed from phenyl-hydrazine and ethyl cyanate (Fischer, A. 190, 109). Monoclinic tables (from dilute alcohol) $a:b:c = .827:1:1\cdot146$; $\beta = 61^\circ$. Gives a bluish-black pp. with cold Fehling's solution, and Cu_iO on warming. Its nitrosamine crystal-lises from a etone in yellow needles [86:5°]. PHENYL ETHYL CARBONATE C, H, O, i.e.

C, H, O.CO. Et. (c. 234°) (P.). S.G. 2 1 1134 (P.) Formed from KOPh and ClCO, Et (Fatianoff, Z. 1808, 77). Formed also by the action of AlCl, on a mixture of phenol and ClCO, Et (Paw-laws): B. 17, 1902. lewski, B. 17, 1205). Liquid. By long heating at 300° it is split up into Ph₂CO₂ and Et₂CO₃. (Bender, B. 19, 2268).

Reference .- NITRO-PHENYL ETHYL CARBONATE. PHENYL-ETHYL-CYANAMIDE. by boiling phenyl-ethyl-hic-urea in benzene with Pbo (Weith, B. 8, 1650). Vitreous mass. DI.PHENYL-ETHYL-TRICTANIDE C,N,Ph.Et. V.D. 129. [67°]. (234° at 15 mm.). Formed by the action of AlCl. on a mixture of

henzonitrile and propionyl chloride at 70° (Krafft a. von Hausen, B. 22, 806). - B"H. PtCl.

PHENYL-ETHYLENE v. STYRENE. s.Di-fhenyl-ethylene C, H₁₃, i.e. CHPh:CHPh, Stilbene. Mol. w. 180. [124°]. (307° i.V.). H.C.v. 1,775,600. H.C.p. 1,777,300 (from dia-

Tri-phenyl-ethyl-amine CPh₂CH₂NNI₂ mond) (Berthelot a. Vieille, A. Ch. [10] 4, 50); [116°]. Formed by reducing CPh₂CN with zinc and HClAq (Elbs, B. 17, 700).—B'HCl. [247°].

Tri-phenyl-tri-ethyl-amine N(CH₂CH₂Ph)₃.

A product of the action of zine and HCl on e25, 616; Maercker, M. 136, 91; Anschütz, A. A product of the action of zine and HCl on e25, 616; Maercker, M. 136, 91; Anschütz, A. e25, 616; Maercker, 21. 130, 91; Auschutz, 2. 235, 296).—2. By distilling benzoic aldehyde with Na (Williams, Z. 1867, 432).—3. By heating benzoic aldehyde with phenyl-acetic acid and NaOAc at 250°; the yield being 55 p.c. (Michael, Am. 1, 313).—4. From s-di-phenylethane and Cl (Kade, J. pr. [2] 19, 465).—5. By heating benzylidene chloride with Na or with alcohol and zinc-dust (Limpricht, A. 139, 318; hipmann, J. 1877, 405).—6. By passing s-diphenyl-ethane through a red-hot tube (Otto a. Droher, A. 154, 177).—7. By heating benzoin with zinc-dust (Limpricht, A. 155, 80).—8. By passing teluene over heated PbO (Behr a. Dorp, B. 6, 754). - 9. By heating di-phenyl-acetylene with HI and P at 175° (Barbier, J. 1874, 421) .-10. By distilling lead phenyl-acetate with sulphur (Radziszewski, B. 6, 390). -11. Together with benzonitrile by the action of zinc-dust and HCl on C.H., CSNH. (Bamberger, B. 21, 55).-12. By heating di-phenyl-fumarate or di-phenyl-cinnamate (Anschütz, B. 18, 1945).—13. By heating CHPhBr.CHPhBr with alcoholic KSH in a sealed tube at 100° (Auwers, B. 24, 1779). 14. By heating thio-benzoic aldehyde at 190' (Baumann a. Klett, B. 24, 3308).

Properties .- Monoclinic plates, v. sol. ether, sl. sol. cold alcohol. Combines with N2O4 forming C₂H₂Ph₂N₂O₄ [c. 300°] crystallising in needles, sl. sol. hot alcohol (Gabriel, B. 18, 2438). Picryl chloride forms a combination $C_{14}H_{12}C_{4}H_{2}(NO_{2})_{3}Cl$ [71°] (Liebermann, B. 8, 2438).

Reactions.-1. Yields phenanthrene and toluene when passed through a red-hot tube (Graebe, B. 6, 126) .- 2. Reduced by HIAq at 150° to s-di-phenyl-ethano (Limpricht a. Schwanert, A. 145, 333).—3. Bromine added to an ethereal solution forms a product containing C₁H₂Br₂O₂ [121°] which gives rise to C₁H₂Br₂O₂ [150°] and C₁H₂Br₂O₂ [206°] and when dissolved in alcohol and reduced by solutions of the containing the contain when dissolved in alcohol and teather by soldium-amalgam yields C₁,H₁₀O₂, crystallising from alcohol in flat plates [172°], whence PCI, forms C₁,H₂ClO₂ [58°), C₁,H₂Cl₂O₂ [87°], and C₁,H₂Cl₂O₂ [190°] (Limpricht a. Schwanert, A. 153, 121).—4. Fuming HNO, added to an ethergal solution forms $C_{11}H_{11}N_{1}O_{2}$ [220°], which is converted by boiling alcohol into $C_{22}H_{22}N_{1}O_{1}$ [57°-73°] (Lorenz, B. 7, 1097; 8, 1050).

u-Di-phenyl-ethylene CH₂:CPh₂. (277°); (162° at 15 mm.). Formed by boiling CHPh₂:CH₂Cl with alcoholic potash (Hepp, B.7, 1409). Formed also by the action of benzene and AlCl. on

CH₂:CBr₂ and on CHBr:CBr₂ (Demole, B. 12, 2245; Anschütz, A. 235, 154. Liquid. Oxidised by CrO, to benzophenone. Combines with Br, forming CPh,Br,CH,Br, which readily gives off HBr, and forms bromo-di-phenyl-ethylene [40°] (c. 170° at 11 mm.).

Isomeride. [190°]. A product of the action of alcoholic potash on exo-chloro-di-phenylethane (Hepp, B. 7, 1412). Small plates (from ether). v. sl. sol. alcohol.

ether), v. st. soi. atconor.

Tetra-phenyl-ethylene C₂H₂₀ i.d. U.Ph₄.

Mol. w. 392. [221°]. (193° at 30 mm.).

Formation.—1. By heating CPh₂Cl₂ with finely-divided silver (Behr, B. 3, 751; 5, 277).—

The Lating herosphane with sing-dust nnely-divided silver [bein, B. 3, 101, 0, 21].—
2. By heating benzophenone with zinc-fust (Staedel, B. 6, 178, A. 194, 307).—3. By strongly heating chloro-di-phenyl-ethane (Engler a. Bethge, A. 174, 194, —4. From CPh.Br. by repeated distillation (Friedel a. Balsohn, Bl. [2] 33, 337).—5. A by-product in the prepara-tion of tri-phenyl-methane from benzene, chloroform, and AlCl, (Schwarz, B. 14, 1526).

Preparation.—1. By adding Br to di-phenyl-

methane and warming the resulting CIIPh, Br; the yield is 80 p.c. (Boissieu, Bl. [2] 49, (31).—

b. By heating di-phenyl-methane (20 g.) with sulphur (8 g.) for 9 hours to 250°, and finally for one hour to 290°, exhausting with ether, and recrystallising the residue from benzene; the

yield is 75 p.c. (Ziegler, B. 21, 780).

Properties.—White needles, v. sol. hot benzene and CS, v. sl. sol. other. Yields benzophenone (2 mols.) on oxidation (Anschütz, A. 235, 221). Yields a tetrasulphonic acid.

Isomeride C13H10? [244°]. Formed by heating (a)-benzpinacolin with soda-lime at 370° (Zincke a. Thörner, B. 11, 1397). Needles (from alcohol). Perhaps identical with the preceding. References .- DI-AMIDO-, BROMO-, DI-CHLORO-,

DI-IODO-, NITRO-, NITRO-AMIDO-, and OXY- PHENYL-RTHYLENE.

PHENYL-ETHYLENE-DIAMINE PHENYL-ETHYLENE-DIAMINE C₈H₁,N₂ i.e. C₈H₄NH.CH₂.CH₂.NH₂. (262° uncor.). Formed by boiling phenyl-amido-ethyl-phthalimide (got from bromo-ethyl-phthalimide and aniline) with conc. HClAq (Gabriel, B. 22, 2224). Liquid, miscible with water, forming an alkaline solution. Absorbs CO, from the air, forming a crystalline carbonate.—B"2HCl: small greenish needles, acid in reaction.— B"HCl. Neutral to methyl-orange. B"H_Br2. -Picrate [143°]. Flat yellow tables.

Di-acctyl derivative C₈H₁₀Ac,N₂. [116°]. Crystals, v. e. sol. Aq (Newman, B. 24, 2193). Di-benzoyl derivative. [143·5°]. Prisms.

Phenyl-di-ethylene-triamine C₁H₃N(C₂H₁NH₂)_r (above 300°). Formed by the action of boiling conc. HBr upon its di-phthalyl derivative NPh(C₂H₁N:C₂H₄O₂)_r [211°], which is a product of the action of aniline on bromo-ethyl-phthalimide at 100°-180° (G.). Thick ammoniacal liquid, miscible with water.

Absorbs CO₂ from the air.—B'H₂Br₂.—Pierate. [202²]. Needles (from alcohol).

**Oi-phenyl-ethylene-dismine C₁₄H₁₆N₂ i.e. C₁H₄(NHPh). [63²]. Prepared by heating ethylene bromide (1 mol.) with aniline (4 mols.); the yield being 80 p.c. of the theoretical (Morley, B. 12, 1794; cf. Hofmann, Pr. 10, 104; Gretillat, M. S. [3] 3, 383). Plates, v. sol. alcohol. Yields a di-nitrosamine C2H4(NPh.NO)2 [157°]. Reacts with benzoic amenyue forming the compound C.H. (NPh) .: CHPh [1870], while cuminic. salicylic, anisic, isobutyric, and heptoic aldeh les yield corresponding compounds [125°], [116°], [164], and [95°] respectively (Moos, B. 20, 732).—B"2HCl.—B"H.PLCl.—Mono-acetyl derivative. [128°]. Got

by heating the base with chloro-acetic acid and Na()Ac at 170° (Bischoff a. Nastvogel, B. 22, 1783).

Qi-acetyl derivative. [158°]. Crystals. Di-phenyl-ethylene-diamine C₁:H₁₆N₂ i.e. CHPh(NH.).CHPh(NH.). [121°]. Formed, together with benzoic aldehyde, by the action of boiling HClAq on C₂₈H₂₄N₃, which is a product of the action of New York, when the second of the section of New York, when the second of the section of New York, when the second of the section of New York, when the second of the section of New York, when the second of the section of New York, when the second of the section of New York New Y of the action of Na on amarine Grossmann, B. 22, 2299). Formed also by the action of cammonia on the hydrocyanide of benzoic alde-hyde (Limpricht a. Müller, A. 111, 142). Is per-haps identical with lophine. Plates (from hot water). Reacts with henzoic aldehyde forming CHPh:N.CHPh.CHPh.N.CHPh [164], m-nitrobenzoic aldehyde forming C₂₄H₂₂N₄O₂ [161°], with salicylic aldehyde forming C₂₄H₂₄N₂O₂ [205°], and with cuminol forming a compound [168° B"2HCl. White needles (from hot water).-B"H_PtCl, : dark-yellow crystals

Di-acetyl derivative. [above 350°]. Phthalyl derivative C_a I.: C_aO_a : N_aH_a : C_aH_a Ph_a. [213°]. Minute crys-

Di-phenyl-di-ethylene-diamine C18H18N2 i.c. NPh C.H. NPh. Diphenylpiperasine. Diphenylpyrazine hexahydride. [163°]. (c. 300°). Prepared by heating ethylene bromide (1 pt.) with aniline (1 pt.) and NaOAc, and by the action of ethylene bromide on di-phonyl-ethylene-diamine at 120° (Morley, B. 12, 1795; Bischoff, annue at 120 (arriey, B. 12, 1735; Bischoll, B. 22, 1777; cf. Hofmann, Pr. 9, 277; 10, 104; Lellmann a. Schleich, B. 22, 1387; Bischoff, B. 22, 1778). Formed also by heating pyrazine hexahydride (1 pt.) with bromo-benzene (11 pts.) at 270° (Schmidtea. Wichmanf, B. 24, 3239). Needles, sol. alcohol and ether . Its solutions are neutral to litmus. Yields a crystalline di-nitroso-derivative which may be reduced by tin and HCl

to C₆H₃(NH₂)N<CH₂.CH₂NC₆H₃NH₂, which, when diazotised and combined with naphthylamine sulphonic acid, yields a colouring matter which dyes cotton.—B"2HCl.—B"H₂PtCl₆.

Methyl-iodile B'MeI. Crystalline. Yields B'2Me2PtČl6.

Ethylo-iodide BEil. [100°]. B',Et,PtCl.

References .- NITRO- and OXY- DI-PHEN TO-ETHYLENE-DIAMINE.

• DLPHENYL . ETHYLENE . DI . BENZYL . DI . AMINE CHPh(NICH,Ph). CHPh(NHCH,Ph), [153°]. Formed by reducing the compound CHPh(N:CHPh). CHPh(N:CHPh) [163°], which is itself got by reducing amarine with Na (Grossmann, B. 22, 2301). White meelles.

DI PHENYL - ETHYLENE - DICARBAMIC

DI PHENYL BIR ACID C4H (NPh.CO.H).

Ethyl ether Et,A". [88°]. N

Chloride C4H (NPh.COCI). 188°1. Needles. [183°] Formed from di-phenyl-ethylene-diamine and COCl. (Hanssen, B. 20, 781). Prisms.

DI-PHENYL-ETHYLENE DI-o-CARBOXY-C,H,(CO,H).CH:CH.C,H,CO,H. ACID LIG [264°]. Formed by heating for four hours at 215° CO CoH CH.CH, CoH, COH (2 pts.) with KCy (5 pts.) (Hasselbach, A. 243, 258). Small needles (from dilute HÖAo). Changes on heating into the parent acid [196°]. Reduced by conc. HIAq to C.H. (C.H., CO.H), [185°].—Ag.A". Floculent pp.

Ethyl ether Et.A". [80°]. Needles. Isomeride v. DI-PHENYL-MALEÏC ACID. References.—Nitro- and Oxy- Di-Phenyl-ethylene carboxylic acids.

DI - PHENYL - ETHYLENE - DI - ETHYL -DIAMINE C₁₈H₂₄N₂ i.e. C₂H₄(NPhEt)₂. [70"].
Formed from di-phenyl-ethylene-diamine and

EtI (Hofmann, Pr. 10, 104).—B"2HI.— B"H,PtCl, needles.

PHENYLETHYLENE-GLYCOL v. DI-0xx-

ETHYL-BENZENE. DI-PHENYL-ETHYLENE-DI-HYDRAZINE C14H18N4 i.t. C2H4(NPh.NH2)2. [90°]. Formed from sodium phenyl-hydrazine and ethylene bromide in benzene (Burchard a. Michaelis, B. 21, 3202; A. 254, 116). Prisms or olates. Aldehyde forms C.H.(NPh.N:CHMc). [82°]. Benzoic aldehyde forms an analogous body [193°]. Acetone and acetophenone form analogous compounds [72°] and [118°]. Phenyl-thiocarbinade forms NH,NPh.C.H,NPh.NH.CS.NHPh [164°] forms NH_NFI...TI, MALCS.NIIPh)₂ [194°]. Yields a crystalline nitroso derivative [160°]. SOCI₂ forms C₂H₄(NPh.N:SO). [123°] (Michaelis a. Ruhl, A. 170, 122).—B"H.Cl., [212°]. Necdles, sl. sol. HClAq.—B"H₂SO₄—B"2HNO₄ [173°].— SOCl₂

B"H₂C₂O₄ [183²].

Acetyl derivative C₁₁H₁₆Ac₂N₂ [222²].

Succinyl derivative C₁₁H₁₆N₂:C₁H₄O₂.

[c. 126°].

Succinoxyl derivative .

Succinoxyl derivative .

C₂H₁(NPh.NH.CO.C₂H₁.CO.H)₂. [203°].

Oxalyt derivative C₁₄H₁₆N₂:C₂O₂.

Di-phenyl-di-ethylene-dihydrazine

(C₂H₄),(N₂HPh)₂. [178°]. Got by heating phenyl-hydrazine with C₂H₄Br₂ and alcohol (Marckwald, C. C. 1888, 1410). DI-PHENYL ETHYLENE DIKETONE

C.H., CO.CH., CH., CO.C., H., Diphenacyl. Succinophenone. [134°] (A.); [140°] (C.); [142°-145°] (P.). Formation.—1. Together with the isomeric CH. CO by the action of succinyl chloride and AlCl₃ on benzene (Auger, A. Ch. [6] 22, 312 : Claus. B. 20, 1374) .- 2. From acctophenone by treatment with fuming HNO, and reduction of the resulting $Q_{10}H_{10}N_{10}O_{10}$ by zinc-dust and HOAc (Hollemann, B. 20, 3301).—3. By the action of KOHAq on di-benzoyl-propionic acid suspended in alcohol (Paal, B. 21, 3056).

Properties. - Needles, v. sol. ether.

Oxim Q.H. (CPh:NOH). [2014].

Phenyl. hydrazide C.H. (CPh:N.HPh).

O']. Needles, v. sol. ether.

DI. PHENYL ETHYLENE DIKETONE

CARBOXYLIC ACID v. PHENACYL-BENZOYL-ACETIC ETHER.

Di-phenyl-ethylene diketone di-o-carboxylic cid Ci.H.O. i.e. C.H.(CO.O.H.,CO.H). [172°].

Obtained by boiling di-phthalyl-ethane with

alkalis (Gabriel a. Michael, B. 10, 1561, 2199; Roser, B. 17, 2622; 18, 803, 8115; Baumann, B. 20, 1486). Prisms (from water), v. sol. alcohol. Reconverted by conc. H₂SO₄ into di-phtralyl ethane C.H₂(C₄O₄C₄H₄)₄. A boiling alcoholic solution of phenyl-hydragine forms C₃₀H₂₂N₄O₂ [237°]. Hydroxylamine at 100° gives rise to $C_2H_4(C < C_0H_4 > CO)_2$ [270°] (Baumann, B. 20,

1492).—Ag₂A": small plates, sl. sol. hot water.
(a).An hydride C₁, H₁₂O₂. [230°]. Got by heating the acid alone, or together with diphthalyl-ethane, by heating it for a short diphthalyl-ethane, by nearing time with HCl. Needles (from alcohol).

by more from great the acid with HCl, and also, together with the (a)-isomeride, by heating the acid by itself. Prisms (from alcohol). Both anhydrides are reconverted into the acid by boiling alkalis, and into di-phthalylethane by elimination of H.O.

Isomeride v. DI-BENZOYL-SUCCINIC ACID.

PHENYL ETHYLENE OXIDE CHPh>O. (260° at 50 mm.). Formed by heating di-oxyetts:1-lienzene with dilute H₂SO₁ (Breuer a. Zincke, B. 11, 1402). Oil. Converted by PBr, into CHPhBr.CH.Br.

Tetra-phenyl-ethylene oxide v. Benzpinaco-

PHENYL-ETHYLENE SULPHIDE

CHPh>s. S.G. 16 1.099. Formed from PhCHBr.CH,Br by successive treatment with alcoholic KSHAq (Spring a. Marsenille, Bl. [3] 7, 13). Oil with strong smell, sol. alcohol-ether. Oxidised by CrO, to benzoic acid.

CHPh>s. Di-phenyl-ethylene sulphide [169°]. A product of the distillation of benzyl sulphide (Barbier, J. 1876, 421). Needles.

Di-phenyl-ethylene disulphide C₂H₄(SPh)₂.

J. Formed from NaSPh and C₂H₄Br₂

(Ewerlöf, B. 4, 716). Needles, insol. water. DI-PHENYL-ETHYLENE DISULPHONE

C₂H₄(SO₂C₆H₅)₂. [180°]. Formation.—1. By oxidation of C₂H₄(SPh)₂ (Ewerlöf, B. 4, 717).—2. By boiling sodium benzene sulphinate (100 pts.) with C.H.Br. (58 pts.) in alcohol (Otto, B. 13, 1279; J. pr. [2] 30, 174).

3. By adding CH., CCl., CO., Na (1 mol.) to C., H., SO., Na (2 mols.) in weak alcoholic solution, kept neutral by Na CO₂ (Otto, J. pr. [2] 40, 531). 4. By heating CH₂CCl₃ with C₈H₅.SO₂Na at 160° (Otto, B. 21, 1691).

Properties .- Triclinic needles or plates, sl. sol. water, m. sol. alcohol, v. sol. HOAc.

Reactions.—1. Sodium-amalgam reduces it to alcohol and C.H. SO.Na, which is finally reduced to C.H.SNa.-2. Chlorine in diffused daylight forms $C_2H_1Cl_2$ and benzene sulphonic chloride. In sunlight the products are $C_2H_1Cl_2$, SO₂Cl₂, and chlorinated benzenes.—3. Boiling aqueous KOH splits it up into C,H,SO,K and C.H. SO, C.H. OII. Conc. KOHAq forms's C₀,H₀,SO₂C₂H₁,Cil. Conc. K(HAq forms a compound [88°] crystallising from alcohol.—4. Aqueous NH, forms C₀H₀,SO.ONH, and (C,H₀,SO₂CH₂CH),NH [78°] which yields B'HCl [193°], B'₂H₂PtCl₁, a nitrate [190°], and the derivatives (C₀H₁,SO₂CH₂CH₁)₂NMc and (C₀H₀,SO₂CH₂CH₁)₂NMcHCl [221°].—5. Aqueous

C.H.SO,NH,Et ethulamine forms and C_eH₄,SO₂C₂H₄NHEt, an oil which yields B'HCl [180°].—6. Alcoholic KCy forms C_eH₃SO₂K and C.H.(CN)...

PHENYL-ETHYLENE-THIO-UREA

CS<NPh>C2H. [155°]. Formed from phenylethylene-diamine and CS, (Newman, B. 24, 2191). White plates, v. sol. alcohol.

Di-phenyl-ethylene-ψ-thio-urea

 $C_{H} < \frac{NPh}{S} > C_{S}NPh.$ [136°]. (above 4800°).

Formed by heating di-phenyl-thio-urea with ethylene bromide (Will, B. 14, 1490; 15, 343). Plates (from alcohol), KClO, and HClAq form C,H,N,SO, [187°] (Andreasch, M. 4, 134).—B'H,SO; thick prisms, v. sol. water.

Di-phenyl-ethylene-di-thio-di-urea

[193°]. C16H16N4S2 i.e. C2H4(NH.CS.NHPh)2. Formed from C₂H₄(NH₂)₂ and phenyl-thio-carbimide in alcohol (Lellmann a. Würfiner, A. 228, 234). White scales, insol. alcohol, sl. sol. HOAc. Decomposed by heat, giving di-phenyl-thio-urea and a crystalline body [164°]

PHENYL-ETHYLENE-UREA

C₂H₄<NPh>CO. [161°]. Formed from phenylethylene-diamine hydrochloride and potassium cyanate, NH, being given off (Newman, B. 24, 2192). Plates, v. sol. alcohol, insol. cold water.

Di - phenyl - ethylene - urea CH...NPh CO.

[209°]. Formed by the action of COCi, in benz. ene on C2H, (NHPh)2; an intermediate body being C₃₁H₂₈N₄Cl₂O₃ (Michler a. Keller, B. 14, 2183; Hanssen, B. 20, 784). Plates.

PHENYLETHYL-ETHYL-PYRIDINE

 $\mathbf{C_{1b}H_1,N} \text{ i.e. } \mathbf{N} \leqslant \begin{matrix} \mathbf{C(CH_2.CH_2Ph).CH} \\ \mathbf{CH:CEt} \end{matrix} \qquad \qquad \mathbf{CH}. \quad (316^{\circ} \text{ cor.}). \end{matrix}$ S.G. 9 1.016. Formed by reducing styryl-ethylpyridine with HIAq at 165° (Plath, B. 21, 3003; 22, 1057). Oil, v. sl. sol. water, v. sol. alcohol 22, 1037), OH, V. S. SOI, WALET, V. S. SOI, ARCHOM.

[1282] whence AgOAc forms C, H, (OAc), N

(815°-820°). — B', H, l'tCl. [168°]. Vellow

meddles. — B'HHgCl. [136°]. Needles. —

B'HAUCl. aq: crystalline mass.

Hexahydfide C13H28N. (314°). S.G. 9663. Got by reducing the preceding body in alcohol with Na. Oil, sl. sol. water, miscible

with alcohol and ether.

PHENYL-ETHYL-FURFURANE

C.H., CH., CH., C,H.,O. (241°). A product of the action of Na on an alcoholic solution of C.H.O.CH:CPh.CN, which is formed by condensation of furfuraldehyde with phenyl-acetonitrile (Freund a. Immerwahr, B. 23, 2848). smelling like CH. Ph2.

DI-PHENYL-ETHYL-GUANIDINE

C₁₈H₁₁N₂ i.e. NHEt.C(NPh).NHPh. Got from phenyl-ethyl-cyanamide and aniline at 100° (Weith, B. 8, 1531). Crystalline.—B'2H2PtCls.

*PHENYL-ETHYL-HYDANTOIN C₁₁H₁₂N₂O₂
i.e. CHPh NH.CO . [94°]. Formed from phenyl-hydantoin, alcoholic KOH, and EtI (Pinner, B. 21, 2325). Prisms, v. sol. alcohol, al. sol. cold water. Decomposed by baryta into ethylamine and phenyl-amido-acetic acid.

Phonyl-ethyl-\psi-hydantoin

CHPh CO.NEt Separates from a dijute alkaline solution of the preceding isomeride on standing. Slender needles, insol. water, nearly insol. alcohol. Decomposed by heating with baryta-water into NH, NH,Et, and a-oxyphenyl-acetic acid.

u-PHENYL-ETHYL-HYDRAZINE C.H.,2N. i.e. NPhEtaNH, (230°). Formed by reducing the nitrosamine of ethyl-aniline with zinc-dust, HOAc, and alcohol (Fischer, B. 8, 1642; A. 199, 325; Philips, B. 26, 2485). Formed also from EtBr and NPhN&NH, in benzene (Michaelis a. Philips, A. 252, 270). Oil. Reduces Febling's colution on manufacturing Ovidious two Hoads. solution on warming. Oxidised by HgO to solution on warming. Oxidised by HgO to diphenyl-di-ethyl-tetrazono NPhEt.N:N.NPhEt [108]. SOCI, forms oily NPhEt.N:SO (Michaelis, B. 22, 223).—B'HCl. Plates.

**Acetyl derivative NEIPh.NHAC. [80°].

Ebby lo-bromide NH, NPhEt, Br. Trimetric prisms (from alcohol); a:b:c = 822:1: 827. V. e. sol. water, insol. ether. Decomposes at 193°. Insol. KOHAq. Converted by moist Ag₂O into a caustic hydroxide. Yields also (NH₂APhEt₂)₃H₂Fe₂Cy₁₂2aq (Fischer, A. 190,

Ethylo-chloride NH, NPhEt.Cl. [198°]. Needles, v. e. sol. water. B' Et.PtCl.

Ethylo-iodide NH. NPhEt,I. s-Phenyl-ethyl-hydrazine NHPh.NHEt. Formed, together with the preceding isomeride, by heating phenyl-hydrazine with EtBr. The crude product is dissolved in water mixed with NaOHAq, and the ppd. oil extracted with ether. The ethereal solution is freed from phenylhydrazine by HCl and the filtrate oxidised by HgO. On addition of HCl it deposits di-phenyldi-ethyl-tetrazone, and the mother-liquor yields by steam-distillation oily C.H.N:NEt 4175°... 185°). The NRh:NEt is then reduced by sodium-

amalgam (Ehrhardt a. Fischer, B. 11, 613).

Properties.—Oil, sol. alcohol and ether.

Readily reduces Mehling's solution and HgQ. Zinc-dust and HOAc yield aniline and ethyl-

amine. -B'H.C.O.: needles, v. sol. hot water.
DI-PHENYL-ETHYLIDENE DIAMINE

Ethylidene-di-aniline, vol. ii. p. 496. DI - PHENYL - ETHYLIDENE - DI - ETHYL-DIAMINE C₁₈H₂₁N₂i.c. CHMe(NPhEt)₂. Formed from ethyl-aniline and aldehyde (Schiff, A. 140, 95; cf. Schultz, B. 16, 2601). Thick liquid .-

B',H,PtCl. PHENYL-ETHYLIDENE DI-ETHYL DI-SULPHONE CH3.CPh(SO2Et)2. [101°]. Formed from benzylidene di-ethyl di-sulphone, Mel, and EtONa (Fromm, A. 253, 154). Needles.

PHENYL-ETHYLIDENE-HYDRAZINE CH, CPh:N.NH2. (255°). Formed from acetophenone and hydrazine hydrate (Curtius, J. pr.

phenome and nyarane nyarane counts, J. Pr. [2] 44, 540). Liquid. Yields CH., CPh:N.N:CHPh [59°] and N., CPh.CH.), [121°].

DI-PHENYL ETHYLIDENE DISULPHONE CH., CH(SO,Ph)., [102°). Got by oxidising CH., CH(SPh)., CO,Ph with dilute (1 p.c.) KMnO. (Escales a. Baumann, B. 19, 2915). Needles or thin lamella, insolv water, acids, and alkalis, sl. sol. alcohol and ether.

Not attacked by alcoholic potash at 140°. PHENYL - ETHYLIDENE - DI - THIO - DI CH. CPh(S.CH,.CO.). GLYCOLLIC ACID

[186°]. Got by the action of ZnUl, on a mixture of acetophenone and thioglycollic acid (Bongastz, B. 21, 483). Needles, sol. hot water. CHCl., and HOAc.

Dilactone C. H. OCO.

PHENYL-ETHYL-IMESATIN v. Di-phenyl-

di-ethyl-diamide of Isatyn.

PHENYL ETHYL KETONE C, H, O i.e. C.H..CO.C.H. Propiophenone. [210]. cor.) (M. a. G.). V.D. 464 (obs.). S.G. 2 1.009

(W.). Formation .- 1. By distilling a mixture of calcium benzoate and propionate (Barry, B 6, 1006). 2. From BACI and Calct. (Freund, A. 118, 20; Kalle, A. 119, 166). 3. By the action of Na on a mixture of BzCl and Etl (Bechi, B. 12, 463). - 4. By the action of propionyl chloride Green, B. 17, 3018; Pampel a. Schmidt, B. 19, 62896).—5. By the decomposition of propylene phenyl-ethyl-ketate by HI or H.SO, (Morley a. Green).—6. By oxidising CHPhEt.OH (Wagner, J. R. 16, 325).—7. From benzoyl cyanide and J. R. 16, 325).—7. From benzoyl eyanide and which is got from phthalyl-malonic ether and ZnEt, either directly or by oxidising the product NaOEt (Wislicents, A. 242, 58). Oil.—Ag,A'v. (Frankland a. Louis, C. J. 37, 745).—8. From PHENYLETHYL METHYL KETONE v.

phenylallylene (Körner, B. 21, 277).

Properties. Tables. Does not combin with NaHSQ.. Yields benzoic acid on oxidation. Reduced by sodium-amalgam to CHPhEt.OH (211°).

Oxim CPhEt:NOH. Oil.

Phenyl hydrazide. Oil.

Phenyl ethyl diketone C.H., CO.CO.C.H., Propionyl-benzoyl. (239°). Got by distilling its mono-oxim (obtained from ethyl benzoylacetic other) with dilute H.SO, (Müller a. Pechmann, B. 22, 2131). Pungent liquid, volatile with steam, m. sol. water.

Reference. - NITRO- and OXY- PHENYL ETHYL KETONE.

PHENYL ETHYL KETONE DIBROMIDE v. DI-BROMO-CUMENE.

PHENYLETHYL KETONE o-CARBOXYLIC ACID C.H., CO.C., II., CO.H. Propionyl-benzoic zeid. [92°]. Formed by boiling phthalyl-propionic acid with KUHAq (Gabriel, B. 11, 1014; 10, 840). Needles (From. Elitherhelm). 19, 840). Needles (from dilute alcohol) .-- AgA'.

Anhydride C, H, CCCHMe) >0.

Formed by heating phthalic anhydride with succinic acid and NaOAc (G.). Formed also by listilling the anhydride of the dicarboxvlic acid Roser, B. 18, 3117). Plates (from water). Com-

bines with N₂O₄ forming C₁₆H₈N₂O₆ [90°].

A mide C₆H₄(CO.NH₂).CO.C₂H₃. Formed from the anhydride and alcoholic NII. Isomerides v. Benzoyl-propionic acid, vol. i.

o. (87.

Phenyl ethyl ketone dicarboxylic acid J.H.,CO.CH, CH(CO.H), β-Benzoyl-isosuccinio wid. [180°]. Obtained by saponifying its ether which is formed from w-bromo-acetophenone and sodium malonic ether (Bischoff, B. 16, 1044; 19, 99; Kues a. Paal, B. 18, 3321). Needles, v. sol. alcohol and ether. Yields β penzoyl-propionic acid when heated. - A . A": needles. - Et. A": oil.

Phenyl hydrazide J.H..C(N.HPh).CH.CH(CO.H). Phonyl ethyl ketone dicarboxylic acid

C.H.CH.CH.C.H.Et. [90°]. Formed by boilC.H.CO.H.CO.CH.CO.H. [137°]. Formed ing CH.Ph.CH(OH).C.H.Et[1:4] with dilute
by bolling its dilactone with water or aqueous H.SO. (Söllscher, B. 15, 1681). Plates.

[1860]. Got by the action of ZnCl, on a mix- | alkalis. Small six-sided prisms, re-converted by

product of the action of phthalic anhydride on succinic acid and NaOAc. at 2503 (Roser, B. 17. 2770; 18, 804, 3115). Needles, sl. sol. cold water. At 260° it gives off CO, and changes to C.H. COO C:CHMe. HIAq and P at 190° reduce it to C₀H₁(CO,H),CH₂CH₂CH₂CO₂H, Cold NH₃Aq forms CO,NH>CCH,CH₂CO₂H |225°]. Boiling alcoholic NII, forms C, II, NO, [c. 205°]. Sodiumamagam reduces it to phthalyl-propiotic acid $C_{11}H_{12}O_{4}$. Phenyl bydrazine forms $C_{11}H_{11}N_{2}O_{4}$ [210°] which gives CaA'₂ aq.

Isomeride v. Benzöyl-succinic Aold.

Phenyl ethyl ketone tetracarboxylic acid C,H,CO,H),CO.C(CO,H),CH,CO,H. Formed by the action of chloro-acctic ether on C. H. NaO.

BENZYL ACETONE. Diphenylethyl methyl ketone CH, CPh, CO.CH, [415]. (311° i.V.). A product of the action of zine and HCl on an alcoholic solution of acctophenone (Zincke a. Thörner, B. 11, 1989). Prisms (from alcohol).

PHENYLETHYL-METHYL-PYRIDINE $C_{11}H_{13}N$ i.e. $C_{1}H_{1}Ph.C_{1}H_{3}MeN$. (290°-295°). S.G. (10283. Formed by reducing styrylmethyl-pyridine with HIAq at 160° (Bachér, B. 21, 3076). Oil, volatile with steam. B',H,PtCl, [168°]. -B'HH₅Cl, aq. [95°]. Silky needles. -B'C_aH,N,O₂. [156°]. Yellow needles Hexahydride C₁₁H₄N. (c. 288°). S.G. ⁹

19775. Got by reducing styryl-methyl-pyridine

in alcohol with Na. Liquid, v. sl. sol. water. **PHENYL-ETHYL-**(β)-**NAPHIHOTRIAZINE** DIH TORIDE C10 H11 N3 i.e. C10 H1 N:CHEt [219°]. Formed by adding propionic aldehyde to benzene azo-(B)-naphthylamine in alcohol (Goldschmidt a. Poltzer, B. 21, 1006). needles, v. sol. alcohol. B'HCl. [258°].—
B'₂H.PtCl. Small yellow crystals.
PHENYL-ETHYL-OXAMIDE C_{1n}H₁₂N₂O₂ i.e.

NHPh.CO.CO.NHEt. [170°]. Formed by the action of ethylamine on phenyloxamic ether or of aniline on ethyloxamic ether (Wallach, A. 184, 66; 214, 259). Needles (from alcohol). Converted by PCl, (2 mols.) into a base which forms the salt (C10H,N.Cl)2H2PtCl.

Di-phenyl di-ethyl oxamide v. vol. iii. p. 651. PHENYL - ETHYL - PHENOL v. Oxy - DI-PHENYL-ETHANE.

PHENYL-p-ETHYL-PHENYL-ETHANE C.H.CH., CH., C, H. C H. (294°). Formed by reduction of CaH CH CO.CaH Et with HI and P (Söllscher, \vec{B} . 15, 1681). Liquid.

Isomeride. Got by the action of zinc-dust on a mixture of cthyl-benzene and a-bromo-ethyl-benzene (Radziszewski, B. 6, 811; 7, 140). Gives p-henzoyl-benzoic acid on oxida-

PHENYL-ETHYLPHENYL-ETHYLENE

PHENYL p-ETHYLPHENYL KETONE C.H., CO.C., H.Et. (831°) at 720 mm. Prepared by the action of AlCl, on a mixture of BzCl and ethylbenzen (Söllscher, B. 15, 1632; Smith, B. 24, 4029). Liquid, sol. algohol and ether. Yields two oxims [108°] and [142°], both giving the same acetyl derivative [95°]

PHENYL-ETHYL-PHENYL METHANE v.

BENZYL-ETHYL-BENZÉNE.
PHÉNYL - ETHYLPHENYL - THIO - UREA NHPh.CS.NH.C.H.Et. [104°]. Formed from p-ethyl-phenyl-thiocarbimide and aniline in alcohol (Mainzer, B. 16, 2020). Plates.

PHENYL-DI-ETHYL-PHOSPHINE

PHENYL-DI-ETHYL-PHOSPHINE
PEt.C.H., (222° cor.). S.G. ¹² -957. Formed
from C.H., PCl., and Z.MEt., (Michaelis, B. 8, 493;
A. 181, 845). Oil. Absorbs oxygen from air,
yielding O.P.Et., C.H., [50°]. Combines also with
Ol and S. forming crystalline C.₁H.₁, PCl. and
C.₁H.₁, PS. — B'2HCl. — B', H., PtCl., — B'HI. —
B'ELI. [115°].—B', 2Et., PtCl., — B'MI. [95°].—
W.M.S. PtCl. B',Me,PtCl,

Di-phenyl-ethyl-phosphine PEtPh,. (298°). Formed from Ph.Pol and ZnEt, (Michaelis a. Link, A. 207, 214). Liquid, sol. alcohol and ether. Yields OPEIPh, on oxidation. Etl yields Ph.PEt.I [204°] which gives (Ph.PEt.Cl),PECI, [218°]. MeI gives Ph.PEtMcI [181°] S. 1·5 at 22°; 50 at 100°, which gives (Ph.PEtMcCl),PtCl, [220°] and Ph, PEtMe.O.C, H, (NO,), [86°

Di-phenyl-ethyl-phosphine oxide PEtPh.O. [121°]. Formed as above, and also by the action of Ag.O on Ph, PEtl (Michaelis a. Soden, A. 229, 817). Prisms, sol. ether and ligroin.

PHENYL-DI-ETHYL PROPENYL TRISUL-PHONE PhSO₂CH₂.CMc(SO₂Et)₂. [128°]. Got from EtSH and PhS.CH₂.CO.CH₃, the product being oxidised (Autenrieth, B. 24, 169). Plates.

Di-phenyl ethyl propenyl trisulphone

Bi-paenyi etayi propenyi atsunanace EtSO_CH_CMc(SO_Ph)_ [139°]. Made in like manner from PhSII and EtS.CH_CO.CH_.

Needles (Auterrieth, B. 24, 1513).

TRI PHENYL ETHYL PROPYL-DI-THIO-BIURET C_5_N_Ph_EtPr. The (a)- compound [166°] is formed by the action of di-phenylpropyl-thio-urea on CICS.NPhEt, while the (B)compound [165°] if got from di phenyl-chyl-thio-urea and CICS.NPhPr (Billeter a. Strohl, B 21, 109). Both crystallise in needles, v. sol. hot alcohol

DI - PHENYL - ETHYL - PROPYL - THIO-UREA NPhEt.CS.NPhPr. [66"]. Formed by the action of CSCl, on propyl-aniline followed by ethyl-aniline or vice versa (Billeter a. Strohl,

B, **21**, 103).

PHENYL-ETHYL-PYRAZOLE C, H, N, i.e. NPh < CEt:CH (274°). S.G. 15 1.064. Formed from phenyl-hydrazine and propionyl-acetic aldehyde (Claisen a. Stylos, B. 21, 1148). Oil. PHENYLETHYL-PYRIDINE

cor.). S.G. 2 1 0465. Formed by reducing styrylpyridine with HI (Baurath, B. 21, 821). Liquid, sl. sol. water, volatile with steam. B'aH.PtCl. [186°]. B'HAuCl., [150°]. Long yellow needles.

B'HHgCl., [149°].

Hexahydride C₁₈H₁₈N. (288° cor.). S.G.

9.9874. Got by reducing the preceding base in alcohol with Na. Liquid, smelling like piper-

idine, sl. sol. water. Turns moist litmus blue Has toxic properties similar to those of conine Forms an oily hitrosamine. Yields pariding carboxylic acid on oxidation.—B'HCl. [155°]
-B'₂H₂PtCl₄. [189°].—B'HAuCl₄. [134°].

TETRA-PHENYL-ETHYL-PYRROLE

NEt CPh: CPh. [221°]. Formed by heating bidesyl with aqueous NBtH2 at 150° (Fehrlin B. 22, 555). Needles (from enloroform) of plates (from HOAc).

DI-PHENYL-ETHYL-PYEROLE DI-o-CARB-

OXYLIC ACID C., H., NO., i.e.

NEt C(C, H., CO, II):CH [220°]. Formed by heating C, H. (CO, C, H., CO, II), with ethylamine solution (Baumann, B. 20, 1488). Yellow plates from alcohol), insol. water. - Ag2A".

PHENYLETHYL QUINOLINE

cducing styryl-quinoline with HI (Heymann a. Königs, B. 21, 1426). Crystals.—Picrate. [c. 130°]. Yellow prisms, sl. sol. alcohol.

PHENYL-ETHYL SULPHIDE Ph.S.Et. (201° i.V.) at 744 mm. S.G. 1.0 :1.032. Formed by heating PhSNa with EtI in sealed tobes at 120° (Beckmann, J. pr. [2] 17, 457). Obtained also by the action of H₂S at 50° on C₆H₂.SO.OEt (Otto a. Rössing, B. 20, 2275) and by the action of EtSH on C, H, N,Cl (Stadler, B. 17, 2078). Liquid, with nasty smell.

Sulphonic acidC2H3.S.C6H4.SO3H. Formed by boiling C.H.S.N., C.H., SO, Na with

alcohol. - NaA': plates.

Phenyl ethyl disulphide PhS,Et. Formed together with Et.S. by heating C.H.SO.H with EtSII at 100° (Otto a. Rössing, B. 19, 3135; 20, 189). Heavy oil. Decomposed by alcoholic potash into EtSII, Ph₂S₂ C₄H₃SO₂H, and ethane sulphinic acid.

PHENYL ETHYL SULPHONE C, H, SO, i.e. C.H., SO., C.H., [43°]. (above 300°). Formed from C.H., SO, Na and Ethr er C.H., OBr., CO., Na (Otto, B. 13, 1274; J. pr. [2] 40, 535). Formed also from C.H., C.H.(SO, Ph.). C.O., H by the action of alkalis and by oxidising PhSEI with dilute KMnQ, (Beckmann, J. pr. [2] 17, 458). Monoclinic plates (Fock, B. 19, 1230), sol. hot water, v. sol. alcohol.

a-Carboxylic acid C.H., SO, CHMe, CO.H. a-uarboxynic acia C_aH₁,NO_aCHMo.CO_aH.

Phenyl sulphono-propionic acid. [116°]. Formed
by saponifying its ether, which is got from
C_aH₃SO_aNa and CH_aCHBr.CO_aEt (Otto, J. pr.
[2] 40, 548). Groups of needles, v. sol. how

water.—NaA'.—BaA', 2aq: leafy aggregates,

Ethyl ether Eth'. [c. 17°]. Oil.

B₂Carboxylic acid C_aH₃SO_aCH₄CH₂CO₂H.

[124]. Formed from benzene sulphinic acid

[124]. Formed from benzene sulphinic acid and \$\beta\$-iodo-propionic acid (Otto, \$\bar{B}\$. 21, 95). Plates, sl. sol. cold water, m. sol. ether.

PHENYL-ETHYL-THIAZOLE C,H, NS i.e. N CEt.S (296° cor.). Formed from thiopropionamide and bromo-acetophenone in alco-

hol (Hubacher, A. 259, 231). Oil.—B.H.PtCl. [129³].—B'HBr. [70³]. White needles.
TRI-PHENYL-DI-ETHYL-DI-THIO-BIURET
NPhEt C(NPh).S.OS.NPhEt. [158³]. Formed from NPhEt.CS.Cl (2 mols.) and aniline (1 mol.)

billeter a. Strohl, B. 21, 108). Yellow needles, aniline hydrochloride and potassium sulpho-. sol. alcohol.

PHENYL-ETHYL-THIOCARBAMIC ACID PhEt.CS.OH.

Ethyl ether Eth. [18]. (143° at 12 m.). S.G. 15 1066. Formed from NPhEt.CS.Cl nd NaOEt (Billeter a. Strohl, B. 20, 1629; 21, 04). Crystals.

Phenyl-ether PhA'. [69°]. Formed from he chloride and phenol. Flat needles.

the chloride and phenon. The last little of the Philades Philades Philades (Prisms (from groin), Converted by alcoholinto (NPhEt.CS), O 143°], S. (alcohol) 7 at 15°.

Phenylethyl-thiocarbamic acid. Phenylthylamine salt

PIELCS.SH. Ethyt ether Eth.* [67°]. (305° 315). Phonyl-dischtyl-4-thio-urea
**Corned by heating NPh:C(NPhet).Set with body and Etl (B.). B'HI. -B.H.PtCl., [148°].
S. at 160° (Bernthsen a. Friese, B. 15, 568, B'C.H.N.3O., [170°]. Formed also from NPhEt.CSCl and VaSEt (B. a. S.). Prisms (from ether). Forms rerystalline compound with MeL.

Phenylether PhA'. [127]. Formed from PhEt.CS.Cl and PhSH (B. a. S.). Needles.

PHENYL-ETHYL-THIO-SEMI-CARBAZIUE NHEt.CS.NH.NHPh. [1227]. Formed from ethylhiocarbimide and phenyl-hydrazine (Dixon, C. J. 55, 302). White crystals, v. sl. sol. water. FeCl, gives a red colour changing to blackishgreen.

NHPh.CS.NH.NHEt. Isomeride Formed from phenyl-thiocarbimide and ethylaydrazine (Fischer, A. 199, 296). Needles.

Di-phenyl-ethyl-thio-semi-carbazide NPhENH.CS.MIII. [149°]. Formed from a phenyl-ethyl-hydrazine and phenyl-thio-4-phenyl-ethyl-hydrazino and phenyl-thio-arbimide (Alchaeis a. Philips, A. 252, 273).

PHENYLETHYL-THIO ARBIMIDE

C.H.Ph.NCS. Formed from phenylethyl-amine by successive treatment with CS, and HgCl, (Neubert, B. 19, 1825). Yellow oil.

PHENYL ETHYL DITHIOCARBONATE

CS(OEt)(SPh). Formed by mixing solutions of C.H. N.Cl and potassium ethyl dithiocarbonate at 0° (Leuckart, J. pr. [2] 41, 186). Reddishyellow oil, sl. sol. water, slightly volatile with steam. Converted by heating with alcoholic NH_a into phenyl mercaptan and ammonium sulphocyanide.

PHENYLETHYL-THIOHYDANTOIN

 $C_{2}H_{*}Ph.N;C<_{NH,CO}^{S-CH_{2}}$ UnH,2N2SO CS < N(C,H,Ph).CH, The hydrochloride B HC)

[138°] is formed from phenylethyl-thio-urca and chloro-acetic acid (Neubert, B. 19, 1822). PHENYL-ETHYL-THIOPHENE C, High i.e.

S<CPh:CH CH:CEt [40°]. Obtained by heating CH_Bz.CHEt.CO,Na with P.S. (Dittrich a. Paul, B. 21, 3457). Small plates. Gives a cherry-red colour with Satin and H.SO, and a bluishgreen colour with phenanthraquinone and prisms, m. sol. cold water. HOAc.

HENYL-ETHYL-THIO-UREA C.H. N.S. i.e. NPhEt.CS.NH, [1180]. Formed from ethyl- (Gebhardt, B. 17, 3039). Needles.

evanide (Gebhardt, B. 17, 2094). Large pearly prisms (from alcohol).

Benzoyl derivative NPhEt.CS.NHBz. 134°]. Formed from chylaniline and benzoyl-thiocarbinide (Dixon, G. J. 55, 305). Palelemon-yellow prisms, insol. water, sol. alcohol. NHPh.CS.NHEt

s-Phenyl-athyl-thio-urea [99°]. Formed from phenyl-thiocarbimide and NH.Et and from ethyl-thiocarbimide and aniline (Weith, B. 8, 1524; Michael a. Palmer, Am. 6, 260). Monoclinic crystals.

Phenylethyl-thio-urea NH. CS. NH. C. H. Ph. [123°]. Formed from phenylethyl-amine hydrochloride and potas ium sulphocyanide (Neubert, B. 19, 1822). Plates (from dilute alcohol).

H. Ph.NH.CS.SNH, C₂H.Ph [130°]. Formed rom phenylethylamine and CS₂ (Neubert, B. 19, 1823). Flate (from diffure alcohol).

Phenyl-ethyl-di-thio-carbamic acid (PhEt.CS.SH.

Phenyl-ethyl-di-thio-carbamic acid (PhEt.CS.SH.

Phenyl-diethyl-di-thio-urea and Ed. (Bertram, B. 25, 55). Yields mercaptan on treatment with alkalis. B'HI. [103°]. B'C₂H₂N₂O₂. [196°].

Phenyl-diethyl-d-thio-urea

B'C_cH_aN₃O₇. [170°]. Phenyl-tri-ethyl-ψ-thio-urea

NPhEt.C(SEt):NEt. (c. 275°). Got from the preceding and Etf (B.). B'C, 11, N, O, [c. 96°]... B', H, PtCl, . [1352]

Di-phenyl-ethyl-thio-urea NHPh.CS.NPhEt. [89]. Formed from phenyl-thiocarbimide and ethyl-aniline (Gebhardt, B. 17, 2090). Crystals.

Di-phenyl-cthyl-4-thio-urea NHPh.C(SEt):NPh. [79°]. Formed from diplicingle-thio-urea and EtBr (Rathko, B. 14, 1776) and by the action of mercaptan on C(NPh), in the cold (Will, B. 15, 1308). Needles (from dilute alcohol). Decomposed by heat into C(NPh), and EtSH. Cl passed into a solution of its hydrochloride yields ethane sulphonic acid. BHCl.- B'2H,PtCl,2aq.-B'III aq. [157.5°] (Bernthsen, B. 15, 266, 567).

Di-phenyl-di-ethyl-thio-urea CS(NEtPh), [75.5°]. Formed from NPhEt.CSCI and ethylaniline at 100' (Billeter, B. 20, 1631). White tables (from ligrom) or needles (from alcohol).

Di-phenyl-di-ethyl-thio-urea CS(NH.C. II.,Ph). [84°]. Formed from phenylethyl-amine and alcoholic CS. (Neubert, B. 19, 1824). Plates (from alcohol), insol. water.

Acetyl derivative C19H22N2SO. [73°].

Di-phenyl-di-ethyl-v-thio-ur-a NPhEt.C(SEt):NPh. Oil. The hydro-iodide. got by heating di-phenyl-ethyl-v-thio-urea with Etl at 130°, is crystalline (B. a. F.).

u-PHENYL-ETHYL-UREA NPhEt.CO.NIL. [626]. Formed from ethyl-aniline hydrochloride and potassium cyanate (Gebhardt, B. 17, 2095).

s-Phenyl-ethyl-urea NPhH.CO.NEtH. [99°]. Formed from ethyl cyanate and aniline (Wurtz, O. R. 32, 417). Needles (from dilute alcohol). Yields a nitrosamine NPhH.CO.NEt.NO [60°] crystallising in monoclinic prisms (E. Fischer, A. 199, 286).

Phenylethyl - urea NH .. CO.NHC.H.Ph. [112°]. Formed from B-phenyl-ethyl-amine and potassium cyanate (Spica, G. 9, 568). Flat

Phonyl - di - ethyl - urea NHPh.CO.NEt, [85°]. Formed from phenyl evanate and NHEt,

Di-phenyl-ethyl-urea NHPh.CO.NPhEt. [91°]. Got from phenyl cyanate and ethylaniline (Gebhardt, B. 17, 2093). Prisms.

s-Di-phenyl-di-ethyl-urea CO(NPhEt)...
[79°]. Formed from NPhEt.COCl and ethylaniline at 130° (Michler, B. 9, 712). Crystals. NPh. CO.NEt. u-Di-phenyl-di-ethyl-urea

1.11-pnenyl-al-etayl-ures NPh, CO.Nitt.

[54]. Formed from NPh, COCl and NHEL.

Dippenyldiethyl-ures NH, CO.N(C,H,Ph),

[109]. Formed from diphenyldiethylamine hydrochloride and potassium cyanate in aqueous solution (Spica, G. 9, 568). Prisms, sol. hot Aq.

Tri - phenyl - ethyl - urea NPh...CO.NPhEt. [899]. Formed from NPh.COCl and ethylaniline (M.). Formed also from NPhEt.CeCl and diphenylamine (Kaufmann, B. 14, 2185).

PHENYL-FORMAMIDE v. vole ii. p. 568.
DI-PHENYL-FORMAMIDINE C₁₃H₁₂N₂ i.e. CH(NPh)(NHPh). Di-phenyl-methenyl-diamine. Mol. w. 196. [138°]

Formation .- 1. By heating chloroform with aniline for 12 hours at 190° (Hofmann, Pr. 9, 229) .- 2. By heating aniline with phenyl-carbamine, with orthoformic ether, or with formic acid (Weith, B. 9, 454; Wichelhaus, B. 2, 116).—3. By passing gaseous HCl into heated formic anilide (Wallach, B. 15, 208) .- 4. From formic anilide and PCI, (Wallach, A. 214, 233). 5. From CH(NPh)SEt and aniline (Wallach a. Wüsten, B. 16, 146). -6. From aniline and CH(NH,Cl)OEt (Pinner, B. 16, 358).

Properties. - Needles (from ether). Yields

B'HCl and B',H,PtCl,

PHENYL-FORMAMIDOXIM C,H,NO i.e. CH(NOH), NHPh. [116°]. Formed from thioformanilide and hydroxylamine (Müller, B. 22, 2411). Needles, m. sol. water. -B'HCl; needles. --B',H,PtCl,: yellow needles.

Bensoyl-derivative CH(NOBz)(NHPh). Needles, m. sol. alcohol and ether.

DI-PHENYL-FORMAZIDINE C₁₇H₁₇N, i.e. CH(N,HPh).N,H,Ph. [185°]. Formed from CH(NH,Cl).OEt and phenyl-hydrazine (Pinner, B. 17, 2002). Yellow plates, v. sol. hot PHENYL-FORMYLACETIC ETHER Yellow plates, v. sol. hot alcohol.

CHO.CHPh.CO₂Et. (145° at 16 mm.). Got, together with an isomeride [71°], by the action of NaOEt on a mixture of formic and phenylacetic ethers (Wislicenus, B. 20, 2931). Liquid. FeCl, colours its alcoholic solutions bluishviolet. Phenyl-hydrazine forms oxy-di-phenylpyrazole.

DI-PHENYL-FUMARAMIC ACID v. FUMARIO ACID.

PHENYL-FUMARIC ACID C, H,O, i.c. CO.H.CPh:CH.CO.H. [161°]. Got by heating bromo-cinnamic ether with alcoholic KCy for 8 hours at 150° (Barisch, J. pr. [2] 20, 186). Got also by heating CO.H.CPh(OH).CH. CO.H (Alexander, A. 258, 82). Nodules (from water).

Di-phenyl-fumaric acid

CO2H.CPh.CPh.CO.H. [c. 260°]. Formed from its ether, which is got, together with di-phenyl-malete ether, by the action of Na on a-bromo-phenyl-acctic ether (Rügheimer, B. 15, 1626). Crystals, decomposing at 260° into water and di-phenyl-maleïc anhydride.

Nitrile CN.CPh:CPh.CN. [158°]. Got by adding alcoholic NaOEt to a-chloro-phenylapetonitrile (Michael a. Jeanprêtre, B. 25, 1680).

DI-PHENYL FURAZANE $\begin{array}{c} \text{CPh:N} \\ \text{CPh:N} \end{array} > 0. [94]$ Formed by heating the (a)-di-oxim of benzil with water at 210° (Dodge, A. 264, 180). Crystals At 300° it forms di-benzenyl-azoxim. H2SO

and HNO, give a di-nitro derivative [220°]. CH:CPh CH:CPh DI-PHENYL-FURFURANE

[91°]. (345°). Formed by heating CPh:C.CH(6O₂H).CO.C₆H, or CH₂Bz.CH₂Bz with conc. HClAq at 160° for 3 hours (Kapf a. Paal, B. 21, 1490, 3057). Got also by heating its dicarboxylicacid (WeH. Perkin, jun., a. Schlosser, C. J. 57, 954). Pates, insol. water.

Tetrahydride C₁₆H₁₆O. (321°). Got by reducing with Na and alcohol. Oil.•

Octohydride C16H20O. Oile Tri-phenyl-furfurane C22H16O i.e.

CPh:CH O. [93°]. Mol. w. 263 by Raoult's CPh:CPh method (calc. 296). Formed by boiling CPhBz:CHBz with HIAq (Japp a. Klingemann, method C. J. 57,675). Got also from desyl-acetophenone by successive treatment with H.SO, and water (Smith, C. J. 57, 645). Needles (from alcohol). Tera-phenyl-furfurane v. LEPIDEN.

DI-PHENYL-FURFURANE CARBOXYLIC ACID CO2H.C:CPh O. [217°]. Formed by boiling CPh:C.CHBz.CO.H with conc. HClAq and alcohol (Kapf a. Paal, L 21, 1489, 3059) Formed also by heating the dicarboxylic acid (W. H. Perkin, jun., a. Schlosser, C. J. 57. 952). Needles (from alcohol), insol. water. May be

Macades (from account), insot. water. May be distilled. Bryields C₁₇H₁₂Br₁O₃.—NaA': needles.

Ethyl ether Eth. [82]. Formed by boiling CH₂Bz.CHBz.CO₂Et with alcohol and HClAq. Crystals (from ether). Yields on reduction a tetrahydride which does not react with AcCl.

Di-phenyl-farfurane dicarboxylic acid C₁₈H_{1.}O₅ i.e. CO₂H.C:CP₂h O. [236]. Formed by dissolving di-benzoyl-succinic ether in H2SO, and boiling the product with alcoholic potash (W. H. Perkin, jun., C. J. 47, 262; 49, 168; 57,

951). Needles, sol. alcohol and ether. FeCl, gives an orange colour in its alcoholic solution. Yields acctophenone on distilling with sodalime. - Ag₂A"

Ethylether Et.A". [86°]. Formed from dibenzoyl-succinic acid and H₂SO₄. Yellow prisms, v. sol. alcohol. Its solution in H₂SO₄ turns violet on heating.

Anhydride C₁,H₁₀O₄, [255']. Formed by heating the acid alone or with Ac₂O. Plates, sl. sol. hot alcohol. Its alcoholic solution c₂. hibits violet fluorescence.

PHENYL - FURFURYL - ACRYLIC Nitrile. C.H.O.CH:CPh.CN. [43°]. Formed from phenyl-acctonitrile, furfuraldehyde, and NaOEt in alcohol (Frost, A. 250, 159). Yields C.H.O.CHBr.CBrPh.CN [114°] ctstallising in orange plates.

Reference. - NITRO-PHENYL-FURFURYL-ACRYLIC PHENYL - FURFURYL - (\$) - NAPHTHO -

TRIAZINE. Dihydride C21H13N2O i.e. C, H, < N.CH.C, H,O Formed by [241°]. warming benzene-azo-(A)-naphthylamine with furfuraldehyde in alcohol (Goldschmidt a.

Poltzer, B. 24, 1007). Needles. - B'HCl: plates.
-B'_H_2PtCl_. Light-yellow crystalline pp.
(B)-PHENYL-(\gamma)-FURFURYL-PROPYLAMINE C,H_3O,CH_CHPh.CH_NH_. (283°).
Formed from pheny facetonitrile and furfuraldehyde, the product of condensation of these bodies C.H.O.CH:CPh.CN being reduced by Na and dry alcahol (Freund a. Immerwahr, B. 23, 2850). Oil, with alkaline reaction. Converted by nitrous acid into the liquid alcohol C₄H₂O.CH₂.CHPh.OH.OH. Phenyi thiocarbin-ide forms C₄H₂O.C₄H₂Ph.NS.CS.NHPh [113]. - B'HCl. [176°]. Crystalline, v. sol. water. Reacts with potassium cyanate forming C4H4O.C3H.Ph.NH.CO.NH2 [101]. - Mercury Gitj.O., Il., rantoo. ang. [137]; needles. — Picrata [152]. Yeflow crystalline powder. PHENYL-FURIDANE. Dihydride

CPh CH.CH. CH₂ • (250° at 721 mm.). Formed by heating its carboxylic acid at 2000 (Perkin, G. J. 51, 731). Oil. HBr forms CH.CO.CH.Br.

PHENYL-FURIDANE DIHYDRIDE CARB-

CO2H.C CH2CH2CH2 ACID · OXYIJC

Phenyldchydrohe cone carboxylic acid. [c. 144]. l'ormed by saponifying its ether, which is ot by the action of NaOEt on a mixture of trimethylene bromide and benzoyl-acetic ether (Perkin, C. J. 51, 726). Monoclinic prisms -AgA': needles (from water).

Ethyl ether Eth', [60°]. Prisms. PHENYL-GLUTARIC ACID $C_0H_{12}O_1$ i.e. CHPh(CH2.CO2H)2. [1382]. Formed by heating sodium malonic ether with alcohol and cinnamic ether at 100°, saponifying the resulting ether CH(CO_Et)_CHPh.CHNa.CO_Et, and heating cthera to the control of the acid at 110 (Michael, J. pr. [2] 35, 352; Am. 9, 110). Needles, sl. sol. water, m. sol. alcohol. -AgA*: amorphous pp.

Di-phenyl-glutaric acid Clf_(CHPh.CO.H), [164*]. Formed by saponifying its nitrile (Zelinsky a. Feldmann, B. 22, 3292). Needles. Nitrile CH_(CHPh.CN), [71*]. Formed by heating CH_Ph.CN with CH_L and dry NaOH, PHENYL-GLYCERIC ACID v. fit-oxy.

PHENYL-PROPIONIC ACID.

TRI-PHENYL GLYCERYL TRIKETONE CH_Bz.CHBz.CH_Bz. Tri-benzeyl-propane. [137°]. Formed from tricarballylic chloride, benzene, and AlCl₃ (Emery, B. 21, 601). Strawyellow needles. Yields a phenyl-hydrazide [57°-60°].

PHENYL-GLYCIDIC ACID C.H.O., i.e. O CHPh Phenyl-pyravic acid? [155] Formed by boiling benzoyl-imido-phenyl-propionic acid NBz CHPh with aqueous HCl or with KOH (Plöchl, B. 16, 2817; 19, 3167). Formed also by boiling phenyl-oxalactic acid with dilute H₂SO₄ (W. Wisticenus, B. 20, 592). Plates, v. e. sol. alcohol and ether. FeCl, colours its alcoholic solution green. Sodium smalagm reduces it to geoxynbenyl-propionic amalgam reduces it to a oxy-phenyl-propionic seid. Yields an oxim and a phenyl-hydrazide CHPh.C(N,HPh)CO.H [161]. Tolylene-o-di-amine forms a quinoxaline (Erlenmeyer, jun., B. 19, 2576; 20, 2465; 22, 1482). Aniline forms C,H,Ph(NHPh)(OH).CO,H.

 (β) -Phenyl-glycidic acid. Formed from C.H.CH(OH).CHCl.CO.H and cold alcoholic potash (Glaser, A. 147, 98). Oil, crystallising at 0°. Decomposes, even at 15°, into phenylacctic aldehyde and CO.. Boiling dilute H.SO. forms CHPh(OH).CH(OH).CO.. It and phenylacetic aldehyde (Erlenmeyer a. Lipp, 4. 219, 181)? Yields β-oxy-phenyl-propionic acid on reduction with sodium-amalgam. - NaA' .-- KA'. -AgA': crystalline powder.

Ethyl other EtA'. (280° cor.). Oil. References .- NITRO- and OXY- PHENYL-GLY-

CIDIC ACID. PHENYL-GLYCOCOLL v. PHENYL-AMIDO-

ACETIC ACID.

PHENYL-GLYCOL v. DI-OXY-ETRYL-BENZENE.
PHENYL-GLYCOLLIC ACID v. Phenylderstative of GLYCOLLIC ACID and MANDELIC

Di-phenyl-glycollic acid v. Benzillo acid. PHENYL-GLYCOLLIC ACRYLIC ACID v. Carboxy-methyl derivative of Coumanic Acid.

PHENYLGLYCOLYL-TROPEINE C18H21NO. Homo-atropine. [98"]. Formed by heating tropine mandelate with HClAq (Ladenburg, A. 217, 82). Deliquescent prisms (fron ether), m. sol. water. Less poisonous than atropine .-B'HAuCl. -B'HBr. -B'C, H, N, O, Yellow plates. TETRA-PHENYL-GLYCOSINE v. GLYCOSINE.

PHENYL-GLYOXAL C.II. CO.CHO. (142° (from ether); a:b:c=2.638:1:3.398; $\beta=74.3.44$ '. •at 125 mm.). Formed by allowing a mixture of its mono-oxim (30 g.) with NaIISO, (120 g. of a 35 p.c. solution) to stand till all is dissolved, and then adding H.SO, and distilling (Müller a. von Pechmann, B. 20, 2904; 22, 2557). Oil. Forms a crystalline hydrate [73°]. Converted by HNO, into phenyl glyoxylic acid, and by potash into mandelic acid. Ammonia forms C₂₂H₁₉N₃O or C₂₂H₁₀N₃O crystallising in plates [193] which can be distilled. Hydroxylamine

gives C₁₅H₁₃N₃O₃, [219°], sol. alkalis. Mono-oxim C₅H₅.CO.CH:NOH. acetophenone. [128°]. Formed from acetophenone, isoamyl nitrite, and alcoholic NaOEt (Claisen, B. 20, 656, 2194; Braun, B. 22, 556). Monoclinic tables (from chloreform), sl. sol. cold water, v. sol. alkalis. Yields C.H., CO.CN on warming with Ac.O. Boiling NaOHAq forms NaCy and NaOBz. Its acetyl derivative is converted by NaOHAq into CHBz(OH).CO.CO.C.H. [170°] crystallising in minute needles (Söder-

baum, B. 24, 1386, 3034). Di-oxim CaH, C(NOH).CH(NOH). phenyl-amphi-glyoxim. [162°] (S.); [168°] (R.). Formed by the action of hydroxylamine on the mono-oxim, or on mono- or di-bronio- acetophenone (Schramm, B. 16, 2183; Strassmann, B. 22, 419; Russanoff, B. 21, 3501). Small needles, v. sol. alcohol, insol. CHCl,; subliming below 160°. N₂O, gives C₆H₂.C₂HN₂O₂ [c. 90°] crystallising in colourless prisms (Scholl, B. 23, 3504). By dissolving in ether and treating with HCl it is converted into an isomeride [180°]. This body, called phenyl-anti-glyoxim, is v. sol. Ac₂O and yields a di-acetyl derivative [92°]. Phenylanti-glyoxim is only stable in acid solutions being readily re-converted into the original di-oxim [168°]. By treatment of the di-oxim [168°] NaOHAq and CO₂ at -10° there is formed a

second isomeride (148°-154°) called phenyl-synglyoxim which yields an oily di-acetyl deriva-tive.—AgC, H,N,O,. Curdy pp.

Phenyl-hydrazide C,H, C(N,HPh).CHO.
[148]. Yellow plates (M. a. P.).

Phenyl-hydrazide C,H,.CO.CH;N2HPh. [129°]. Formed by the action of warm dilute KOHAg on the compound got by treatment of sodium benzoylacetic ether with diazobenzene chloride (Stierlin, B. 21, 2123). Yellow plates. p-Tolyl-hydrazide CHBz:N.H.C.H.,Me.

Got in like manner, using p-diazotolucne chloride. Yellowish-brown plates, v. sol. ether.

Di-phenyl-di-hydrazide C.H.C(N,HPh).CH(N,HPh). [1522]. Got by heating phenyl-glyoxal or, better, the phenyl-hydrazide of benzoyl-cathinol with phenylhydrazine hydrochloride and NaOAc at 100°

(Laubmann, A. 243, 247). Yellow plates.
Di-phenyl-di-methyl-di-hydraz?de
Cath, C(N_Mclh), CH(N_Mclh). [151*]. Formed
from w-bromo-acctophenone and phenyl-methylhydrazine (Culmann, B. 21, 2597). Prisms.

Di-phenyl-glyoxal v. Benzu. PHENYL-GLYOXALINE C, II, N2 i.e. •

 $C_{\bullet}H_{\bullet}N <_{\mathrm{CH};N}^{\mathrm{CH};\mathrm{CH}}$. [13°]. (276°). Formed by

warming sulphydro-phenyl-glyoxaline [181°] with dilute HNO, or HClAq (Wohl a. Marek-wald, B. 22, 576, 1353). Crystalline, miscible with alcohol. B'HAuCl₄.—B'₂H₂PtCl₆.—Picrate B'C₆H₃N₃O₇. [152°]. Yellow needles (from alcohol).—B, AgNO, —B'MeI. Syrup.

Phenyl-glyoxaline NII CH :CH (c. 340°). Formed by distilling its dicarboxylic acid, which is got from di-nitro-tartaric acid, benzoic aldehyde, and NH, (Maquenne, C. R. 111, 742). Plates (from benzene). - $B'_{2}H_{2}C_{2}O_{1}$. Needles. - $B'_{2}H_{2}PtCl_{6}$.

Di-phenyl-glyoxaline $\mathrm{CH} \leqslant_{N-CPh}^{NH,CPh}$. [227°].

Formed by the action of formic aldehyde and ammonia on benzil (Japp, C. J. 51, 559). morphous. Crystallises with di-phenyl-methylglyoxaline as (C₃N.H₂Ph₂)C₃N₂HMePh₂ [218]. -B'2H2P(Cla: small flat yellow needles.

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PHENYL-GLYOXIM v. Oxim of PHENYL-GLYOXAL.

PHENYL-GLYOXYLIC ACID C.H.O. C.H. CO.CO.H. Benzoyl-formic acid. [66°].

Formation .- 1. From benzoyl evanide and conc. HClAq in the cold (Claisen, B. 10, 429, 844, 1663; 12, 626, 1505) or HOAc saturated with HCl (Buchka, B. 20, 395).—2. From dioxy-ethyl-benzene (phenyl-glycol) and nitrio acid of S.G. 1-38 (Zincke, A. 216, 305).—3. By saponitying its ether, which is got by heating COCLCO. Et with HgPh, for several hours at 150°; the yield being 40° p.c. of the theoretical (Glaisen a. Morley, B. 11, 1596). - 4. By oxidising acctopherone with alkaline KMnO, at 0°; the yield being 20 p.c. of the theoretical amount (Glückmann, M. 11, 248).

Properties. -- Prisms, v. e. sol. water and ether. Decomposed by distillation into benzoic acid and CO, and partly also into benzoic aldehyde and CO. Phenyl-hydrazine added to its solution in dilute HCl forms a bulky yellow pp.

of phenyl-hydrazide (Ebers, A. 227, 340). When mixed with benzene (containing thiophene) i gives with conc. H.SO, a red colour changing t violet. On adding water, the layer of benzen becomes crimson.

Reactions. 1. Sodium amalgam reduces i to mandelic acid.— 2. HI and P at 160° reducit to phenyl-acetic acid.—3. Phenyl mercaptar and gaseous HCl form C₈H₂C(SPh). CO₂E [142^o], sl. sol. benzene (Baumann, B. 18, 891) Phenyl mercaptan alone forms a crystalline powder C₀H₁,C(OH(SPh).CO₂H [69°]. Salts.—NaA'O—KA'aq: dimetric tables.—

NH₄A'.—CaA'₂aq₁flat prisms.—BaA'₂.—SrA'₂aq —CuA'₂.—ZnA'₂2aq.—PbA'₂.—PbA₂aq.—AgA' Methyl ether MeA'. (218°). Ethyl ether EtA'. (257'). S.G. 175 1·121. Forms a crystalline compound with NaIISO₂. Redets in alcoholic solution with hydrazine neates in actionic solution with hydrate forming C, H₁₂N₂O₁ [120°] and C₂₂H₂₂N₂O₁ [135°] (Curtius, J. pr. [2] 44, 566).

n. Propyl ether PrA. (174° at 60 mm.).

Isoanyl ether. (174° at 38 mm.).

Isoanyl ether. (182° at 40 mm.).

(a) Amide C.H. CO.CONH. [91]. Formed from benzoyl cyanide and cold HClAg. On solution and re-ppn. by CO2 it forms an unstable

hydrate C_sH NO. aq [65°] (so-called (β) amide).

• (γ) - Amide (C_sH , NO.). [134°]. Formed by adding an alcoholic solution of the (a)-amide to dilute HClAq (Claisen). Formed also, together with the (a) amide, by the action of HOAc saturated with HCl upon BzCy (Buchka). Prisms.

Nitrile v. BENZOYL CYANIDE. (a) - Oxim C, II, C(NOII).CO, II. Isonitrosophonyl-acetic acid. [127]. Formed by the action of hydroxylamine on the Na salt (A. Müller, B. 16, 1617) or on the acid at '0° (Hantzsch, B. 23, 2333; 24, 42). Thick wisms, v. e. sol. water. Yields a amido-phenyl-acetic acid on reduction. - KA'ag: very soluble crystals. -BaA', 1 aq. -AgA'.

Acety derivative. [119]. Prisms.

(β) - O. rim C₆H₃, C(NOM), CQ₂H• [145⁸]. Formed by the action of HCl on an ethereal solution of the (a) oxim. Formed also by warming phenyl-glyoxylic acid with hydroxyl-Tri-phenyleglyoxaline v. Lophine, vol. i. amine and potash. White needles composed of dimetric prisms.

Acetyl derivative. [1250]. Tables. Methyl ether of the oxim

CPh(NOH).CO.Me. [139°]. Got from the Ag salt and McI (Müller, B. 16, 2987). Converted by NaOEt and MeI into Clh(NOMe).CO.Me [56°], sol. alcohol, insol. alkalis.

Ethyl ether of the oxim CPh(NOH).CO₂Et. [113°]. Formed from phenylglyoxylic ether and hydroxylamine (Gabriel, B. 16, 519). Needles (from hot water).

Nitrile of the oxim C,H,.C(NOH).CN. 129°]. Formed from phenyl-acetonitrile, amyl nitrite, and alcoholic NaOEt (Frost, A. 250, 163; Meyer, B. 21, 1306). Formed also by the action of hydroxylamine on dibromo-acctophenone in dilute alcohol at 60° (Russanoff, B. 24, 3505). Thin plates, v. sol. alcohol.—C.H., C(NONa).CN: yellow powder, v. sol. water. Yields an acetyl detivative [58°].—KA'.—CuA'₂—Pb_A₂O.—AgA'.

Phenyl hydrazide C.H., C(N₂HPh).CO.H.
[153°]. (F.); [153°-1642] (Yon Pechmani, B.
25, 1054). Yellow needles, al. sol. hot water

(Fischer, B. 17, 578; Ebers, A. 227, 340). May be reduced to C.H., CH(N.H., Ph).CO.H [158°], and finally to aniline and a amido-phenyl-acetic

Phenyl-methyl-hydrazide C₆H₃.C(N₂MePh).CO₂H₂ [116°]. Plates (from alcohol). Its amide C₆H₃.C(N₂MePh).CONH₄. [156°] is crystalline.

Phenyl-gthyl-hydrazide C.H.,C(N,EtPh).CO.H. [109°]. Formed, to-gether with its amide C.H.,C(N,EtPh).CO.NH. [111°], by the action of phenyl-cthyl-hydrazino in dilute HOAc on phenyl-glyoxylic acid. Yellow plates, sl. sol. water. Yields ethyl-aniline and benzoic aldehyde when heated with conc. HClAq.

References. -- AMIDO-, NITRO-, and OXY-

PHENYL - GLYOXYLIC o - CARBOXYLIC ACID.

ACID C_aH₁(CO₂H).CO.CO.H. [140°]. Formed by oxidising the oxyquinone C_aH₁₀O₃ or indonaphthene dibydride carboxylic acid with alka line KMnO, (Scherks, B. 18, 378; cf. Zineke, A. 226, 53, 240, 142). Yields CO, and phthalic anhydride on heating. May be reduced to phthalide carboxylic acid. -- K, A". Ban" 2aq. -Cu,A"(OH), 6aq. -Ag A": crystalline pp.

PHENYL-DIGUANIDE C, II, N. i.e. NH:C(NHPh).NH.C(NH2):NH. [c.237°]. Formed by the action of alcoholic ammonia and AgNO, or HgCl₂ on guanyl-phenyl-thio-urea (Bamberger, B. 13, 1582). Formed also by heating aniline hydrochloride with di-cyan-di-amide in alcohol at 100° (Smolka a. Friedrich, M. 9, 232). Plates, v. sol. water and alcohol; absorbs CO. from air. When boiled with baryta-water it yields NH, aniline, phenyl-urea [147], phenylguanidine, guanidine, and urea (Emich, M. 12, 15).—B'HCl: prisms. Yields phenyl-carbamine

15).—B HOI: prishes. Then phenyl-carbanine when warmed with alcoholic potash and CHCl₃.

Salts.—B'HNO₃. [209°].—B' [H SO₄.—Cu(C₃H₁₈N_{\$\)}, 14aq: red powder, sol. hot water.

— CuA'₂H₁Cl₄ 14aq.—CuA'₂H₂SO₄, 1½aq.

— CuA'₂H₂CrO₄aq.—NiA'₂.—NiA'₂H₂SO₄, 1½aq.

— NiA'₄H₂SO₄ 1¹ aq.—CoA'₂ 1½aq.

— CoA'₂H₃SO₄ aq: crimson needles.

(a) Pi neared distancial of M. M. S. (b) Pi neared distancial of M. M. S. (c) Pi neared distancial of M. M. S. (d) Pi n

(a) Di-phenyl-diguanide C₁H₁N₅ i.c. NPh:C(NHPh).NH.C(NH₂):MH. Formed by the action of AgNO, and aniline on guanyl-phenylthio-urea (Bamberger, B. 13, 1581). White solid, m. sol, water and alcohol, alkaline in reaction.—B'HNO₃. [231°]. White needles. (B)-Di-phenyl-diguanide

NH:C(NPh.).NH.C(NH.):NH. [c. 162°], Formed by heating diphenylamine hydrochloride with di cyan-di-amide (Emich, M. 12, 21). Thin medles, with alkaline reaction. - B'HNO_x. [203°]. Prisms. -B'23H2SO4.

Tri-phenyl-diguanide CzoH, No. Formed from guanyl-tri-phenyl-thio-urea, NH3, and AgNO. Formed also from di-phenyl-guanidine and phenyl-cyanamide [78°] in ether (Rathke a. Oppenheim, B. 23, 1672). Prisms (from alcohol). With CS₂ at 100° it yields triphenyl-thio-ammeline C_nH_nN,S. — B'HCl: prisms, v. sol. alcohol.—B'H.PtCl.

PHENYL-GUANIDINE C,H,N, i.e. NH:C(NH₂)(NHPh). Formed by desulphuration of phenylethio-ures in presence of alcoholic NH₂ (Feuerlein, B. 12, 1602). Formed also by the action of baryta-water on phenyl-diguanide

(Emich, M. 12, 11). Decomposes on standing into phenylcyanamide and ammonia. — Picrate B'C,H,N,O,. [208°-214°] (Prelinger, M. 13, 99).

Di-phenyl-guanidine C13H13N3 i.c.

NH:C(NHPh)... Melaniline. [147°]. S. (90 p.c. alcohol) 9.25 at 21°.

Formation.—1. From aniline and CyCl or CyBr (Hofmann, A. 67, 129; 74, 8; Weith a. Ehert, B. 8, 912). - 2. By the action of PbO on As solution of di-phenyl-urea in alcoholic NH, (Hofmann, B. 2, 452, 688; Weith, B. 7, 937; Rathke, B. 12, 772).—3. By boiling phenyl-thiourea with HgCl(NHPh) and alcohol (Forster, B. 7, 2291; A., 175, 35). -4. Together with thiourea, by the action of aniline on mercuric fulminate (Steiner, B. 7, 1244; 8, 518). 5. By confibination of di-phenyl-cyanamide with NH₃ (Weith, B. 7, 10).

Properties. Monoclinic prisms (Arzruni, P. 152, 284), se sol. cold water.

Reactions.—1. Ac.O at 100° yields acetyl-phenyl-uren [185']. At 150° the product is acetyl-di-phenyl-uren [115°] (McCreath, B. 8, 1181) 2. Phenyl thiocarbimide forms, in the NHPh.CS.NPh.C(NH).NHPh [150°], weak base, sl. sol. benzene. 3. HClAq at 250° forms CO., NII, and aniline. -4. Cyanogen passed into its alcoholic solution forms C15H13N3 which crystallises from alcohol in yellowish needles [151°], decomposed by HClAq into crystalline melanoximide $C_{13}H_{11}N_{3}O_{21}$ which is split up by alcoholic potash into oxalic acid and diphenylguanidine, and by alcoholic HCl into NH, and di-phenyl-parabanic acid.

Salts. The hydrochloride is gummy. B'HAuCl₁: golden needles. -- B'2H2PtCl₆. B'HBr: stellate groups of needles, v. sol. water. - B'HI. - B'HNO₃. - B'₂AgNO₃: geodes. - B'₂H₂SO₄: stellate groups of plates. - B'H₂C₂O₄. -Sulphocyanide: [115]; m. sol. water.

Dibenzoyl derivative C27 II21 N8O2 [102°]. Monoclinic (McCreath, B. 8, 383). Tri-phenyl-guanidine C, II, N, i.c.

NPh:C(NHPh)₂. Mol. w. 287. [143°]; [147°] (F. a. W.). S. (alcohol) 4.5 at 0°.

Formation. - 1. By adding I to an alcoholic solution of di-phenyl-thio-urea alone or mixed with aniline (Hofmann, B. 2, 453). - 2. From diphenyl-thio-urea and HgCl(NHPh) (Forster, B. 7, 291). - 3. From di-phenyl-cyanamide C(NPh)2 and aniline (Weith, B. 7, 10).-4. Together with phenyl-thiocarbimide by heating diphenyl-cyanamide with di-phenyl-urea (Weith, B. 9, 810).—5. By boiling di-phenyl-urea with inverted condenser (Barr, B. 19, 1765). -6. By heating di-phenyl-thio-urea with aniline, with Cu, or with PhCl₂ (Merz a. Weith, Z. [2] 4, 513, 609; 5, 583, 659; Gir: id, Bl. [2] 46, 506), or with Italian 145° (Buff, B. 2, 498).—7. By heating di-phenyl cyanamide (2 mols.) with phenyleneo-diamine (1 mc!.) at 210° (Keller, B. 24, 2505). 8. By the action of aniline on CCI, or chloropicrin (Hofmann; Basset, C. J. 18, 31). - 9. By the action of PCl₂ (1 mol.) on a mixture of diphenyl-urea (3 mols.) and ardline (3 mols.).—10. By the action of PCl, (2 mols.) and CO, (3 mols.) on aniline (9 mols.) at 170° (Merz a. Weith, Z. [2] 6, 160).—11. By fusing di-phenylurea with NaOH (Hentschel, J. pr. [2] 27, 500).

12. From phenyl thiocarbimide by chlorinating

and heating the product NPh:CCl₂ with aniline (Sell a. Zierold, B. 7, 1231). The base got is possibly an isomeric tri-phenyl-guanidine.— 13. A product of the action of CSCl, on CS(NHPh), and benzene (Freund a. Wolf, B. 25, 1464).

Properties .- Trimetric six-sided prisms (from alcohol); a:b:c = .670:1:.558, nearly insol. boiling water. Occurs also in an amorphous form (Giraud, Bt. [2] 46, 505). Decomposed above 250° into online and C(NPh). KClO, (1, pt.) and HCl give a greenish solution, depositing dark flakes which dissolve in alcohol with violet

Reactions.—1. CS at 170° forms CS(NPIM), and phenyl thiocarbimide—2. H.S passed through it at 170' forms aniline and di-phenyl-urea (Morz a. Weith, Z. [2] 6, 72).—3. Water at 175° forms aniline and di-phenyl-urea.—4. Conc. KOHAq or conc. HClAq yield aniling and CO2 on heating .- 5. Cyanogen passed into the alcoholic solution forms crystals of CnH1,N3 which is decomposed by HClAq into NH1 and which is decomposed by Holly NPh.CO [c. NPh] NPh.CO 230°] which is itself decomposed by boiling with alcohol and HClAq into aniline and di-phenylparabanic acid (Hofmann, B. 3, 701; Stojentin, J. 7r. [2] 32, 1).—6. Chloro-glywylic ether COCLCO, Et forms a carbonyl derivative

C(NPh) NPh CO which forms the salts B'HCl [190°] and B'HNO, [185°] (Stojentin). - 7. COCI, forms the above (?) carbonyl derivative C₂₀H₁₀N₂O, which crystallises from CS₂ in tables [134°] and forms a hydrate B' aq [141°] (Michler a. Keller, B. 14, 2181).

Salts.—B'HCl aq [242°] (Weith, B. 9, 810); [245°] (F. a. W.). S. 2 at 0°,—B'IINO,; lamine.—B'_2H_1PtCl, S. 09 at 0°,—B'II.SO,: broad needles. B'HOAc. B'H, C,O,: lamina. B'C, H, N, O,. [178°]. S. 0082 at 15° (Prelinger,

Acetyl derivative C(NPh)(NPhAc). [181°]. Crystals (MacCreath, B. 8, 383). Benzoyl derivative C(NPh)(NPhBz)2.

[185°]. Plates (from alcohol).
(β)-Tri-phenyl-guanidine
C(NH)(NHPh)(NPh.). [131°]. Formed heating phenyl-cyanamide (cyanilide) CN.MIPh with diphenylamine at 125° (Weith a. Schröder, B. 8, 912). Regular tablets, nearly insol. water. Its solution in cone. H.SO, becomes violet on heating.

Reactions.-1. Conc. HClAq or KOHAq at ! 260° forms CO, NH, aniline, and NHPh... CS₂ at 160° forms the sulphocyanide, H.S. phenyl-thiocarbimide and NHPh.

Salts.-B'HCl aq. S. (of B'HCl) 284 at

23°.-B',H,PtCl,: crystalline.

Dicyanide C₂₁H₁₇N₃. [173°]. A product of the action of cyanogen as an alcoholic solution of aniline (Hofmann, A. 66, 129; B. 3, 763). Got also by boiling the compounds of cyanogen with di-phenyl-guanidine or (a)-triphenyl-guanidine with aniline hydrochloride (Landgrebe, B. 10, 1593; 11, 973). Dark-brown needles (containing aq) with violet iridescence (from alcohol).—B'HCl 3aq: brown needles.

Tetra - phenyl - guanidine C(NH)(NPh2)2. [181°]. Formed by passing gaseous cyanogen

chloride through diphenylamine at 160° (Weith, B.7, 843). Pyramids (from ligroïn), insol. water, v. sol. alcohol and ether. Conc. H.SO, forms a colourless solution turned violet-red by heat. CS2 at 260° forms tetra-phenyl-thio-urea. Solid KOH at 200°, and con HClAq at 340°, yield NH3, CO., and NHPh2.

Salts.—B'HCl 5aq. Efflorescent tablets.—B'_H_PtCl_s.—B'HNO_s.

References. - DI-BROMO-, DI-CHLORO-, DI-10DO-, and NITRO- PHENYL-QUANIDINES.

DI-PHENYL-GUANDINE CARBOXYLIC ACID C(NH)(NH, h).NH.C, H, CO, H. Phenyl-guanido-benzoic acid. [165°]. Formed by heating m-cyanamido-benzoic acid or cyancarf bimidoamido-benzoic acid with aniline (Traube, B. 15, aq), nearly insol. alcohol and ether, sol. hot water, aqueous alkalis and acids.-HA'IICl aq.

Reference. - Amido - di - Phenyl - Guanidine CARBOXYLIC ACID.

PHENYL-GUANIDO-ACETIC ACID

[260' uncor.] Formed from phenyl-cyanamide and glycocol (Berger, B. 13, 992). Crystals, DIPHENYL-DI-GUANIDO-DI-TOLYL-SUL-

PHIDE S(C,II, NII.C(NII).NHPh)2. Thio-ptolyl-di-phenyl-di-gnanidine. [1539]. Formed by heating di-phenyl-di-uramido-di-tolyl sulphide with alcoholic NH, and HgO (Truhlar, B. 20, 675). Small white needles (from ether-ligroin). V. sol. alcohol, benzene, and ether.—B'II,Cl,PtCl,: yellow amorphous powder.

Tetra-phenyl-di-guanido-di tolyl-sulphide S(C,II, NH.C(NPh).NHPh). Thio-p-tolyl-tetraphenyl-di-guanidine. [106°]. Formed by heating di-phenyl-di-uramido-di-tolyl sulphide with aniline and HgO (T.). Amorphous powder.

PHENYL-HEPTADECYL-THIO-UREA C. H. NH.CS.NI[C., Hx., 179"]. Formed by boiling heptadecyl thiocarbimide with aniline and

alcohol (Turpin, B. 21, 2091).

PHENYL HEFTADECYL UPEA C2, H1, NO. i.e. C6, II, Nfl.CO.NHC1, H3, [99]. Formed by heating heptadecylamine hydrochloride with COCl₂ in benzete at 100°, the product being heated with aniline (Turpin, B. 21, 2492).

PHENYL-HEPTANE v. HEPTYL-BENZENE. Disphenyl-heptane C.H.; CHPh. (191° at 13 mm.). Formed from CeH13.CHCl benzene, and AlCl₃ (Auger, Bl. [2] 47, 48; Krafft, B. 19, 2986). Needles.

PHENYL-HERTENOIC ACID C .: H .: O. i.e. Ph.CEt.CEt.CO.H (?) Oil. Got by passing CO over a heated mixture of NaOEt and sodie cinnamate (M. Schroeder, A. 221, 52).

PHENYL HEPTYL KETONE CARBOXYLA ACID C.H., CO.CH. CH(C.H.,).CO.H. [103°]. Furned by heating phenacyl-isoamyl-malonic acid (Paal a. Hofmann, B. 23, 1504). Plates, insol. water, sl. sol. ligroïn. On repeated dis-

Ethyl ether Eth. (200°). Oil.

PHENYL-HEXINENE v. BUTENIL-SIYEENE. DI-PHENYL-HEXOIC CH_Ph.OPhPr.CN. [63°]. (330° 340°). Formed from C₆H₂.CHPr.CN, benzyl chloride, and NaOH (Rossolymo, B. 22, 1236). Needles. ACID.

TETRA PHENYL-HEXUNENE & CPh CH.CH CPh [269°]. Formed by heating di-benzyl-carbinol with MeI at 265° (Bogdanowska, B. 25, 1273). Needles, insol. alcohol and ether, sol. CHCl.

PHENYL-HEXYL-TRIAZOLE CARBOXYLIC

ACID CH₂(CH₂), C NNPh [126°]. tained by saponifying its nitrile, which is got from phenyl-hydrazine dicyanide and heptoic aldehyde (enanthol) (Bladin, B. 25, 186). Silvery plates, v. sol. alcohol. -CuA', aq. -HA'HCl.

Amide. [82.5°]. White plates.

Thio-amide C₁₁H₁₈N₁CS.NII... [77°].

Formed from the crude nitrile and alcoholic ammonium sulphide. Yellow plates, sol. alcohol.

DI-PHENYL-HEXYL-TRICYANIDE

 $N \leqslant_{\mathrm{CPh}:N}^{\mathrm{CPh}:N} \searrow_{\mathrm{C.}(\mathrm{CH_2})_s,\mathrm{CH_3}}^{\mathrm{CPh}:N}$ [44°]. 15 mm.). Cot from heptorl chloride, benzonitrile, and AlCl, at 70° (Krafft a. Hanssen, B. 22, 808).

PHENYL HEXYL KETONE C.H. CO.C. H. [17]. (267°) at 740 mm. Formed by the action of AlCl₃ on a mixture of benzene and heptoyl chloride (Auger, Bl. [2] 47, 50; Krafft, B. 19, 2987). Leaflets. Yields an oxim [55]. PHENYL-HEXYL-(β)-NAPHTHOTRIAZINE.

Dihydride C ... H ... N i.e. C .. U .. N. NPh ... N. NPh

[176.5°]. Formed by heating benzene-azo-(A)naphthylamine with conanthol and alcohol (Goldschmidt a. Poltzer, B. 24, 1007). Needles, sol. alcohol.—BHCl. [226°]. White needles.
—B'_2H_P(Cl_c. [225°]. Granules.
PHENYL-HEXYL-PYRAZOLE C_6H_0N_2 i.e.

 $\mathbf{C}_{a}\mathbf{H}_{13}$. $\mathbf{C} \leqslant \frac{\mathbf{CH} - \mathbf{CH}}{\mathbf{NPh} \cdot \mathbf{N}}$. (319°).Formed from heptoyl-acetic aldehyde and phenyl-hydrazine (Claisen a. Stylos, B. 21, 1149). Oil.

PHENYL-HEXYL-THIO-UREA C₁₃H₂₀N₂S i.c. (N #Ph).NH.CHaCHEt., [53°]. Formed CS(NRPh).NH.CH.cHet. [53°]. Formed from hexylamine and phenyl-thiocarbinide (Freund a. Herrmann, S. 23, 195). Prisms.

PHENYL-HEXYL-UREA C17H20N.O i.c. CO(NHPh).NII.CH,.CHEt₂. [705]. Formed from hexylamine and phenyl cyanate (Freund a. Herrmann, B. 23, 194). Needles.

PHENYL-HOMO-ITAMALIC ACID v. Oxy-BENZYL PYROTARTARIC ACID.

PHENYL-HYDANTOÏC ACID

NH₂.CO.NH.CHPh.CO₂H. [178°]. Got by boiling (a)-phenyl-hydantoin with baryta (Pinner,

B. 21, 2326). Prisms, sl. sol. cold water.

A mide NH₂:CO.NH.CHPh.CO.NH₂. [223°]. Formed by adding the compound got from urea and the cyanhydrin of benzoic aldehyde to H SO4 and pouring into water at 0' (Pinner a. Spilker, Br 22, 697). Prisms (from dilute alcohol). lields phenyl-hydantoin on heating.

PHENYL-HYDANTOIN C, H, N, O, i.e. CO NH .CO [192°]. Formed by fusing urea with phenyl-amido-acetic acid (Schwebel, B. 10, 2045). Needles, v. sl. sol. water, sol. alkalis.

(a)-Phenyl-hydantoin CO NH.CO Dioxy-phenyl-glyoxaline. [178°]. Formed by heating the cyanhydrin of benzoic aldehyde with mandelic nitrile at 100° (Pinner, B. 21, 2321). Formed also from phenyl-uramido-acethe ether and KOH (Kossel, B. 24, 4150). Needles (from HClAq). KOH and MeI yield C.H.MeN2O2 [1620], crystallising in needles .-KA': needles, v. sol. water.

Acetyl derivative C.H.AcN.O. [145°]. Small needles (from benzene), insol. water.

C(NH) < NH.CO Phenyl-\psi-hydantoin*

[above 300°]. Got by dissolving (a)-phenylhydantoïn in alcoholic potash and then adding HCl. Crystalline. $-K\Lambda'$: almost insol. water.

Atotyl derivative C(NH) CNAc.CO White prisms (Pinner a. Spilker, B. 22, 698). Decomposes at about 290".

PHENYL-HYDRAZIDO-ACETIC ACID

C, 17, NH. WH. CH, .. CO, H. (159°). Formed by reducing the pheny hydrazide of glyoxylic acid (Elbers, A. 227, 353). Formed also by reducing phenyl-osotriazole carboxylic acid with sodiumamalgam (Pechmann, A. 262, 288). Hexagonal tables, sol. hot water. Re-oxidised by Fehling's tables, sol. hot water. Re-oxid solution to NHPh.N:CH.CO₂H.

u-Phenyl-hydgazido-acetic acid

NH2. NPh.CH2.CO H. [131°]. Got by saponifying its ether [127°], which is formed by heating phosyl nydrazine with chloro-acetic ether at 100° (Reissert a. Kayser, B. 24, 1519). Needles.

PHENYL-HYDRAZIDO-BUTYRIC ACID C₁₀H₁₄N₂O₂ i.e. CHEt(N₂H₂Ph).CO₂H. Formed by reducing the phenyl-hydrazide of ethyl-glyoxylic acid (Japp a. Klingemann, A. 247, 217). Needles (from McOII). Softens at 165%.

Phenyl-hydrazido-isobutyric acid

CMe₂(N₂H₂Ph).CO₂H.

Anhydride N.HPh CO. [175°]. Got by gently heating the nitrile with H.SO, and pouring into water (Reissert, B. 17, 1458). Crystals, v. sol. alcohol. -B'HCl: crystals.

Nitrile CMe2(N2H2Ph).CN. [70°]. Got by heating the cyanhydrin of acctone with phenyl-

With pients with p of the nitrile. B"H3Cl3: crystals.

Phenyl-hydrazido-butyric acid

NH.,.NPh.CHMe.CH,.CO.H. [1110]. Formed phenylfrom potassium \$B-bromo-butyrate, hydrazine and NaOAc in aqueous solution (Lederer, J. pr. [2] 45, 87). Plates (from alcohol), v. sol. hot Aq. Converted by conc. H₂SO₄ into oxy-phenyl-methyl-pyrazole dihydride.

PHENYL - B - HYDRAZIDO - CROTONIC ETHER CH3.C(NH.NHPh):CH.CO2Et. [50°]. Formed from acctoacetic ether (1 mol.) dissolved in other by adding phenyl-hydrazine (Nef. A. 266, 70; cf. Knorr, A. 238, 147). Colourless needles, v. e. sol. ether, sl. sol. ligroin. Turns yellow in air. Split up by conc. HClAq into phenyl-hydrazine and acetoacetic ether. When heated in vacuo at 200° it changes to oxy-phenylmethyl-pyrazole. Conc. H.SO, followed, after 10 minutes, by water forms methyl indole carboxylic ether [134°]. HgO oxidises it to the azo-compound CH, C(N₂Ph):CH.CO₂Et crystallising from light petroleum in red needles [51°]. AcCl forms a di-acetyl derivative CH, C(NAc.NAcPh): CH.CO Et (245°-250° at

150 mm.). PHENYL-HYDRAZIDO-METHYL-QUINOL-

INE C.H.MeN(N.H.Ph). [197°]. Formed from

(Py. 3) methyl-quinoline and phenyl-hydrazine (Ephraim, B. 24, 2820).

PHENYL - HYDRAZIDO - METHYL - THIAZOLE. Dihydride C₁₀II₁₂N₃S i.e.
CHMe.S
C.NH.NHPh. Phenyl-propylene-ψthio-semicarbazide. [93°]. Formed by heating
phenyl-allyl-thio-usea with cone. HClAq at 100°
(Arenarius, B. 24, 269). Yellowish plates (from
ligroin).—B'HCl. [202°]. Concentric crystals.
—Picratte. [167°].

PHENYL-HYDRAZIDO-PHENYL-ACETIC ACID C_{1.}H_{1.}N_.O₂ i.e. NHPh.NH.CHPh.CO.H. [158°]. Got by reducing the phenyl-hydrazide of phenyl-glyoxylic acid (Elbers, A. 227, 315). Crystalline, v. sl. sol. cold water, v. sol. alcohol.

PHENYL-HYDRAZIDO-PROPIONIC ACID C.H., N.O., **.c. NH., NPh. CHM.6.CO., II. [187]. Formed by boiling its amide with NaOHAq (Reissert, B. 17, 1454; 20, 3110; 22, 2021). The ether is got by heating lactic ether with phenyl-hydrazine. Needles. *Yields phenyl-a-amido-propionic acid on reduction.

Ethyl ether ELA. [116].—EtA'HCl. Nitrile. [58]. Formed by heating • CH,CH(OH).CN with phenyl-hydrazine at 100°. Amids. [124]. White crystals.

Phenyl-hydrazido-propionic acid
NHPh.NH.CHIMo.CO₂H. [172°]. Formed by
reducing the phenyl-hydrazide of pyruvic acid
with sodium-annalgam (Pischer a. Jourdan, B.
16, 2244; Japp a. Klingemann, B. 20, 3281; A.
247, 211). Needles (from MeOII). Re-oxidised by
cold Pehling's solution to NHPh.N:CMc.CO₂II.

PHENYL-HYDRAZIDO-QUINOLINE
C,H,N.NII.NHPh. [191°]. Formed from (Py. 3)chloro-quinoline and phenyl-hydrazine (Ephraim,
B. 24, 2818). Needles, v. sol. chloroform. Reduced
by HI and P to (Py. 3)-amido-quinoline.

PHENYL-HYDRAZINE C, H, N₂ i.e.
NHPh.NH₂. [23°]. (241.5° i.V.) at 750 mm.
S.G. 27 1097 (E. Fischer, A. 236, 198). H.C.v.
805,240. H.C.p. 806,300. H.F. 34,200 (from diamond) (Petit, A. Ch. [6] 17, 168).

Formation.—(E. Fischer, B. 8, 589, 1005, 1641; 9, 111, 880; A. 190, 67).—By the action of zine and HOAc on diazo-benzene anilide or diazo-benzene diethylamide.

Preparation.-1. A cold solution of 71 pts. of sodium nitrite in 50 pts. of water is slowly added to a well-cooled mixture of 10 pts. of aniline and 200 pts. of HCl (30 p.c.). To the diazo-benzene chlorido solution so prepared a cold solution of 45 pts. of stannous chloride in 45 pts. of HCl is now added, when the mixture immediately becomes a thick magma of phenylhydrazine hydrochloride, which is filtered off, basified, and distilled (Meyer a. Lecco, B. 16, 2976).—2. Aniline (28 g.) is dissolved in K.CQ. (21 g.) and water (500 c.c.) by passing in SO. The solution is mixed with a cold solution of NaNO₂ (25 g.) exactly neutralised by HOAc. After two hogrs the product is warmed till dissolved, acidified by HOAc, and reduced with zinc-dust and HClAq (Reychler, B. 20, 2463). By adding diazo-benzene nitrate to a cold aqueous solution of KHSO, heating the resulting C.H., N. SO.K with excess of KHSO., and de-composing the C.H., NH.NH.SO.K, thus formed, by heating with HClAq.

Properties.—Oil, solidifying to monoclinic tables; v. sl. sol. hot water, almost insol. KOHAq. Miscible with alcohol, ether, benzene, and CHCl. Volatile with steam. Reduces Fehling's solution in the cold, N, aniline, and benzene being formed. When heated for a long time at 150° it is gradually split up into aniline, NH_a, benzene, and N (Reissert a. Kayser, B. 23, 3703). Reduces ScO₂ to Se (Hinsberg, A. 260, 42). Gives benzene and N when boiled with CuSO₁. It is very poisonous. Reactions.—1. H₂O₂ forms benzene and diazo-

benzene imide PhN₃ (Wurgter, B. 20, 2633).— 2. Yellow HgO adued to its ethereal solution forms aniliue, N, and HgPh₂ (Fischer, 4, 199, 320). HgO added to a solution of the sulphate forms diazo-benzene sulphate and imide.— 3. SOCL in other forms in the cold NPhH.N:SO, which crystallises in yellow prisms [103]; v. sol. cther, volatile with steam. Thionyl-phenyl-hydrazine is hardly attacked by HCl, but is converted by NaOHAq into phenyl-hydrazine and Na. SO. Br forms NPhBr. NBr. AcCl forms diazo-benzene chloride, S, and HOAc (Michaelis, B. 22, 2228; A. 270, 115).-4. SO, passed into an ethereal solution of phenyl-hydrazine forms NHPh.NH.SO, as a crystalline pp. SO, passed into an alcoholic solution of phenyl hydrazine forms (NHPh.NHL) SO2; v. sol. water and alcohol, igsol, ether, crystallising in tables which shrink together at 70°, but decompose at a higher temperature (Michaelis a. Ruhl, B. 23, 474). SO₂ passed into a benzene solution at 75° forms NHPh.N:SO, which when heated with phenylhydrazine gives Ph.S., benzene, and N.--5. Dry CO, forms solid phenyl-hydrazine phenyl-carbazate (NHPh.NH.) CO. or N.PhH. CO.O.N.PhH, which is crystalline; sl. sol. water and ether, decomposed by hot water. - 6. CS, forms the corresponding N.PhH., CS.S.N.PhH, [97°], which at 110° splits up into H.S, and di-phenyl-thiocarbazide. COS forms crystalline COS(N.H.Ph). (Fischer, B. 22, 1935). -7. Zinc-dust and conc. HClAq slowly form aniline and NH3 -8. Excess of phenyl-hydrazine acts upon iodine, forming HI, aniline, and PhN₃ (Fischer, B. 10, 1335). Excess of I forms iodo-bonzene, N, and HI (E. von Meyer, J. pr. [2] 36, 115). This reaction may be used for the volumetric estimation of phenylhydrezine .- 9. Sulphur above 80° forms aniline. H.S. N. Ph.S., Ph.S. PhSH, benzene, and NH2-10. Nitrous acid forms PhN₃. KNO₂ added to the hydrochloride at 0° forms a yellow crystalline pp. of NPh(NO)NH .- 11. Alcoholic potash and chloroform form, on heating, $C_{14}H_{12}N_{*}$ [180°], mol. w. 236. This body crystallises in white needles; sol. alcohol, scarcely affected by HClAq at 200°, and yielding crystalline C, H,1N, NO 2 and C₁₁H₁₁N₁.SO₂H (Ruhemann a. Elliott, C. J. 53, 850)—12. EtBr forms NPhEt.NH₂, NPhH.NHEt, and NPhEt, Br. NH2.-13. Aqueous diazobenzene nitrate added to a cold solution of the hydrochloride ppts. PhN₃, aniline nitrate remaining in solution.—14. Reacts with aldehydes and ketones, forming phenyl-hydrazides; e.g. (Fischer, B. 17, 572) CH₂CHO+NPhH.NH.
- H₂O+CH₂CHN.NHPh. Thus a solution of phenyl-hydrazine hydrochloride (2 pts.) and crystallised sodium acetate (3 pts.) in water (20 pts.) gives a pp. of the phenyl-hydrazide when added to an aqueous solution of an aldchyde or ketone, either in the cold, or, in the case

of aromatic compounds, on warming. These phepyl-hydrazides are decomposed by acids into the original components, and, in alcoholic solution, by sodium-amalgam and HOAc into aniline and a base. The phenyl-hydrazides of ketones are converted by ZnCl₂ into derivatives of indole. The phenyl-hydrazides of aldehydes and ketones are described under the aldehydes, and ketones from which they are derived .- 15. Diketones containing the group CO.CHX.CO yield derivatives of phenyl-pyrazole. Saturated γ -liketones in ethereal solution usually form a mono- or di- phenyl-hydrazide; in HOAc the product is the anhydride of the mono-phenyl-hydrazide, a derivative either of CH.CH:N or of CH:CH-NN.NHPh (Klingemann, A. 265, 108) .- 16. Acetacctic ether forms a phenyl-hydrazide, which at 140° changes to oxyphenyl methyl-pyrazole TPh CO.CH. by loss of alcohol. Acetyl-propionic acid forms the com- occurs with benzoic, glyceric, and lactic acids. pound CH, C(N, HPh), CH, CH, CO, H [108]. Benzoylacetic ether forms two compounds [1320] and s[165°] (Bender, B. 21, 2495).—17. Leacts with sugars as with aldehydes; thus a solution of glucose gives CH (OII).(CH(OII)), CH:N_HPh [145"] on heating with phenyl-hydrazine, while galactose gives C₆H₁₂O₅(N_.HPh) [158] (Fischer, B. 20, 824). On heating these compounds with aqueous phenyl-hydrazine acetate at 100° 'osazones' are formed, e.g. phenyl-glucosazone CH,OH.(CH.OH), C(N HPh).CH:N, HPh [204] and the isomeric phenyl-galactosazone [c. 191"]. 18. By heating with phenyl-hydrazine hydrochloride and NaOAc arabinose is converted into C₁, H₂₀N₄O₃ [158°; formose into C₁, H₂₂N₄O₄ [·. 144°]; acrose (the product of the action of NaOHAq on glyceric aldehyde) into C_{ls}H₂N₁O₁ [c. 217°] and an isometade [159°2...-19. Phenyl [c. 217°] and an isomewde [159°].—19. Phenyl hydrazine acetato reacts with the product of oxidation of glycerin with Na CO, Aq and Br forming glycerosazone $C_{i_1}H_{i_2}N_iO$ crystallising from benzene in yellow plates [131°] (Fischer a. Tafel, B. 20, 1089, 3386). 20. Erythrite, after oxidation by dilute HNO, yields with phenylhydrazine hydrochloride and NaOAc the compound C₁H₆O₂(N.HPh)₂ [167°]. 21: Mannite on oxidation with HNO₃ yields levulose (mannitose) and mannose, which with phenyl-hydrazine forms $C_1H_1N_2O_2$ [195°-200°] (Fischer, B. 21, 1805).—22. The acetate reacts with the preduct of oxidation of dulcite by bromine and Na CO Aq with formation of the 'phenyldulciteosazone' $C_{18}H_{22}N_4O_4$ [206]. -23. Isodulcite heated with phenyl-hydrazine hydrochloride and sodium acetate at 100° forms 'phenyl-isodulcite-osazone' $C_{1a}H_{22}N_4O_4$ or $C_6H_{16}O_4(N,HPh)_2$ [180°]. Solutions of isodulcite and phenyl-hydrazine form, on mixing, C,H,,2O,(N,HPh)[150°] (Fischer a. Tafel, B. 20, 2574; Raymann, Bl. [2] 47, 760).—24. Sorbin heated with aqueous phenyl-hydrazine hydrochloride and NaOAc at 100° forms the osazone C, H,N,O, [164].—25. Milk sugar heated with aqueous phenyl-hydrazine flydro-chloride and NoOAc forms C,H,N,O, [200] and C₂₁H₂₀N₁O₅ [224°].—26. Mallose forms C₂₁H₂₂N₁O₅ [191°].—27. The acetate gives with glyorylic, fhenyl-glyoxylic, and pyruvic acids the corresponding phenyl-hydrazides [137°], [153°], and [192°] respectively.—28. Phenyl-

hydrazine in HOAc (50 p.c.) gives with a dilute solution of gluconic, galactonic, and arabinose carboxylic acids compounds C₈H₁O₈N₂H₂Ph [200°], [203°], and [216°] respectively (Fischer a. Passmore, B. 22, 2760). These compounds are m. sol. hot water. Saccharic acid gives a similar compound CaH11OsN2H2Ph [165'] which, as well as the compounds from mucic and metasaccharic acid, is almost insoluble. The compound from nucle acid melts at 240°. All these compounds contain the group CO.NH.NHPh. Compounds containing this group are also obtained by the action of phenyl-hydrazine and dilute HOAc at 100° on formic, succinic, malic, tartaric, Cinnamic, and callic acids, but not from glycollic, lacta, and glyceric acids. The compounds got from precinic, malic, gallic, and tartaric acid melt at 218, 223, 187, and 240 respectively. Acetyl-phonyl-hydrazine is produced when aqueous phenyl-hydrazine acetate is heated at 130°; and a similar reaction Compounds containing the group CO.NH.NHPh give a reddish-violet colouration with H2SO4 and a Iftle FeCl, and they are readily decomposed by KOHAq and by baryta into phenyl-hy-drazine and a salt of the acid (Fischer, B. 22, 2728). - 29. Glucose carborylic lactome yields C, H₁₃O, N₂H₂Ph [172°], while mannose carboxylic acid gives an isomeric body [223°].- 30. The acetate gives with rhamnose carboxylic acid the compound CallarOaNaHaPh [c. 210°], while \$1. Maionic acid heated at 100' with phenylhydrazine and dilute HOAc forms $C_{13}I_{43}N_1O_2$ [143°] and $CO_2H.CH_2.CO.N_2H_2Ph$ [154°], which when heated with water and phenyl-hydrazine at 200° yields $\text{CH}_2 < \frac{\text{CO}}{\text{CO}} > \text{N}_2 \text{HPh} \quad [128^\circ]. - 32.$ Lactic other forms, on heating, phenyl-hydrazido-propionic ether. a-Oxy-butyric acid at ido-propionic ether. a -Ory-bulpric acid at 160° forms $C_{11}H_{11}N_{1}O_{2}$ [152°], while mandelic acid $^{\bullet}$ yields $C_{11}H_{11}N_{1}O_{2}$ [182°] (Reissert a. Kayser, B. 22, 2924). -33. γ -Oxy-valeric dectone at 100° forms $C_{2}H_{10}O_{1}N_{2}P_{11}H_{1}$ [79°] (Wislicenus, B. 20, 402). -34. Benzoyl-carbinel gives N₁HPh₁CPh₁CH₂OH [112°] osazone N.HPh:CPh.CH:N.HPh aubmann, A. 243, 244). and the 243, [192] (Laubmann, A. 243, 244). — 35. Boiling aqueous itaconic acid forms the acid NHPh.N CH. CH. CH. CO. CH. [194°] (Scharfenberger, A. 254, 150) .- 36. Cinnamic acid forms C13H14N2O [183], which on distillation yields C15H12N2O[251] (Knorr, B. 20, 1107). -37. Acrolein reacts forming phenyl-pyrazole dihydride NPh< N:CH [52] (274") (Fischer a. Knoevenagel, A. 239, 194) .- 38. Mesityl oxide yields NPh CMe, CH, phenyl-tri-methyl-pyrazole (F. a. K.) .- 39. Chloro-acetone in alcoholic solution at -18° fo ans $C_{24}H_{23}N_{6}$ [158°] which yields an acetyl derivative $C_{24}H_{25}AcN_{8}$ [220°] (Bender, H. 21, 2496). s-Tetra-chloro-ecctons forms C_{1,H1,N}, [126°] converted by fuming HNO₃ into C_{1,H1,N}, 0, [235°] and by SnCl₂ to two bases C_{1,H1,N}, [77°] and [193°] (Levy a. Witte, A. 252, 343; Zincke a. Kegel, B. 22, 1478).—40. Tetrabromo-di-benzyl-ketone heated with alcoholic phenyl-hydrazine at 150° forms C,Ph₂(N,Ph), [70°] (Bourcart, B. 22, 1369).—41. Di. bronw-acete

crystallising from alcohol in yellow prisms (B.). 420 Bromo-acetyl-propionic ether mixed with an alcoholic solution of phenyl-hydrazine forms OH, C(N,4HPh).CH.CH.O.Et [117.5°], which on reduction with tin and HCl forms methyl-indole carboxylic acid (Bender). Bromo-acetyl-propionic acid forms. CH., C(N., IIPh). CH.CH.CO., H. 157° (Decker, B. 21, 2937). — 43. Di-chloromaleic imide at 100° forms C₄O₂(N₂H₂Ph)₂NH crystallising from acetone in orange-red needles (Giamician, B. 22, 2495).—44. Amides react thus: N₂H₂Ph + R.CO.NH₂ = NH₂ + R.CO.N.H.Ph (Just, B. 19, 1201).—45. Carbanic ether forms, (3018), B. 13, 1201).—45. Caroanuc etter forms, on heating, di-phenyl-carbazide CO((H.N.HP!h)₂ [151°] (Skinner a. Ruhemann, B. 20, 3372).—46. Reduces alloxan to allexantin, N and benzene being formed (Pellizzari, G. 17, 254). In this reaction the first product is the compound CO NH.CO C(OH). N., H., Ph (Skinner a. Ruhemann, C. J. 53, 550) .- 47. Perabanic acid with phenyl-hydrazine hydrochloride and NaOAc yields C₁₆H₂₀N₆O, [170°], which on boiling with water forms NH₂CO.NH.CO.CO.N₂H₂[1 [215°] (S. a. K.).—48. Urca heated with phenylhydrazine hydrochloride at 160° forms phenylurazole NPh

CO.NH [263°]. — 49. Reduces nitroso-aniline to p-phenylene-diamine and $C_{12}H_{12}N_1O$ (Fischer, B. 21, 2610). 50. The acetate (2 mols.) acting on nitroso-dimethylaniline (3 mols.) forms $C_{11}H_{16}N_1O$ [103°]. An ethereal solution of phenyl-hydrazine converts nitroso-di-methyl-anilino into di-methyl-amidobenzene-azo-di-methyl-aniline and phenylenebenzene-azo-di-metnyi-antine and pnenyiene-di-methyl-diamine. In alcoholic solution there is formed NHPh.C., II., NMe., [130°] which yields a nitrosamine C₁₄H₁₅N₂O [116°] (O. Fischer, B. 21, 2609).—51. Di-nitroso-acctone (1 mol.) mixed with phenyl-hydrazine (1 mol.) in hot alcoholic control of the c solution forms CH(NOH).C(N.HPh).CH(NOH) [145°]. Di-nitroso-acetone boiled with excess of phenyl-hydrazine acetate forms C15H12N4 or phenyi-nyarazine acctate forms $C_{13}H_{12}N_4$ crystallising in yellow plates $[122^2]_- = 52$. Diazoacetic ether at 100° gives off N and forms a colourless compound $[136^\circ]_- = 53$. p-Diazobenzene sulpkonic acid forms the compound · N3C6H4.803NaH4Phaq crystallising in plates (Griess, B. 20, 1528). -54. Di-acetyl-succinic ether fused with phenyl-hydrazine at 100° forms CO₂Et.CH(CMe:N₂PhH).CHAc.CO₂Et [91°] and CO₂Et.CH(CMe:N₂PhH).CO_Et which on heating with toluene at 180° gives diwhich on neating with tollene at 100° gives all coxy-di-phenyl-di-methyl-dipyrazyl (q.v.). — 55. Dioxims form additive compounds; c.g. glyoxim yiolds C,H_(NOH),N,H,Ph [110°]. di-phenyl-glyoxim yields C,Ph_(NOH),N,H,Ph [150°], while the di-oxim of (β)-naphthoquinone forms C₁₀H₆(NOH),N,H,Ph [138°] (Polonowsky, B. 21, 182).—56. Phloroglucin kept for five days with an alcoholic solution of phenyl-hydroxine in the an alcoholic solution of phenyl-hydrazine in the cold forms C_cH₁(OH)(N_cH_.Ph), [144°] which may be oxidised by FeCl, to C_cH₁(OH)(N_.Ph), [177°] (Baeyer B. 22, 2891).—57. Thio-acetoacetic ether forms S(CH CO-NPh) 1 Modern etner with CMe; N) 2 [183°], together with the compounds NHPh.N:C CMe:N 8,(CH<CO -NPh). and di-oxy-di-phenyl-di-

phenone forms N. HPh: CPh.CH: N. HPh [148°],

methyl-dipyrazyl (Sprague, C. J. 59, 332).—5i
Cyanogen passed into an emulsion of phenyinydrazine in cold water forms the dicyanide (infra).—50. Cyanogen passed into an alcoholi solution forms PhN.H. C(NH).C(NH).N.PhH [225°], crystallising in white plates (from alcohol). The same compound is formed by the action of phenyl-hydrazine on cyananiline. I gives a rose-red colour with calcoholic NH. Cone. H.So.; is coloured indigo-blue. Dry HC forms the hydrochloride C., H., N., 2HCl [188°]. Drute HCl forms PhN.NH.CO.C(NH).NHNHP! [180°].—60. Cyananiline in chloroform sclution forms, after boiling, matted needles of the compound C2, H2, N.Cl. [200°-212°]. This body is perhaps (PhH.N., CHCl.C., H1, 18, 2HCl (Senf. J. pr. [2] 35, 533).—61. PCl., in ether form amorphous NHIB.N.P.NH.NHPle converted by water into (NHPh.NH).POH, a yellowish-white powder [92°] which reduces Fehling's solution in the cold (Michaelis a. Oster, A. 270, 126). This body is split up by acids into phenyl-hylazine and H.PC., oasily decomposed by acids and alkalis (Michaelis, A. 270, 135).—63. PSCl., forms, in like manner, PS(NH.NHPh), [154°].—64. AsCl., forms, (N.PhH.), BCL., o. 65. BCl., forms, in like manner, (N.PhH.), BCL., v. sol. water, decomposed at 242°.—66. C.H., PCl., in ether forms NHPh.N.PC.H., [152°] crystallising from EtOAc in plates (Michaelis, 2. co., E. BCl., forms, in like manner, (N.PhH.), BCL., v. sol. water, decomposed at 242°.—66. C.H., PCl., in ether forms NHPh.N.PC.H., [152°] crystallising from EtOAc in plates (Michaelis a. Oster, A. 270, 129). It reduces hot Fehling's solution, and is split up by acids into PhPO_H2, and phenyl-hydrazine.

Salts.—B'HCl. Plates, m. sol. water. Got by ppg. an alcoholic solution of the base by HCl, and washing the pp. till it is colourless.—B'HBr. Needles (from water).—B'_HSO. Plates, v. sol. water.—B'C.H.M.O. Yellow needles.—B'_HLGO. Plates.—Benzene sulphinate; [131] (Escales, B. 18, 895).—Dinitro-(a)-naphthol sulphonate: lighthrown needles, sl. sol. hot water (Richardson, C. N. 58, 39).—Sulphocyanide: sparingly soluble plates. Changes at 160°-170° into phebyl-thio-semicarbazide.—B'H,PO. [118°] (Michaelis, A. 270, 127, 133).—B'_HPO. [121°].—B'C.H.PHO. [135°]

B'C_H_PH_O__ [135°].

Sodium derivative C_H_NNa.NH_ Formed by dissolving 8g. of sodium in 70g. of warm phenyl-hydrazine. The H evolved reduces some of the phenyl-hydrazine to NH, and aniline when the reaction is complete the aniline and excess of phenyl-hydrazine are distilled off by heating the product in an oil-bath to 200° 210° (not higher) in a current of H. It is a yellow hygroscopic powder. When finely divided it sometimes takes fire in the air. Decomposed by water into phenyl-hydrazine and NaOH. Readily reacts with alkyl haloids, giving unsymmetrical phenyl-alkyl-hydrazines (Michaelis, B. 19, 2448; A. 252, 266).

Formyl derivative NHPh.NH.CHO. [145°]. Formed by heating formamide with phenyl-hydrazine at 180°. White scales.

Acetyl derivative NHPh.NHAc. [1284].
Formed by heating phenyl-hydrazine with MOAc
or acetamide (Fischer, A. 190, 129; Just. B.

19, 1201). Formed also from the sodium-derivative and Ac.O at 0° (Michaelis a. Schmidt, A. 252, 3017. Six-sided prisms, sl. sol. cold water.

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Di-acetyl derivative NPhAc.NHAc. [108°]. Formed from NPhNa,NH, and AcCl in ether. Tables or needles, v. e. sol. alcohol. Completely reduces hot Fehling's solution.

Chloro-acetyl derivative NHPh.NH.CO.CH,Cl. [115°]. Formed from the base and CH.Cl.COCl in ether (Gattermanu, B. 25, 1081).

Propionyl derivative NHPh.NH.CO.Et. 6158°] (Freund a. Goldschmidt, B. 21, 2161).

n-Butyryl derivative. [114°]. Scales, v. sol. ether (Michaelis a. Schmidt, A. 252, 308).

Isovaleryl derivative NHPh.NH.CO.CH.Pr. [101°]. Formed from the base and accto-valeric anhydride (Auten-Formed from

rieth, B. 20, 3190). Plates, v. sl. sol. cold ligroin. Hexoyl derivative [117°]. Needles.

s-Benzoul derivative [169°]. Formed from phenyl-hydrazine by adding BzCl in ether at 0° (Fischer, A. 190, 125), or by heating with benzamide (Just, B. 19, 1203). Formed also by warming phenyl-hydrazine with BzCy (Hausknecht, B. 22, 329). Prisms, sl. sol. hot water. Yields NPhMe.NHBz on methylation. Reduces HgO. Phthalic anhydride at 180° forms an addition-compound $C_{21}H_{10}N_{2}O_{1}$ [1722], crystallising from alcohol in prisms. It is probably $CO_{2}H.C_{0}H_{1}.CO.NPh.NIBz$. At 250° it splits up into benzoic acid and (3)-phthalyl-

 $\textbf{phenyl-hydrazine} \ C_{_{0}}H_{_{4}};C_{_{2}}O_{_{2}} \diagdown \Big| \\ NPh$

NPhBz.NH. u-Benzoyl derivative [70°]. A product of the action of BzCl in benz-[70°]. A product of the action of B251 in action on NPhNa.NII, at 0° (Michaelis a. Schmidt, B. 20, 23, 1718; A 252, 310). Needles (from water). Reduces hot Fehling's solution but not HgO. Conc. HCl at 150° gives HOBz and phenyl-hydrazina. HNO, forms in acid solution benzanilide and N.O. but in neutral solution it forms N₃Ph and HOBz. Reacts like phenylhydrazine with aldehydes and ketones; thus acetone yields NPhBz.N:CMe₂ [115^{-5°}], aceto-phenone forms NPhBz.N:CMePh [124°], and benzoic aldehyde gives NPhBz.N:CHPh [122°]. Salts.—BHCl. [202°]. Needles, m. sol. HClAq. water.—B'HNO, [145°].—B'C₆H₁N₅O, [122°]. Needles, sl. sol. cold water.—B'₂H₂SO, [191°]. Needles, sl. sol. cold water.—B'HNO, [145°].—B'C₆H₁N₅O, [122°]. Di-benzoyl derivative NPhBz.NHBz.

[178°] (Fischer, A. 190, 128; M. a. S.). Prisms, v. sl. sol. water, sol. alkalis. On methylation it yields NPhBz.NHBz.—NPhBz.NBzNa: plates.

Benzoyl - acetyl derivative NPhBz.NHAc. [153°]. Got from NPhBz.NH, and Ac.O. Needles (from dilute alcohol).

p-Nitro-benzoyl derivative NHPh.NH.COC, H., NO2. [198]. Formed from phenyl-hydrazine and C,H,(NO2)CN (Haus-knecht, B. 22, 328). Yellowish-red needles.

o-Amido-benzoyl derivative. [170°]. Got by warming phenyl-hydrazine with an alcoholic solution of isatoic acid (Meyer, J. pr. [2] 83, 20). Yellow needles, v. sl. sol. other.

n Amido-benzoyl derivative NHPh.NH.CO.C.H., NHA [151°]. Formed by

heating phenyl-hydrazine (1 mol.) with m-amidobenzoic acid (1 mol.) at 165° (Pellizzari, G. 16, 200). Scales, insol. cold alkalis, sol. acids.

Amido-toluyl derivative [3:6:1] C.H.Mc(NH.).CO.N.H.Ph., [198°]. Formed from methyl-isatoic acid and phenyl-hydrazine (Panactovitch J. pr. [2] 33, 68). Prisms (from chloroform), sl. sol. ether.

Phenyl-acetyl derivative N2H2Ph.CO.CH2Ph. [169°]. Got by heating phenyl-scetic acid with phenyl-hydenzine at 150° (Bülow, A. 236, 196). Needles (from alcohol), sl. sol. water.

Cinnamoul derivative N.H.Ph.COC.H.Ph. [258°). Got by Heating cinnamic acid with phenyl-hydrazine at 190° (Knorr, B. 20, 1708). Forms, on distillation, a compound C₁H₁₂N₂O [258°], crystallising in needles with green fluorescence.

Of alyl derivative C.O. (N.H.Ph), [278°]. Described in vol. iii. p. 655.

Ethyl-malodyl derivative

CHEt(CO.N.H.Ph). [233°]. Got by heating ethyl-malonic amide with phenyl-hydrazine at 220° (Freund a. Goldsmith, B.21, 1242). Needles (from HOAc). Converted by COCl, into C₁₉H₁₆N₄O₄ [113°].

Succinyl derivative C,H,:C,O,:(N,H,Ph), [218°]. Formed from succinyl chloride (1 mol.) and phenyl-hydrazine (2 mols.). Formed also by heating C2H4:C2O2:S with phenyl-hydrazine and HOAc (Zanetti, Rend. Accad. Linc. [4] 5, i. 225). Plates (from HOAc) (Freund, B. 21, 2456; Fischer a. Passmore, B. 22, 2734). When succinic anhydride is heated with phenyl-hydrazine at 160° there is formed C₂H₄:C₂O₂:N.NHPh [155°], which yields a nitrosamine C₂H₄:C₂O₂:N₂Ph.NO [84°] (Hötte, J. pr. [2] 35, 293).

(a) - Phthalyl derivative C.H. C.O.: N.NHPh. [179°]. Formed from phenylhydrazine and phthalyl chloride in ether (Pickel, A. 232, 233). Formed also by heating phenylhydrazine (1 mol.) with phthalimide (1 mol.) at 120° (Pellizzari, G. 16, 203; Just, B. 19, 1204); or with phthalic anhydride (1 mol.) at 150° (Hötte, J. pr. [2] 33, 99; 35, 268). Prepared by boiling an alcoholic solution of phthalic anhydride with phenyl-hydrazine. Colourless needles (from alcohol), insol. water and alkalis. Conc. H₂SO₂ forms a violet solution, turning brown. Reactions.—1. Converted by boiling alcoholic potash into N.H₂Ph.CO.C₂H₄.CO₂H₄ [166°], an acid of which the benzoyl derivative acid of which the benzoyl derivative NHPh.NBz.CO.C.H.,CO.H [172°] is formed by heating NHPh.NHBz with phthalic anhydride at 180°.—2. Boiling aqueous KOH or HClAq at 150° splits it up into phthalic anhydride and phenylhydrazine. —3. Benzoyl chloride at 160° forms C.H.;C.O.;N.NPhBz [193°].—4. Nitrous acid passed into its solution in diluted HOAc forms the nitramine CoH,:C2O2:N.NPh.NO2 [148°]; but in boiling HOAc it forms the di-nitro-derivative C, H, N, O, [182°]. Nitrous acid passed into phthalyl-phenyl-hydrazine suspended in ether forms the nitrosamine C₄H₁:(2O₂:N.NPh(NO) [154°].—5. Alcoholio NH₄ at 80° forms unstable NH₂CO.C₆H₄:CO.NH.NHPh [146°], which decomposes at 170° into NH₃ and (β)-phthalyl-phonyl bytessize (212°) phenyl-hydrazine [210°].

(B) - Phthalyl derivative

 $C_2H_4:C_2O_2 < NH_1$. [210°]. Formed at the same time as the (a) isomeride by heating phenylhydrazine with phthalimide or phthalic anhydride, being the chief product when the temperature is above 163° (Pellizzari, G. 16, 204; 17, 278; Hötte, J. pr. [2] 35, 284). Monoclinic tables (from benzene) or prisms (from alcohol), sol. alkalis. Ammoniacal AgNO. ppts. C.H.:C.O.N.PhAg.

Reactions. - 1. NaOMe and MeI at 100° form C₆H₄(C₂O₂:N₂PhMe [125°], which is decomposed by cone. HClAq into phthalic acid and NHPh.NHMe. 2. KOEt and Ett give C₆H₄O₂:N₂PhEt [106°].—3. BzCl at 200° forms C₆H₄O₂:N₂PhAe [122°].

Phthulyl derivative C,H4(CO.NH.NHPh)2. [191°]. Formed by heating phenyl-hydrazine (2 nols,) with hithalic anhydride (1 nol.) at 150° (H.). White tables. At 170° it gives the (β)-phthalyl deri vative [210°].

Nitrosamine NH, NPh.NO. Formed by adding NaNO, to an aqueous solution of plenylhydrazine hydrochloride at 0° (Fischer, A. 190. 92). Pale-yellow plates. Very poisonous. Converted by hot alcoholic potash into diazobenzene-Alcoholic HCl acts in like manner. Exhibits Liebermann's reaction.

Dicyanide C_xH_xN₄ i.e. NH_x,NPh.C(NII).CN? Separates as colourless flakes when evanogen is passed into an emulsion of phenyl-hydrazine and cold water (Bladin, B. 18, 1544). Monoclinic lamine, v. sol. alcohol and ether. Decomposes above 160°. Yields a formyl derivative C,H,(CHO)N, [193].

Reactions. -1. By heating with Ac₂O it is converted into C₁₀II₈N₄ [108], which on saponification yields an acid C₁₀H₉N₃O₂ [177°], which on heating loses CO2, leaving oily CaHaNO3 (c. 240°).—2. By heating with propionic anhydride it is converted into $C_1H_{10}N_4$ [38'].—3. By treatment with nitrous acid, followed by boiling with water, it yields C.H.N., crystallising in needles [56°], v. sl. sol. water .- 4. Acetic aldehyde in alcohol and HCl give CH3.CH:N.NPh.C(NH).CN • [96.5°], crystallising in pale-yellow plates, v. e. sol. alcohol and ether, insol. water; converted by alcoholic AgNO, into phenyl-methyl-triazole carboxylic nitrile [109] (Bladin, B. 25, 184) .--5. Benzoic aldehyde forms the corresponding CHPh:NNPh.C(NH).CN [129:5°], crystallising from alcohol in prisms, oxidised by FeCl, to C₁₆H₁₀N₄ [166°] (Bladin, B. 22, 796).—6. Pyrawic acid in alcohol forms the above phenyl-methyl-triazole carboxylic nitrile on warming gently (Bladin, B. 19, 2598).—7. Boiling acetoacetic ether forms the compound CO₂H.CH₂CMe:N.NPh.C(NH).CN [209°], the oily ether of this acid, and phenyl-methyl-triazole carboxylic nitrile N NPh.C.CN [109°] (Bladin, B. 25, 190). The acid forms the salts KA' and NH, A', and is converted by nitrous acid CO.H.C(NOH).CMe:N.NPh.C(NH).CN into [218°], [218°], and by potash into the compound CO.H.CH.CMe:N.NPh.CO.CN [188°], from CO.H.CH. CMe:N.NPh.CO.CN [188°], from which potassium nitrite and HClAq form CO.H.C(NOH).CMe:N.NPh.CO.CN [209°].

References .- AMIDO-, LODD-, NITRO-, and OXT PHENYL-HYDRAZINE.

u-Di-phenyl-hydrazine NPh₂.NH₂. [34·5°] (220° at 40 mm.) (Stahel, A. 258, 243). Formed by reducing di-phenyl-nitrosamine NPh, NO ir alcoholic solution with zinc-dast and HOAc (E Fischer, A. 190, 174). Monoclinic tables (from ligroin), partially decomposed on distillation into diphenylamine and NH, Conc. H.SO forms a deep-blue solution. Decomposed by nitfous acid into NPh, NO and N.O. Reduces HgO, forming in the cold crystalline tetra-phenyl-tetrazone, NPh., N:N.NPh. [123°], but if the temperature rises the products are N and diphenylamine. Benzoic aldehyde forms NPh.N:CHPh [122°]. With salicylic aldehyde, furfuraldehyde, glucose, mannose, galactose, and rhamnose it forms di-phenyl-hydrazides, melting at 139°, 90°, c. 162°, c. 155°, 157°, and 134° respectively.
Salts. B'HCl. Needles, v. sl. sol. cold water.

-B'2H2SO; needles, m. sol. dilute H2SO;

Formylderivative NPh. NH.CHO. [116:5°]. Formed by boiling the formyl deriva-tive of phenyl-hydrazine with ammoniacal CuSO₄ (Gattermann, B. 25, 1075). Needles, sl. sol. hot water and ligroin, v. sol. alcohol.

Acctul derivative NPh., NHAc. Formed by boiling NIIPh.NHAc with HOAc and Cu(OAc), (Tafel, B. 25, 413).

Propionyl derivative. [178]. Needles. Benzoyl derivative NPh2.NHBz. [189°] (G.); [192] (Fischer, A. 190, 178). Needles (from acctone), m. sol. alcohol,

Phthalyl derivative C,H,O,:N.NPh... [155°]. Formed by heating di-phenyl-hydrazine with phthalic anhydride at 160° (Hötte, J. pr. [2] 35, 271).

s-Di-phenyl-hydrazine NHPh.NHPh. drazo-benzene. Mol. w. 184. [131°]. H.C. 1,598,000 (from diamond) (Petit, M. Ch. [6] 17, 163). S. (alcohol) 5 at 16° (Moltschanowsky, C. J. 42, 965). Prepared by passing H₂S into a solution of azobenzene Ph.N_x.Ph in alcoholic NH₃ (Hofmann, Pr. 12, 576). Formed also by reducing nitro-benzene with sodium-amalgam or zinc-dust (Alexejeff, Z. 1868, 497; Glaser, A. 142, 364). Laminæ, sl. sol. water, m. sol. alcohol and ether. Yields aniline and azobenzene on distillation.

Reactions .- 1. HClAq converts it into the isomericdi-p-amido-diphenyl (benzidine). H.SO. acts in like manner. 2. Readily oxidised to azobenzene, even by moist air .- 3. Nitrous acid. passed into an alcoholic solution at 0°, yields a nitroso- compound which, when warmed, Violently decomposes into NO and azobenzene (Bacyer, B. 2, 683).—4. On heating with BzCl it yields di-benzoyl-di-p-amido-diphenyl; formic acid gives di-formyl-di-p-amido-diphenyl (Stern, B. 17, 379); and phthalic anhydride yields diphthalyl di-amido-diphenyl (Bandrowski, B. 17, 1181).—5. Boiling benzoic aldehidle forms azobenzene, but benzoic aldehyde and ZnCl2 gives C1.H2(N:CHPh), (Clève, Bl. [2] 45, 188). Benzoic aldehyde, heated with hydrazobenzene at 120°-

150°, forms' benzhydrazoin' CHPh NPh [55°]. The o-nitro- derivative C.H. (NO2).CHN2Ph2 of this body melts at 66°.—8. Furfuraldehyde forms C₄H₃O.CH
NPh [59°] (Cornelius a. Homolka, B. 19, 2240).—7. Phenyl cyanate (2 mols.) and some benzene at 150° forms the compound NHPh.CO.NPh.NPh.CO.NHPh [220] (Goldschmidt a. Rosell, B. 239490).

Acetyl derivative NHPh.NPhAc. [159°]. Formed from s-di-phenyl-hydrazine and Ac.O in the cold (Stern, B. 17, 330). Needles (from alcohol). Decomposed by heat into acetanilide

and azobenzene.

Di-acetyl demivative NPhAc.NPhAc. [105°]. Formed from s-di-phenyl-hydrazine and Ac.O (Schmidt a. Schultz, B. 12, 485; A. 207, 326). Yellowish trimetric crystals (from alcohol); a:b:c = 67:1:56, not affected by dilute HClAq.

Chlofo-derivatives C_aH₃NH.NHC_aH₄Cl. [90°].—N_aH₄(C_aH₄Cl[1:3]). [91°].—N_H(C_aH₄Cl[1:4])₂ [122°] [Claus a. Heu-

(Janowsky a. Erb, B. 20, 361). Tables. Con-Verted by H SO, into bromo-benzidine.

Di-bromo- derivatives N.H. (C. H.Br.). o. [82°]. m. [109°]. p. [130°] (J. a. E.; Gabriql, B. 9, 1406; Werigo, A. 165, 192).

Iodo · derivatives v. vol. iii. p. 41. Nitro-derivatives v. vol. iii, p. 607.

Oxy-derivatives v. vol. iii. p. 743. Chloro-nitro- derivative

NHPh.NHC_H_C(NO.) [1:3:6]. [135°-140°]. Formed from chloro-di-nitro-benzene and phenyl-hydrazine in alcohol (Willgerodt a. Ferko, J. pr. [2] 37, 355). Red prisms.

p-Amido-derivative. The compound NHPhNHLC₆H₁,NHAe [146²] is got by treating C.H.,N.,C.,H.,NHAe with alcoholic ammonium sulphide (Schultz, B. 17, 463). Yellowish plates (from dilute alcohol). Re-oxidised to the azo- compound by air.

Di-m-antido- derivative

N₂H₂(C₆H₄.NH₂)₂, [141°] (Gebe**b**, A. 251, 193). Got by treatment of m-nitro-aniline with alcoholic potash and zinc-dust (Craeff, A. 229, 311), or with sodium-amalgam (Haarhaus, A. 135, 164). Golden needles (from alcohol). Yields $C_{12}H_3Br_3N_4$ [150°] and $C_{12}H_12Ac_2N_1$ [247'].— $B''H_2Cl_2...=B''H_2PtCl_6...=B''2HNO_1...=B''H_1SO_1...=$ B"H,C,O, Prisms, v. sl. sol. water.

Di-y-amido-derivative. [115]. Got by reducing N₂(C₆H₄,NO₂)₂ with alcoholic ammonium sulphide (Gerhardt a. Laurent, A. 75, 7. Lermontoff, B. 5, 232). Yellow crystals. Yields quinone on oxidation. — B"H₂Cl₂.
B"2HNO₂.

Di-diphenyl-hydrazine v. Hydrazo-diphenyl. PHENYL-HYDRAZINE o-CARBOXYLIC ACID C,H,NO2 i.e. NH2.NH.C,H,CO2H. Hydrazido-benzoic acid. Formed from o-amidobenzoic acid by diazotising and treating the product with Na₂SO, (E. Fischer, B. 13, 670; A. 212, 333). Needles, sol. hot water. Reduces Fehling's solution in the cold. -- HA'HCl: needles, sol. hot water.

heating the acid at 220°. Monoclinic plates (from alcohol); a:b:c = 0.072:1: .064; $\beta = 75^{\circ} 18'$.

Sublimes in white needles. -- NaC, H, N,O xaq: silvery plates. — B'HCl: white needles. — B'HgCl: needles (from water). Yields an acetyl derivative C.H.Ac.N.O [112°].

Phenyl-hydrazine m-carboxylic acid

N.H.*C.H.,CO.H. [186°]. Formed by the action of tin and HClAq on C.H.(CO.H).N:N.SO.K, which is got by warming the nitrate of m-diazobenzoic acid with aqueous K2SO, (Griess, B. 9, 1657; Roder, A. 236, 164). Plates, sl. sol. hot Aq.

Reactions. -1. Acetone forms $G_{so}H_{12}N_2O_2$ [150], which gives EtA' [91°]. -2. Benzow addehyde forms CHPh: N.NH.C.H .. CO.H [172°] .-3. Pyruvic acid reacts with formation of CO_H.CMq.N.NH.C, H₁CO₂H [208°], which forms whetstone shaped crystals (containing aq), and gives EtA' [102°] .- 4. Glucose, heated with the fives Eth. [103].—4. trucose, neutod with the hydrochloride and MaOAe, gives C₂₀H₂₂N_Q, [208].—5. Phenyl-thicorbinide forms the compand C₁₁H₁₁N₃SO₂ [205°].

Salts.—14A'HCl.—BaA₂' 4aq. Nodales.

Phenyl-hydrazine p-carboxylic acid
Bromo derivative C₆H₃,NH.NH.C₆H₄Br. N₂H₄,C₆H₄,CO₅H. [220²-225²]. Formed, in the
benzene and alcoholic approximation same way as its isomeridae from the control of the control (from water). -HA'HCl : sl. sol. cold water.

s-Di-phenyl-hydrazine di-o-carboxylic acid 1H₁₂N₂O₁ i.e. CO₂H₁C₃H₁NH₂NH₃NH₄CO₂H₅CO₂H₅O₁. w. 272. [205°]. Formed by reducing Mol. w. 272. [205°]. Formed by reducing o-azoxy-benzoic acid with sedium-amalgam (Griess, B. 7, 1609; Homolka, B. 17, 1904). Small colourless plates. Oxidised by moist air to o azobenzoic acid.

s-Di-phenyl-hydrazine di-m-carboxylic acid, Hydrazo-benzoic acid. Formed by boiling m-azobenzoic acid with FeSO, and NaOHAq (Strecker, A. 129, 141). Insol. water, sl. sol. hot alcohol. In alkaline solutions it absorbs O, being oxidised to azobenzoic acid. Boiling conc. HGAq forms azobenzoic acid and amidobenzoic acid. Yields orange-red crystals of BaA". On warming with SnC and HClAq at 100° it yields di-amido-diphenyl dicarboxylic acid and two other acids. One of these $C_{11}H_{10}N_{2}O_{3}$ crystallises from hot water in yellowish needles and forms BaA' 77aq and HA'HCl. The other acid C14H12N2O1 crystallises in yellow needles melting above 290°, and forms NaA'4aq, BaA', 2aq, HA'HCl, HA'HBr, and (HA'), H., SO, (Kusseroff, B. 23, 913).

s-Di-phenyl-hydrazine di-p-carboxylic acid C_1,H_1,D_1,O_1 . Formed by boiling p-azobenzoic acid with FeSO, and NaOHAq (Reichenbach a. Beilstein, A. 132, 137; Billfinger, A. 135, 152). Formed by boiling p-azobenzoic Needles (from alcohol), easily oxidised in alkaline solution.

s-Di-phenyl hydrazine tetra-carboxylic acid [1:4:2]C₆H₃(CO₂H)₂.NH.NII.C₆H₃(CO₂H)₂ [2:1:4]. Formed by reducing azoxytorephthalic acid in alkaline solution with sodium-amalgam (Homolka

a. Löw, B. 19, 1092). White crystalline pp., v. sol. alcohol and ether.

PHENYL-HYDRAZINE m-SULPHONIC ACID C₆H₄(N₂H₅),SO₂H. Formed from m-amido-benzene sulphonic acid by diagotisation and subsequent reduction by SnCl₂ at 0° (Limpricht, B. 21, 3409). Crystals (containing 2aq), sl. sol. cold water, nearly insol. alcohol. Converted in alcoholic solution by nitrous acid into

 $N_sC_sH_sSO_sH_s$ Phenyl-hydrazine p-sulphonic acid [1:4]O,H,(N,H,).SO,H.

Formation.—1. From diazobenzene p-sulphonic acid by warming with aqueous K.SO, followed by HOI (E. Fischer, A. 190, 74).—2. By heating phenyl hydrazine sulphate with ClSO, H at 160° (Limpricht, B. 18, 2196).—3. Together with alcohol, by heating phenyl-hydrazine ethyl-sulphate at 160°.—4. By heating phenyl-hydraz-ine (1 pt.) with H₂SO₂ (6 pts.) at 100° (Gallinek a. Richter, B. 18, 3172).

Properties.—Needles (containing aq), sl. sol. water. By boiling with CuSO, it is neatly oxidised to N and benzene sulphonic acid. With acetoacetic ether and dilute (50 p. c.) HOAc at 155° it forms CMe CH. CO. (Möllenhoff, B. 25, 1849), which crystallises with aq.

Salts. - NaA' 1 aq. - NH, A' - BaA', 5aq. -

PbA', 2aq. — ZnA', 4aq: minute tables.

Phenyl-hydrazine v-sulphonic acid. Potassium salt. C.H.NH.NH.SO.K. Formed from stum satt. C_aH₃NH.NH.SO₂M. Formed from diazobenzene nitrate and K₂SO₃ (180mer, Z. 1871, 481) and also by heating pheavi-hydrazine with K₂S₂O₇ (Fischer, A. 190, 97). Crystals (containing aq), sl. sol. cold water and alcohol. Oxidised by HgO to CaHs. No. SOaK. Split up by boiling HClAq into phenyl-hydrazine and KHSO.

Phenyl-hydrazine disulphonic acid NH₂.NH₂C₂H₃(SO₃H)₂. Two acids of this formula are got by further sulphonation of the mand p- sulphonic acids respectively (L.). They both yield BaA" and BaH₂A"₂.

s-Di-phenyl-hydrazine m-sulphonic acid C_eH₂.NH.NH.C_eH₄.SO₂H. Formed by heating the disulphonic acid with water at 200° for 3 days (Limpricht, B. 11, 1048). Yellow needles (containing 2 aq). - KA' 4aq. - PbA', 3aq. BaA', 4aq: yellow plates, v. sol. water. Chloride C₁₂H₁₁N₂SO₂Cl. [240°]. Di-bromo-derivative

C.H.Br.NH.NH.C.H.Br.SO.JI. Formed as a by-product in the exidation of C.H.Br.(NII.)SO.JH 1:3:6:4] by KMnO, (Limpricht, B. 18, 1425).-KA' aq: long needles.

s-Di-phenyl-hydrazife di-m-sulphonic acid N₂H₄(O₂H₄;SO₂H)₂. S. 079 at 22°. Formed by reduction of nitro-, azo-, or azoxy-benzene-sulphonic acid (Limpricht, B. 11, 1048; 21, 3409; 23, 1057; Bruhnemann, A. 202, 344; Mahrenholz a. Gilbert, A. 202, 337; Neumann, B. 21, 8419). White needles, v. e. sol. water, almost insol. alcohol and other. Readily reduces ammoniacal AgNO, and Fehling's solution. Readily reduces HClAq immediately forms benzidine disulphonic

Amide NH(C₆H₄SO₂NH₂).NH.C₆H₄SO₂NH₃. [248]. Formed by reducing N₁(C₆H₁S₀,NH₂), with zine-dust and NH₂Aq or HOAc (Limpricht a. F. Meyer, A. 268, 132). White needles (from 50 p.c. acetic acid), almost insol. water, ether, and toluene. Reduces ammoniacal AgNO, forming a mirror. HClAq converts it into the amide of diamido-diphenyl (benzidine) disulphonic acid, m-amido benzene sulphonic amide and N₂(C₆H₄,SO₂NH₃)₂, — N₂H₄(C₆H₄,SO₂NHK)₂ I₂³aq. Thin needles or plates quickly oxidised by air.— N₂H₄(C₆H₄,SO₂NHNa)₂ 2 aq: needles.

s-Di-phenyl-hydrazine di-p-sulphonic acid N.H.₁(C.H.,SO.H). Obtained, in the same way as the preceding acid, from amido-benzene p-sulphonic acid.—BaH.A".—BaA": crystalline. Isomeride.—V. BENZIDINE TETRASULPHONIC ACID, vol. i. p. 174.

DI . PHENYL . HYDRAZINE v. DI . THIO . CARBOXYLIC ACID NPh., NH.CS.SH. [c. 109°], Formed by dissolving NPh., NH, in CS. (Stabel, A. 258, 249). Golden prisms, v. sol. alcohol, insol. water.

s-Di-phenyl-hydrazine di-m-thiosulphonic acid N₂H₂(C₆H₄,SO₂SH)₂. Formed, together with N₂(C₆H₄,SO₂SH)₂, by adding N₂(C₆H₄,SO₂Cl)₂ to a cold saturated solution of Ba(SH)2 (Limpricht, pp., becoming steky on boiling with water. Oxidised by KMnO₄ to N₂(C₈H₄,SO₄H)₂.—BAA'' 2aq: minute needles, sl. sol. cold water. TRI - PHENYL - HYDRAZOÏN is Benz-

hydrazoin, v. s-DI-PHENYL-HYDRAZINE, Reaction 5. DI. PHEN YL. HYDROQUINONE C. H. 10.2 i.e. C. H., Ph. (OH). [5:2:4:1]. [219°]. Formed by reducing di-phenyl-quinone with aqueous SO. (Müller a. Pechmann, d3. 22, 2131). Colourless cubes (from dilute alcohol).

PHENYL-IMESATIN v. ISATIN. PHENYL-IMIDO-DIACETIC ACID

NPh(CH₂CO₂H)₂. [150°-155°]. A product of the action of aniline on chloro-acetic acid (P. Meyer, B. 14, 1325; Hausdörfer, B. 22, 1796). Formed also by heating phenyl-amido-acetic agid with chloro-acetic acid and NaOAcat 120°-130° (H.). Needles, v. sol. hot water and alcohol. NPhH A'. Needles (from alcohol). Decomposes at 151°.

Mono-anilide

CO2H.CH2NPh.CH2.CO.NHPh. [213°]. Formed together with the dianilide by heating the acid with aniline at 175°. Needles. Its ether CO.Et.CH. NPh.CH. CO.NHPh [122°] is got by heating the anilide of phenyl-amido-acetic acid (q.v.) with other and NaOAc at 140°.

Di-anilide NPh(GH, CO, NHPh)₂. [218°]. Needles, v. sl. sol. alcohol.

TRI - PHENYL - TRI - IMIDO - BENZENE $\mathbf{C}_2,\mathbf{H}_2,\mathbf{N}_3$ i.g. $\mathbf{C}_a\mathbf{H}$ (NHPh)₃. [242°]. Formed by warming $\mathbf{C}_a\mathbf{H}_a\mathbf{C}\mathbf{I}_a$ with aniling (Mohr. M. 11, 22). Golden plates, v. sol. chloroform, insol. water and alcohol. Conc. $\mathbf{H}_a\mathbf{SO}_a$ gives a dark-blue

colour changed to violet by potash.

PHENYL - IMIDO - BENZYL - MALONIC ETHER C.H.C(NPh).CII(CO.Et).. [75°]. Formed, together with (C.H., C(NPh)).C(CO.Et)., by the action of sodium malonic ether on the compound C, H, CCl:NPh (Just, B. 18, 2624). Decomposes at 150° into alcohol and oxyphenyl-quinoline carboxylic ether.

DI-PHENYL IMIDO-DI-ETHYL DISTIL. PHONE NH(CH, SO, C, H), [78]. Got by heating C, H, (SO, C, H, J, with NH, Aq is seaked tubes (Otto, J. pr. [2] 30, 324). Triclinic plates (from alcohol).—Nitrate: [190°].—B'HCl. [193°].— B'.H.,PtCl.; plates, sl. sol. water. PHENYL - IMIDO - METHENYL - 0 - AMIDO-

C_eH₄< NH C:NPh. (c. 230°). PHENOL

Formed by heating $C_eH_4 < {}^{\rm NH}_O > C\delta$ with aniline at 210° (Von Chelmicki, J., pr. [2] 42, 440). Needles, insol. water, sl. sol. cold alcohol. DI-PHENYL-DI-IMIDO-NAPHTHOL v. (β).

NAPHTHOQUINONE, Reaction 5. PHENYL-IMIDO-DINAPHTHYL v. PRENTL DINAPHTHYLENE AMINE.

PHREVIANIDO PHENYL METHYL THI . ZOLE . DIHYDRIDE NPh C(NPh).S

138°]. Formed from di-phenyl-thio-ures and hloro-acetone (Traumann, A. 249, 51). Yelwish prisms, insol. water, v. sol. ether. DI . PHENYL - DI - IMIDO - DI - PHENYL -

LAZTHIOLE TETRAHYDRIDE CaHan,S i.e. C(NPh).NPh . [131°]. Got by oxidising dihenyl-thio-ures with H.O. (Hector, B. 23, 357).
PHENYL-IMIDO ROPIONIC ACID

[123°] H. C(NPh).CO.H. Anilpyrthic acid. by the principle of the property of the proper

Isomeridee, Intro-PHENTI, PROFICIOI ACID.
PHENYI, IMIDO-SUCCINIC ACID
O.H.CH., C(NPh), CO.H. [150°]. Formed by
te action of dilute (1 p.e.) KMnO, on 'pyranilyroic' acid (Anschütz, B. 22, 738; cf. Reissert,

21, 1942). Decomposed on fusion.
PHENYL-IMIDO-THIAZOLE DIHYDRIDE

(NPh) < NH.CH. [124°]. Formed from

H2Cl.OHCl.OEt and phenyl-thio-urea (Näf, A. 55, 125). White needles, sol. alcohol. Yields nitrosamine C₀H₇(NO)N₂S [58°].

Di-phenyl-imido-thiazole dihydride

(NPh) S - CH [105°]. Formed from dichloro-di-ethyl oxide and di-phenyl-thio-urea.

DIPHENYLINE v. DI-AMIDO-DIPHENYL. PHENYL-INDAZINE C, H10N2 i.e.

 $C_dH_4 < \frac{N}{CH} > NPh.$ [84°]. (345° uncor.). Formed by reducing o-nitro-benzyl-aniline with tin and HClAq (Paal, B. 23, 2640; 24, 961). Needles (from scohol). Not affected by distillation over red-hot zinc-dust. Itedweed to a dinydride [98°] by adding Na to its alcoholic solution. Yields a methylo-iodide B'MeI [188°].

PHENYL INDOLE C.H. CH NPh CH. (327° i.V.). Formed by heating its earboxylic acid [176°] (Fischer a. Hess, B. 17, 567; Pfülf, A. 239, 221). Oil, v. sol. alcohol. Its solution in HClAq colours pine-wood intensely violet.

Phenyl-indole C.H. CH SCPh.

phenanthridine. [186°]. (above 360°).

Formation.—1. By boiling w-bromo-acetophenone or phenyl-wamido-acetophenone with aniline (Möhlau, B. 14, 173; 15, 2480; 18, 165). 2. By heating the phenyl-hydrazide of aceto-phenone or of phenyl-acetic aldehyde with ZnCl, at 180° (Fischer, B. 19, 1565; 21, 1071; A. 236, 135).—3. By passing benzylidene-o-toluidino through a red-hot tube (Etard, Bl. [2] 39, 531). 4. By the action of zinc-dust and NH,Aq on C.H.(NO₂).CH₂.CO.C.H₃.(Pictet, B. 19, 1065). Properties. Colourless plates, insol. water.

May be sublimed. Colours pine-wood violet-blue. Yields B'C.H.N.O. [127°]. Nitrous acid forms a nitroso-derivative $C_uH_4 < \frac{C(NO)}{NH} > CPh$ [c. 258°], which yields B'HCl, B'HNO, and NaC, H,N.O, and may be reduced to amidophenyl-indole [174°].

Dahydride CuHush. [46°]. Formed by Vor. 17.

boiling phenyl-indole with zinc-dust, alcohol, and HCl. Colours pine-wood orange. Yields a nitrosamine.

с.н.<СРһ>он. Phenyl-indole Formed by the action of alcoholic HCl on the phenyl-hydrazide of phenyl acetic aldehyde (Fischer, B. 21, 1811). White plates (from ligroin), v. sol. alcohol. Converted by heating for fifteen minutes with ZnCl, into the preceding isomeride [186°]. Yields a picrate [107°] and a nitrosamine C.H. CPh CH [61°] which gives Liebermann's reaction (Ince, A. 253, 87).

Di-phenyl-indole C.H. CPh CPh. [123°]. Formed by heating the phenyl-hydrazide of de-oxybenzoin with ZnCl₂ (Fischer, B. 14, 1566; A. 236, 136). Colourless crystals, v. sol. alcohol. Does not give the pine-wood reaction. Its picrate crystallises in dark-red needles.

Di-phenyl-indob CaH4 < CH > CPh. (above 360°). Got by heating the u-di-phenyl-hydrazide of acetorhenone with ZnCl, at 175° (Pfülf, A. 239, 223). Oil. Colours acidified pine-wood bluish-violet.

PHENYL-INDOLE CARBOXYLIC ACID

 $C_{13}H_{11}NO_2$ i.e. $C_6H_4 < \frac{C(CO_2H)}{N(C_6H_3)} > CH$. Formed by heating the di-phenyl-hydrazide of pyruvic acid with HOAc and HClAq (E. Fischer, H. 17, 567). Needles, v. sl. sol. water, v. sol. alcohol. NaOCl in the cold forms phenyl ψisatin C,H, CO CO. [134°] (Pfülf, A. 239, 222).

PHENYL INDOXAZINE C.H. CH N. [84°]. Got from o-bromo-benzophenone and an alkaline solution of phenyl-hydrazine (Catheart a. V. Meyer, B. 25, 1498). Large crystals. PHENYL-INDULINE C₂,H₁₇N₂ i.e.

ÇH:CH----Ç:N C(NPh).CH:C.NPh C.H., [231°]. Mol. w. (by C(NF)-CHICAPP Raoult's method) 320-370 (calc. 347). Formed from amido-phenyl-induline [152°] by treatment with nitrous acid (Fischer a. Hepp. A. 262, 257; 266, 263). Reddish tables, with blue reflex; v. sol. benzene, insol. ligroin. Heated with HOAc (5 pts.) and HCIAq (25 pts. of 20 p.e.) at 165° for six hours it forms: (a) C₂₁H₁₈N₁O crystallising from benzene in steel-blus plates [218°], forming a brownish-red solution in HClAq, and converted by cone. HClAq at 200° into a compound $C_{10}H_{14}N_2O_2$; (b) the compound $C_{10}H_{14}N_2O_2$ [c. 280°] which crystallises from benzene or alcohol in brownish-yellow prisms or plates, and is both base and phenol. Its hydrochloride crystallises from conc. HClAq in prisms with green lustre; (c) benzolindone $C_{18}H_{12}N_2O$; (d) a body which dissolve in benzene with fiery brown fluorescence, and is perhaps carbazole-fluor-indine (Fischer a. Hepp, A. 266, 249). Benzolindone C₁₅H₁₂N₂O i.e.

CH:CH.C:N CO.CH:C.NPh Co.H. Formed by heating phenyl-induline with HOAc and HClAq at 160°-200° (Fischer a. Hepp, A. 266, 253). Lustrous brown plates, insol. alkalis, sol. dilute HClAq, forming a rose-coloured solution. Its solution in conc. H.SO, is green. Yields phenazine on distillation with zinc-dust.

PHENYL IODIDE v. IODOBENZENE PHENYL IODOMETHYL SULPHONE

C.H., SO. CH.I. [64-52]. Formed from benzene aulphinic acid, NaOEt, and CH.I. at 100° (Michael a. Palmer, Am. 6, 253). Prisms (from alcohol). NaOEt at 75° gives phenyl-methyl sulphone and products of oxidation (Otto, B. 21,

PHENYL-ITACONIC ACID CHPh:C(CO.H).CH. CO.H. [1729]. Formed by the action of Na or NaOEt on phenyl-paraconic acid (Fittig, A. 256, 68). Prisms, sl. sol. cold acid (Fittig, A. 250, 68). Prisms, 81. sol. cold water. Yields phenyl-isocrotonic acid [1799] and 7-0xy-phenyl-futyric lactone [379] when boiled with diluted H.SO. (1:1). Br gives bromophenyl-paraconic acid 6, H.BrO. [999] and arm isomeride [1449].—BAA" 23aq.—CaA".—Ag.A".

Ethyl ether Et.A". (315° uncor.). Oil.
Di-PHENYL-KETONE V. BENGOPHENONE.

Di-phenyl diketone v. Benzil.

Di-phenyl triketone C.H., CO.CO.CO.C.H., [70°]. (248° at 40 mm.). Formed by distilling CBz_Br.OAo in vacuo. Formed also by adding aqueous NaNO, to a solution of the mone oxim in HOAc, and boiling (Pechmann, B. 22, 852; 23, 3375). Hygroscopic golden needles (from ligroin, v. sol. all solvents. Give a blue colour with H2SO, and benzene that contains thiophene.

Reactions .-- 1. Alkalis decompose it, forming benzoin, benzoic acid, and CBzPh(OH).CO2H [118°].—2. Phenyl-hydrazine forms a phonyl-hydrazide C₂₁H₁₆N₂O₂ [c. 135°], benzene-azo-triphenyl-pyrazole C₈H₃.N₂.C≪CPh.NPh CPh:N and a third compound [223°] .-- 3. Aniline gives rise to Compound [225].—5. Antime gives rise to CPh(NPh).C(OH). COPh [100°] and C(OH). (CPh:NPh). [148°].

Hydrate Bz.C(OH). [90°].

Mono-oxim Bz.C:NOH. [146°]. Formed

from Bz,CH, and nitrous acid. Tri-oxim (C.H. C(NOH)), C:NOH. [186°]. Formed from the triketone and hydroxylamine.

Di-phenyl tetraketone C.H. CO.CO.CO.CO.C.H_a. The hydrate [88°] of this body is formed by the action of conc. HNO, on phenyl-glyoxal (Abenius a. Söderbaum, B. 24, 8084).

DI-PHENYL-KETONE CARBOXYLIC ACID v. Benzoyl-benzoic acid.

Di-phenyl ketone dicarboxylic acid v. Benzo-

PHENONE DICARBOXYLIC ACID. Di-phenyl diketone o-carboxylic acid

C.H. CO.CO.C.H. CO.H. Formed by oxidising deoxybenzoin o-carboxylic acid with alkaline KMnO, (Graebe, B. 21, 2003; 23, 1344). Occurs in a yellow modification [141.5°] and a white variety [125°-130°]. The yellow modification is nearly twice as sol. alcohol and chloroform as the white variety, and is converted into the white variety by dissolving in alkali and ppn. by soids. The white modification changes into the yellow one at 115°-125°.

Dicarboxylic acid v. DIPHTHALYLIC ACID. DI-PHENYL-KETOXIM v. Oxim of Benzo-PHENONE

PHENYLLACTIC ACID v. OXY-PHENYL-PRO-PIONIC ACID.

PHENYL-LACTIMIDE v. vol. i. p. 180.

PHENYL-LUTIDINE-CARBOXYLIC ACID & PHENYL-DI-METHYL-PYRIDINE-CARBOXYLIC ACID.

PHENYL-LUTIDONE v. Oxy-phenyl-di-METHYL-PYRIDINE.

PHENYL-MALEIC ACID C, H,O, i.e. CO.H.CPh:CH.CO.H. Formed by dissolving its anhydride in water and extracting with ether (Alexander, A. 258, 77). Prisms, m. sol. water. Begins to lose water below 100°

Anhydride CH .CO O. [119.5°]. Formed by distilling phenyl-malic scid. Needles, insol.

water, v. sol. chlosoform and ether. Di-phenyl-maleïc acid CO2H.CPh:CPh.CO2H. Stilbene dicarboxylic acid. Formed by saponification of its nitrile. Its ether is formed, neation of its nitrie. Its eather is formed, together with di-phenyl-fumaric ether, by the action of Na on a-bromo-phenyl-aceta ether in ether (Reimer, B. 14, 1800; Rügheimer, B. 15, 1626). The free acid splits up at once, on liberation from its splits, into H₂O and anhydrida On distillation with limit in the life. dride. On distillation with lime it yields s-diphenylethylenc.—K₄A": needles, v. sol. water.

—Ag₂A": amorphous pp.—Ag₁A'A, needles,

Ethyl ether Et₂A". [54°]. Prisms,

Linide C₁₀H₁₀O₂(NH). [218°]. Needles,

almost insol. water, v. sol. alcohol.

Phenylimide' C, H10 O2 (NPh). [175°]. Formed by heating the anhydride with aniline at 120° (Anschütz a. Bendix, A. 259, 63).

Nitrile CN.CPh.CPh.CN. Dicyanostilbene. [158°]. Formed by heating a bromo-phenylacetonitrile alone or with alcoholic KCy (Reimer, B. 14, 1798). Plates (from benzene).

Isonitrile. [2420]. Occurs in small quantity in the preparation of the nitrile by heating the product of bromination of phenylacetonitrile. Golden needles (from alcohol). Yields an acid [222°] on saponification.

Anhydride CPh.CO O. [155°].6 (236° at 15 mm.). Formed by adding HCl to solutions of salts of the acid, or by heating di-phenylfumaric acid at 260° (Reimer, B. 13, 742). Trimetric needles (from dilute alcohol), abic = 693:1: 385, insol. water, sol. CS. May be sublimed. Its alkaline solution reduces AgNO. Not changed by NaOHAq into the fumaroid form (Delisle, A. 269, 91). NaOHAq (15 p.c.) at 100 forms a polymeride melting much above 250°, insol. water and other solvents.

Reactions.—1. Reduced in alcoholic solution by zinc-dust and HCl to a mixture of the two diby 2h0-dust and 11c4 to a unxure of the two appenyl-succinic acids.—2. Fuming HNO, gives rise to an amorphous di-nitro derivative (C_aH₄(NO₂))_C(O_a -3. p-Tolyl-acetic acid forms C₁Ph_O₂:CH_C(H, [165°], crystallising in yellow coding at Phone and Castic acid and No. needles .- 4. Phenyl-acetic acid and NaOAc at 225? form CPh.C(CHPh) O [176°], which may be reduced by HI and P to benzyl-di-phenyl. maleïde CPh.CH(CH,Ph) O [128°] (Gabriel a. Cohn, B. 24, 3228, 3854). The compound Cohn, B. 24, 3228, 3854). The compound C,Ph,O₂(CHPh) combines with Br, forming C,Ph,BrO₃(CHPh) [154°], which splits up at 155°-160° into HBr and C,Ph,O₂(CBrPh) [165°]. The compound C,Ph,HO₂(CH,Ph) is converted by potash into CO,H,C,Ph,CH(OH),CH,Ph [174°], and by an alcoholic solution of NEIH, into CO(NHEt).C,Ph,CH(OH).CH,Ph [196°]. The

compound C₄Ph₂O₄(CHPh) is converted by KOH to Me₄C(SO₄Ph), [97°]. — 6. Chloro - acetoms at C₄Ph₂O₄(OH).CH₂Ph [185°], and in benzene reacts on PhSNa in ether, forming acetonylication by HNO₂ into C₄Ph₂O₄(OH).CH(NO₂)Ph phenyl-sulphide PhS.CH₂CO.CH₄ [35°] (209°) [125°] (which yields an acetyl derivative [166°]), and the compound C₂Ph₂O₄(NO₄).CH(NO₂)Ph crystallises in prisms, 8l. sol. hot water, v. sol. 146°], which is converted by boiling sloohol into O,Ph,O,c(NO,)Ph [177°], a body that may be reduced by HI and P to iso-benzyl-diphenylmaleide [118°]. Benzyl-di-phenyl-maleide is sonverted by alcoholic NH, at 180° into CPh.CH(CH,Ph) NH [170°], which yields a

pitrosamine [136°].

PHENYL-MALIC ACID v. Oxy-PHENYL-SUC-DINIC ACID.

PHENYL-MALONAMIC ACID v. MALONIC

DI-PHENYL - MALONIC ACID. Ethyl sther of the nitrile CPh₂(CN).CO₂Et. [50°]. Formed from CPh₂Cl.CO₂Et and HgCy, at 125° (Bickel, B. 22, 1537). Yellowish tables.

Reference.—Di-nitro-phenyl-malonic ethen.
PHENYL-MANDELIC ACID v. Phenyl derivative of Mandelic acid.

PHENYL MELAMINE v. vol. ii. p. 322.
PHENYL MERCAPTAN C.H.SH. Thio-

plenol. Phenyl-sulphydrate. Mol. w. 110. (168°) (L.); (172°) (F. a. C.). S.G. 2 1-078. Formation.—1. A product of the dry distillation of sodium benzene sulphonate (Kekulé, Z. 1867 194; Stenhouse, A. 149, 248; Pr. 17, 62). 2. Together with Ph. S and diphenylene sulphide by heating benzene with S and AlCl, at 75° (Friedel a. Crafts, C. R. 86, 884; A. Ch. [6] 14, 1371.—3. By distilling phenol (10 mols.) with P₂S₃ (1 mol.), the yield being 6 p.c. of the phenol used (Kokulé, Z. [2] 3, 193, 306; Beckmann, J. pr. [2] 17, 456).—4. From Ph.S₂ and K.S in alcohol (Otto a. Rossing, B. 19, 3129).—5. By distilling C.H. SO, Na with NaSH (Stadler, B.

17, 2080). Preparation. - Phenyl ethyl dithiocarbonate, or a mixture of diazobenzene chloride solution and potassium ethyl dithiocarbonate (xanthate) is boiled with alcoholic potash until the solution remains clear on addition of water. The alco-hol is then distilled off and the residue dissolved in water, mixed with a little H.SO, and zinc-dust (to prevent oxidation), and distilled with steam. The distillate is extracted with ether. The yield is 75 p.c. of the theoretical (Leuckart, J. pr. [2] 41, 187).

Properties .- Oil, v. sol. alcohol and ether. Smells like garlic. Attacks the skin. Conc. H.SO, forms a violet solution, changing on warming through cherry-red to blue (Baumann, H. 5, 321; cf. Brunner, B. 4, 984).

Reactions .- 1. Readily oxidised to Ph. S. 2. CH,CCl, and dilute (20 p.c.) NaOHAq form CH,C(SPh), crystallising in white plates; v. sol. hot alcohol (Laves, B. 25, 353).—8. Acetoacetic ether and dry hydrochloric acid form CH, C(SPh), CHaCO, Et [58°], crystallising from alcohol in plates. Not attacked by boiling HClAq, atcohol in plates. Not attacked by colling invividual, but decomposed by alkalis into alcohol, PhSH, and CH_rC(SPh):CH.CO₂H [177°] (Escales a. Baumann, B. 19, \$790).—4. NH_rCOCl forms NH_rCO.NH.CO.SPh [218°] (Gattermann, A. 244, 43).—5. Actions and HCl in the cold give (Ma_rC(SPh)₂ [56°] (Baumann, B. 19, 2804), which is oxidised by KMnO₄ and H_rSO₄

alcohol; combines with KHSO, yields a phenylhydrazide [82.5°], and is converted by oxidation into Ph.SO₂.CH₂.CO.CH₃ [57°]. Acetonylphenyl sulphide may be converted by successive pnenyi sulphide may be converted by successive treatment with HCy, alcoholic hydrochloric acid, and alcoholic potash into the acid PhS.CH."CMc(6H).CO.H [97], which yields CaA'₂ aq, BaA'₂ aq, and AgA', and is oxidised by KMnO₄ to Ph.SO., CH., CMc(OH).CO.H [121].—7. Chiloral forms CCl., CH(OH)(SPh) [53°] decomposed by heat into its components (Baumann, B. 18. 888).—8. Combines with preguence acid. B. 18, 886).—8. Combines with pyruvic acid, ferming CH₂.C(OH)(SIA).CO₂H [87°], but in presence of gaseous HCl it forms the 'marcaptol' CH₃.C(§Ph), CO₂H [117°] which is not attacked by boiling HClA or alcoholic potash.—9. Phenylglyoxylic acid forms C,H,,C(OH)(SPh),CO,H converted by HCl gas into C,H,C(SPh),,CO,H [148°] (Escales a. Baumann, B. 19, 1789).—10. β-Acetylpropionic acid does not combine directly, but propionec acid does not combine directly, but in ptesence of hydrochloric acid it forms CH₂C(SPh)₂CH₂CH₂CQ₂H [69°], which is not attacked by alkalis, but is decomposed by dilute acids into PhSH and acetyl-propionic acid (E. a. B.).—11. CH₂CO.CH₂SPh forms CH₂C(SPh)₂CH₂SPh [55°], crystallising in cubes; v. sol. alcohol, insol. water; converted the acid that in [1] (C(Ph)₂CO) ph. (EL SO Ph. by oxidation in CH₃.C(SPh)(SO₂Ph).CH₂.SO₂Ph by oxidation in CH₂C(Srh)(SO₂Fh)-CH₂SO₂Ph [157°], crystallising in needles, sl. sol. cold alcohol, split up by alkalis into Ph.SO₂CH₃, PhSH, and Ph.SO₂H (Autenrieth, B. 2t, 170).—12. CBr₂(SO₂Et)₂ and NaOHAq form PhSCH(SO₂Et)₂ [86°), crystallising in tables; v. sl. sol. bot water v. sol. alkelia, corrected by v. sl. sol. hot water, v. sol. alkalis; converted by alcoholic NaOH and MeI into PhS.CMe(SO,Et), [113°], crystallising in white needles: m. sol. hot alcohol (Fromm, A. 253, 166; Laves, B. 25, 361). — 13. NaSPh reacts with isobutylene bromide, forming NaBr, Ph2S2, and isobutylene (Otto, B. 23, 1052)

Salts .- NaSPh. When Na is dissolved in an ethereal solution of PhSH containing phenol, a pp. of NaSPh is got while NaOPh remains in solution.—Hg(SPh),: colourless nædles (from alcohol).—ClHgSPh: plates.—Pb(SPh),: yellow crystalline pp., split up on distillation into PbS and Ph.S. Cu(SPh)2: pale-yellow powder.

AgSPh: pale-yellow crystalline pp.

Methyl ether PhSMe. (188°). Formed from Pb(SPh)2 and MeI (Obermeyer, B. 20,

Éthyl ether PhSEt. (204°) at 744 mm. Formed from NaSPh and EtI at 120° (Beckmann, J. pr. [2] 17, 457), and by the action of PhSH on PhN₂Cl (Stadler, B. 17, 2078). Liquid with unpleasant smell.

Allyl ether v. PHENYL ALLYL SULPHIDE. Acetyl derivative PhSAc. (229°). Formed from phenyl mercaptan and AcCl (Michler, A. 176, 177). Oil.

References. - AMIDO-, BROMO-, CHLORO-, CHLORO-NITRO-, NITRO-, and OXY- PHENYL-MERCAPTAN.

PHENYL-MERCAPTURIC ACID C, H, NSO, i.e. NHAc.CMe(SPh).CO2H. [143°]. by reducing bromo-phenyl-mercapturic scid with

sodium-amaigam (Baumarin, B. 15, 1732; 18, 258; H. 5, 835; 8, 190). Tetrahedra, m. sol. alcohol. Lesvorotatory in alcoholic solution. Solutions of its salts are dextrorotatory. Decomposed by dilute H.SO, into HOAc and phenylcystein.—BaA', 3aq; needles.

References.—Brown- and Chloro- Phenyl-

MERCAPTURIC ACID.

PHENYL-MESITYL-CARBINOL v. PHENYL-TRI-METHYL-PHENYL-CARRINGL.

PHENYL-MESITYL-CARBINOL CABBOXY-LIC .ANHYDRIDE v. TRI . METHYL - PHENYL-PHTHALIDE.

PHENYL MESITYL KETONE v. PHENYL TRI-LETHYL-PHENY; KETONE.

PHENYL-METHACRYLIC ACID v. PHENYL-CROTONIC ACID.

PHENYL-METHACRYLIC ALDEHYDE

CHPh:CMe.COH. (150° at 100 mm.). Formed by adding NaOHAq to a mixture of penzoic aldehyde and propionic aldehyde (Miller a. Kinkelin, B. 19, 525). Oil. Reduces ammoniacul AgNO₃. Combines with bisulphite. Yields a phenyl-hydrazide [137°].

PHENYL-METHANE v. Toluene. • Di-phenyl-methane C₁₃H₁₂ i.e. CH₂Ph₂. Mol.

w. 168. [25°]. (c. 263°).

Formation.—1. Together with C, H, (CH, Ph), by boiling benzyl chloride with benzene and zinc-dust (Zincke, B. 4, 298; C. J. 24, 508, 688).

2. By the action of H₂SO₄ and HOAc on a mixture of benzene and benzyl alcohol (Meyer a. Wurster, B. 6, 963) .- 3. By heating bentzophenone with zinc-dust (Staedel, B. 6, 1401; 7, 1480; cf. Barbier, C. R. 79, 812), or by reducing it with HI and P (Graebe, B. 7, 1624), or Zn it with H1 and F (Graebe, B. 7, 1024), or Zn and H₂SO₄ (Zincke, B. 10, 1473).—4. From benzene, CH₂Cl₂, and AlCl₃ (Friedel a. Crafts, Bl. [2] 41, 824; A. Ch. [6] 11, 264).—5. From CH. (OMe), benzene, HOAc, and H.SO. (Baeyer, B. 6, 221).—6. By distilling barium di-phenylacetate with soda-lime (Jena, A. 155, 86).

Preparation. - By adding AlCl, (35 g.) to a mixture of benzyl chloride (100 g.) and benzene (500 g.) (Friedel a. Crafts, A. Ch. [6] 1, 478; Bl.

[2] 33, 337).

Properties.—Prisms, v. sol. alcohol and other, smelling like oranges. According to Reissert (B. 23, 2242) it melts at 23°. Oxidised by chromic acid mixture to benzophenone. Yields diphenylene-methane when passed through a red-hot tube (Graebe, B.-7, 1623). Prolonged treatment with Cl in presence of I forms CCl, and C.Cl. (Ruoff, B. 9, 1048).

Tri-phenyl-methane Cl. H. i.e. CHPh. [92°].

(330°) (Schwarz); (355°) (K. a. F.).

Formation.—1. By heating PhCHCl₄ with HgPh, at 150° (Kekulé a. Franchimont, B. 5, 907).—2. By heating Ph₂CH(OH) with benzene and P₂O₄ at 155° (Hemilian, B. 7, 1203).—3. By heating (8)-benzpinacolin C₂₈H₂₆O with soda-lime at 300° (Thörner a. Zincke, B. 9, 65).—4. Together with a little CH₂Ph₂ by adding AlCl₂ to a mixtus of chloroform and benzene (Friedel a. Crafts, J. pr. [2] 16, 233; A. Ch. [6] 1, 496). 5. With other products, by the action of AlCl, on benzene mixed with CH,Cl, with CCl, with PhCCl, and with CPhHBr. (PhHBr (Magatti, B. 12, 1468; Schwarz, B. 14, 1526; Anschütz, A. 235, 208).—6. By heating benzoic aldehyde 729). Needles, v. sol. alcohol and ether. AAA.

(100 g.) with benzene (147g.) and ZnCl, (100 g.) at 260° for 7 hours (Griepentrog, B. 19, 1876; A. 242, 329).

Preparation.—AlCl₂ (500 g.) is slowly added to a mixture of benzene (1400 g.) and chloroform (400 g.). The mixture is finally heated on the water-bath, water is carefully added, and the oil dried and fractionally distilled. It is finally purified by conversion into the compound with benzene (Allen a. Kölliker, A. 227, 108; cf. Fischer, A. 194, 252; Schwarz, B. 14, 1516).

If the benzene contains toluene the product will contain a homologue (Hanriot, Bl. [3] 1, 773).

Properties. Plates (from alcohol), v. son benzene, ether, and CHCl, m. sol. cold alcohol. Crystallises from benzene in efflorescent rhombo-Crystallises from benzene in emorescent momor-hedra CHPh₂C_H, [76°]. Oxidised by chromic acid to tri-phenyl-carbinol [159°]» AlCl, at 120° decomposes it, but below 80° it forms CH₂Ph₂ (Friedel a Crafts, C. R. 200, 692). On exhaustive chlorination with SbCl, it yields CCl, and C, Cl, (Merz a. Weith, B. 16, 2876). Na has no action at 300°, but K at 200° forms a red substance (CKPh₂). K at 250° Torms a dark mass, whence HClAq liberates C₁₀H₁₄ [148·5°] (360°) (Hanriot a Saint-Pierre, C. R. 108° 1119; Bl. [3] 1, 774). The potassium derivative CKPha absorbs CO, at 200°, yielding CPh, CO,H [264°]. Benzyl chloride acting on CKPh, forms the compound CPh, CH, Ph [140°]. BzCl forms C₂₀H₁₀O [172°] which may be reduced by HI and P to C20H20 [234°].

References. — Amido-, Bromo-, Chloro-, Methyl-amido-, Nitro-, Nitro-amido-, Oxy-AMIDO-, and OXY- PHENYL-METHANE.

DI-PHENYL-METHANE DI-O-CARBOXY-LIC ACID CH₂(C₂H₄CO₂H)₂. [255°]. Formed by reducing the lactone of CH(OH)(C₂H₄CO₂H)₂. with HI and P (Graebe a. Juillard, A. 242, 253).
Crystals (from alcohol). Yields anthraquinone on heating at 280°.—BaA 6aq. S. 47.

Methyl ether Me₂A" [44°].

Isomeride v. BENZYL-ISOPHTHALIC ACID. Di-phenyl-methane tricarboxylic acid

Do-phenyl-methane transformed acid CO_H.CH(C,H,CO_H). [220°] S. 095 at 25°. Got by heating the lactone of the oxyacid CO_H.C(OH)(C,H,CO_H), with HI and P at 170° (Gracbe a. Juillard, A. 242, 235). Crystals (containing aqf. At 270° it forms a red compound C, H, O, [261°].

Methyl ether Me.A". [145°]. Tri-phenyl methane o-carboxylic acid CHPh, C, H, CO, II. [162°].

Formation.-1. By the action of NaOH an zinc-dust on di-phenyl-phthalide (Baeyer, B. 12 644; A. 202, 52).—2. By heating phenyl phthalide with benzene and AlCl, (Gresly, A 234, 242).—8. By saponifying the nitrile, which is obtained from CHCl₂.C.H₄.CN, benzene, and AlCl, (Drory, B. 24, 2572).

AlCi, (Drory, B. 24, 2572).

Properties.—Needles (from alcohol), insol water. May be sublimed. Yields tri-phenyl methane when heated with Ba(OH)₂. CrO_a in HOAc oxidises it to diphenyl-phthalide.

Nitrile CHPh₂C₂H₄.CN. [89°].

"Tri-phenyl-methane-p-carboxylis acid [162°]. Obtained by sandmeyer's reaction from earnide-tri-phenyl-methane [84°] (Fischer a samide-tri-phenyl-methane [84°] (Fischer a samid p-amido-tri-phenyl-methane [84°] (Fischer a Frankel, A. 241, 864; Otto a. Pischer, R. 24,

An isomeric acid melting above 360° was obained by Oppenheimer (B. 19, 2029) by oxidising he corresponding aldehyde with Ag.O.

Tri-phenyl-methane dicarboxylic soid CHPh.C.H.(CO.H), [1:2:5]. [280°]. Formed by reduction of the lacton of tri-phenyl-carbinol dicarboxylic acid by zinc-dust and NaOH (Hemilian, B. 16, 2375). Needles (from HOAc). Conc. H.SO, forms a greenish-yellow solution, which on heating changes through green, blue, and violet to purple.—BaA"4aq.—Ag₂A": pp.

Tri-phenyl-methans dicarboxylic acid CHPh.C.H.(CO.H.), [13:4]. [778°]. Formed by boiling di-phenyl-phthalide dicarboxylic acid with zinc-dust and NaOHAq (Hemilian, B. 19, 3068). Needles (from dilute alcohol). May be sublimed. Yields CHPh, when distilled with Ba(OH), Re-exidised by alkaline KMnO, to diphenyl-phthalide dicarboxylic acid.—CaA" 2aq: needles.—Ag.A": curdy pp.

Reference .- OXY - DI - PHONYL - METHANE CARB-OXYLIC ACID.

DIPHENYL . METHANE DISULPHONIC ACID $C_{13}H_{10}(SO_3H)_2$. [59°]. Got by sulphonation (Doer, B. 5, 796). Deliquescent plates. -K.A" aq: prisms (from dilute alcohol).—BaA".
-CuA" . green plates.

Tri-phenyl-methane trisulphonic acid $C_{19}H_{11}(SO_1H)$. Formed by warming CHPh, with fuming H_2SO_4 (Kckulė a. Franchimont, B_2 , B_3 , B_4 , B_4 , B_5 , B_4 , B_5 , B_5 , B_5 , B_5 , B_6 , B_6 , B_7 , B_7 , B_8 , needles, ppd. by adding alcohol to its aqueous solution.

DI PHENYL METHAZINE C, H12O, i.e. CHPh<\(\frac{N}{N}\) CHPh. [93°]. Formed by shaking a dilute solution of hydrazine with benzoic aldehyde (Curtius, J. pr. [2] 39, 44). Light-yellow prisms, v. sl. sol. hot water, v. sol. hot alcohol. Decomposed by boiling into CHPleCHPh and nitrogen, and by boiling dilute acids into benzoic aldehyde and hydrazine. Reduced in alcoholic solution by sodium-amalgam to di-benzyl-hydrazine, and by excess of Na to benzylamine.

PHENYL-METHENYL-AMIDINE v. BENZ-

· Diphenyl-methenyl-diamine is described as DI-PHENYL-FORMANIDINE.

PHENYL-METHENYL-AZIDINE C.H., N. i.e. NH, CH:N.HPh. [225°]. Formed from phenyl-hydrazine and HCy (Fischer, B. 22, 1934). Insol. water, v. sol. hot alcohol. The nitrate and hydrochloride are crystalline.

PHENYL METHENYL DI-ETHYL TRISUL-PHONE C.H., SO., CH(SO., C.H.). [166°]. S. 2 at 15°. Formed by oxidising PhS.CH(SO.Et). with alkaline KMnO, (Fromm, A. 253, 167; Laves, B. 25, 362). Snow-white needles, v. sol. alkalis.—KA': prisms.—BaA'₂: tables.

TRI PHENYL METHENYL TRIKETONE v. Tri-benzoyl-methane.

TRI.PHENYL METHENYL TRISULPHONE CH(SO,Ph). \$\, 215\circ\$. Formed by oxidising PhS.CH(SO,Ph), with alkaline KMnO, (Laves, B. 25, 348). Tables, v. sol. alcohol, insol. ether, m. sol. water.—KA': tablets.—BaA';—AgA'.

DI - PHENYL - DI - METHYL - ACETYLENE TETRAKETORE . DI-BENZOYL-DI-ACETYL-SHAHE

PHENYL-METHYL-ACRIDINE C.H., N i.e. C.H. C.CH:CMe. [136°]. Formed heating phenyl-p-toluidine with benzoic acid and ZnCl, at 260° (Bonna, A. 289, 62). Needles, sl. sol. water. Its alcoholic solution shows greenish-blue fluorescence. Yields phenylacridine carboxylic acid [253°] on oxidation .-B'HCl: yellow needles. B'HI. B', H. SQ, .-

B'C₆H₁N₃O₇. Red needles.—B'HI.—B'₂H₂SQ₅.—
B'C₆H₁N₃O₇. Red needles.
Phenyl-methyl-acridine dihydride
C₅H₄.—C₅H₄. [104°]. Formed by the action of MeI on phenyl-acridine dihydride; or by reduction of the methylo-chloride of phenyl-acridine with zinc-dust (Bernthsen a. Bender. B. 16, 1816). White needles or prisms. exidation with nitrous soid it gives the methylo-

hydroxide of phenyl-acridine.

PHENYL-METHYL-ALLYL-PYRROLE

CH:CMe
CH:CMe
NC,H, [52°]. (278°). Formed by

Paal, B. 18, 2595). Large colourless plates, Blue fluorescence. Extremely sol. all ordinary solvents.

PHENYL - METHYL - ALLYL - PYRROLE CARBOXYLIC ACID CO.H.C.=CMe>NC.H. [158°]. Obtained by saponification of its ether, which is formed by the action of allylamine upon acetophenone-acetoacetic ether (Lederer a. Paal, B. 18, 2594). Short glistening prisms.

alcohol, ether, benzene, and acetic acid. PHENYL-METHYL-AMIDO-ACETIC C.H., NO. i.e. CH. (NPhMe). CO.H. Phenylmethyl-glycocoll. Formed by heating chloroacetic ether with dimethylaniline and saponifying the product by boiling HClAq (Silberstein, B. 17, 2661). Liquid.—HA'HCl; prisms.

A mids. CH (NPhMe). CO.NH. [168°].

Formed by heating CH_CI.CONH, with NPhMe, or NPhMeH. Crystals, sol. hot water. Its hydrochloride forms easily soluble prisms.

Methylo-chloride CH2(NPhMe2Cl).CO2H. Formed by warming chloro-acetic acid with NPhMe, in ether (Zimmermann, B. 12, 2206). Needles. Moist Ag₂O forms an hydroxide.

Amide of the methylo-chloride CH₂(NPhMe,Cl).CO.NH, Formed by heating chloro-acetamide with dimethylaniline in alco-

PHENONE C.H., CO.CH., NPhMe. Phenacyl-methyl-aniline. [120°]. Formed by the action of NPhMeH or NPhMe, on \(\varphi\)-bromo-acetophenone (Staedel a. Siepermann, B. 18, 842; 14, 983; 21, 2196). Prisms (from alcohol). A solution of its hydrochloride gives a red pp. with dilute HNO, (Weller, B. 16, 27). ZnCl_forms Cl_Hu_N [102°].—B'_H_PtCl_s: tablos.—B'MeI. Crystals.—B'MeOH. Strongly alkaline.

PHENYL - METHYL - AMIDO - BENZENE

ACID NPhMe.C.H.,P(OH), PHOSPHINIC [150.5°]. Formed by the action of NaOHAq on the oily chloride NPhMe.C.H., PCl., which is formed by the action of AlCl, on a mixture of NPh_Me and PCl, (Michaelis, A. 260, 37). Small needles (from water) or plates (from alcohol),—NaHA" 2aq. [265°]. Plates, v. e. sol. water.

PHENYL-METHYL-AMIDO-BENZOIC ACID C₁₄H₁₈NO₂ i.e. C₄H₄(NPhMe).CO₂H. [184°]. Formed from NPh₂Me and COCl₂ (Michler a. Sarauw, B: 14, 2180). Plates.—BaA'₂: pearly plates.—AgA': white pp.

PHENYL-METHYL-AMIDO-ETHANE SUL-PHONIC ACID NPhMe.C.H., SO.H. Formed from CH_Cl.CH_, SO.H and methylaniline at 160° (James, J. pr. [2] 31, 417). Silky crystals (from

PHENYL - METHYL - AMIDO - ETHYL - PHTHALIMIDE C.H.O.N.C.H.NPhMe. [105°]. Formed from brono-ethyl-phthalimide and methyl-aniline at 165° (Newman, B. 24, 2199). Greenish-yellow four-sided tables, a c. sob CaHa.

PHENYL - METHYL AMIDO-METHENYL-AMIDO-PHENOL C, Ho, N,O i.e.

C.H. C.NPhMe. (above 360°). Formed

from C.H. C.SH and methyl-aniline (Kalckhoff, B. 16, 1825). Syrup, with blue fluorescence.—B'2H2PtCle: prisms.

PHENYL - METHYL - AMIDO-DI-METHYL-PYRROLE C₁₈H₁₆N₂ i.e. NPhMe.N CMe:CH [41°]. (310°). Formed by heating its dicarboxylioacid at 231° (Knorr, A. 236, 310). Crystalline mass, v. sol. alcohol. Volatile with steam.

Phenyl-methyl-amido-di-methyl-pyrrole dicarboxylic acid C₁₈H₁₆N₂O₂. Formed by saponification of its oily ether, which is formed from diacetyl-succinic ether and phenyl-methyl-hydrazine (K.). Prisms, decomposing at 231°. -AgA': flocculent pp.

PHENYL - METHYL - p - AMIDO - PHENOL. Methylderivative NPhMe.C.H.OMe. (813°). Formed from phenyl-p-amido-phenol, KOH, and MeI (Philip a Calm, B. 17, 2433), Oil, insol. NaOHAq. PHENYL - TETRA - METHYL - TRI-AMIDO-

DI-PHENYL-NAPHTHYL-CARBINOL

C.H.s.N.O. i.e. NPhH.C., H. C(OH)(C.H., NMc.)... [95°]. Base of Victoria Blue B. Formed by heating tetra-methyl-di-amido-benzophenone (10 pts.) with phenyl-(a)-naphthylamine (9 pts.), and POCIs (7 pts.) at 110° (Nathansohn a. Müller, B. 22, 1890). The base is set free by NaOHAq. Brick-red powder, v. sol. alcohol and benzene. — (C₃₃H₃₂N₃Cl)₂PtCl₄: violet needles. —C₃₃H₃₁N₃C₆H₂(NO₂)₃OH: dark-blue pp.

Phenyl - penta - methyl-tri-amido-di-phenyl-

naphthyl carbinol C₁,H₁,N₃O i.e. NPhMe.C₁₀H₂,C(OH)(C₂H₁,NMe₂)₂. [77°]. The chloride C₃,H₃₄N₁Cl, Victoria Blue 4 R, formed by the action of methyl-phenyl-(a)-naphthyl-amine on CO(C_eH₁NMe_e), in presence of POCl, is v. sol. hot water (Nathansohn a. Müller, B. 22, 1892). The carbinol is a brick red pp., v. sol. alcohol. It forms $(C_{24}H_{24}N_{2}Cl)_{2}PtCl_{4}$ and v. 801. accords. It forms (***14.35.7)2.
C1,1H_g/N,1C,H_g/NO_3,OH crystallising in very small dark-blue needles.
PHENGL - TETRA - METHYL - TRI AMIDO.

DI-PHENYL-NAPHTHYL-METHANE C,1H,1,N, i.e. NHPh.O.,H.,OH(O.H.,NMe.). [125°]. Formed by reducing the carbinol (v. supra) (Nathansohn a. Müller, B. 22, 1891). Flocculent pp., v. sol. hot alcohol. Yields B".H.,PtCl. and B"C.,H.,N.O., both being crystalline.

Phenyl-penta-methyl-tri-amide-di-phenylnaphthyl-methane ("H., N. i.e.

NPhMe.C., H., CH(C.H., NMe.)... [87°]. Formed
by reducing the carbinol (N. a. M.). Amorphous.

Yields crystalline B" H. PtCl, and B"C. H., N.O.,
PHENYL DI METHYL AMIDO TOLYL

KETONE C₆H₃.CO.C₆H₃Me.NMe₂. [67°]. (850°-360°). Formed from benzoic acid, di-methyl-otoluidine, and P.O. (O. Fischer, A. 206, 91).

PHENYL-TETRA - METHYL-DI-AMIDO-DI-

TOLYI. METHANE C₂₁H₃₀N, i.e. CHPh(C₆H₃Me.NMe₂)₂ [109°]. Formed by heating di-meth**9**1-m-toluidine with benzoic aldehyde and ZnCl₂ (Fischer, B. 13, 807). Prisms.

-B"H_PtCl_ 2aq: small yellow crystals.
PHENYL-METHYL-AMINE v. METHYL-ANIL-INE.

Phenyl-di-methyl-amine v. DI-METHYL-ANIL-

Di-phenyl-methyl-amine v. METHYL-DI-PHENYL-AMINE.

Tri-phenyl-methyl-amine TRI-PHENYL CARBINYLAMINE.

PHENYL-METHYL-ANTHRACENE i.e. CoH, Me CH CH [119°]. by distilling phenyl-methyl-anthranol with zince dust (Hemilian, B. 16, 2367). Yellow pointed crystals. Dissolves in alcohol and ether, with a strong greenish-blue fluorescence. By CrO, in acetic acid it is oxidised to phenyl-methyloxanthranol.

PHENYL-METHYL-ANTHRANOL C21H18O i.e. C_eH₃Me<CPh<C(OH)>C_eH₄. [157°]. Obtained by heating di-phenyl-tolyl-methane carboxylic acid with H₂SO₄ (Hemilian, B. 16, 2365). Yellow glistening tables. Sol. ether, boiling alcohol and acetic acid, insol. cold alkalis, but dissolves on boiling to a yellow solution. On oxidation is gives phonyl methyl-oxanthranol. PHENYL-DI-METHYL-ARSINE v. vol. i. p.

DI -PHENYL - DI - METHYL - AZIMETHYL. ENE N₂(CMePh)₂. [1213]. Found by the action of acetophenone on hydrazine hydrate or on CPhMe:N.NH., (Curtius, J. pr. [2] 44, 542). PHENYL-METHYL-BIAZOLE DIHYDRIDE

CH₂. NPh [140°]. Formed by the action OCCMe:N

of tin and HCl on O CCl. NPh [122°], which is made by the action of COCl, on acetyl-phenyl-hydrazine (Freund a. Kuh, B. 23, 2838). Yel-

lowish plates.
PHENYL-METHYL-TRIAZOLE C.H., N. i.e. N.NPh CH. Formed by heating its carboxylic acid to 180° (Bladin, B. 19, 2602). Oil. B'₂H₂PtCl₆ aq. [124°]. Lemon-yellow tables. PHENYL-METHYL-TRIAZOLE CARBOXY-

LIC ACID N.NPh C.CO.H. [177°]. Formed by saponifying its nitrile, which is got by the action of Ac.O on phenyl-hydrazine dicyanide and also by gently warming phenyl-hydrazine dicyanide with an alcoholic solution of pyruvic acid (Bladin, B. 18, 1544; 19, 2598; 22, 1749; 25, 185).

Salts. — CuA', 1 aq. — PbA', 2 aq. — AgA' 1 aq. — HA'HCl; tables (from HCMq).

Ethyl ether Eth'. Oil. Nitrile. [109°]. Prisms. Amêde C₂N,PhMe.CO.NH₂. [170°]. Prisms,

m. sol. water and alcohol.

Amidoxim C2N3PhMe.C(NH2):NOH. [210°]. Formed from the nitrile and hydroxylamine in alcohol. Plates (from alcohol), v. sl. sol. water. FeCl, colours its alcoholic solution deep red. Yields B'HCl and B',H,PtCl, [201°]. Ac,O forms C,N,PhMe.C(NH,):NOAc [148°] and $C_{2}N_{3}PhMe.C < N > CMe [105.5°]$. BzCl forms C₂N₃PhMe.C(NH₂):NOBz [1825°] converted by heat into C,N,PhMe.C N.O CPh [167°].

DI-PHENYL-DI-METHYL-TETRAZONE NPhMe. N.N.NPhMe. [137]. Formed by oxidising phenyl-methyl-hydrazine (Fischer, A. 190, 162; Tafel, B. 18, 1744). Monoclinic plates. With I in CHCl, it forms C, H, N, I, a black crystaltine pp. DI. PHENYL-DI-METHYL-DI-TRIAZYL

N.NPh>C.C≪NPh.N CMe.N>C.C≪N - CMe [223°]. Formed by CMe.N° N — Une heating the cyanide of phenyl-hydrazine with Ac.O (Bladin, B. 21, 3063). Prisms (from alcohol).—B"H₂Cl₂.—B"H₂PlCl₃ laq. Plates.

DIBHENYL METHYL-BENZAMIDINE

C_oH_o.C(NMe).NPh_o. Formed by heating di-phenyl-benzamidine with MeI at 130° (Bernth-

sen, A. 192, 17). Syrup. -B',H,PtCl_a: yellow pp.
PHENYL p.METHYL-BENZYL KETONE
C.H.,CO.CH.,CaH,Me. [94°]. Formed from ptolyl-acetic chloride, benzene, and AlCl. (Strassmann, B. 22, 1231). Yields an oxim [109°].
PHENYL-METHYL-BENZYL-UREA

NHPh.CO.NH.CH.,C,H,Me. [131°]. from m-methyl-benzylamine and phenyl cyanate (Brömme, B. 21, 2700).

TRI-PHENYL-METHYL-BROMIDE

BROMOSTRI-PHENEL-METHANE

PHENYL-METHYL-CARBAMIC ACID.

Ethyl ether NPhMe.CO.OEt. (241°). Formed from methylandine and Cl.CO.Et (Geb-

Formed from methylamine and Ch. O₂Et (Geshardt, B. 17, 3042). Yellow off.

Chloride, NihMe.COCl. [88°]. (280°).

Got by passing COCl₂ into a solution of methylamiline in benzene (Michler a. Zimmermann, B. 12, 1165). Tables (from alcohol), insol. water Reacts with toluene and aluminium chloride, forming NPhMe.CO.C.,H.Me [70°] while AlCl. and o. m., and p. xylene give rise to the compounds NPhMe.CO.C. H.Me. melting at 78°, 54°, and 74° respectively (Lellmann, B. 24, 2114).

Phenyl ether NPhMe.CO.OC, H., [58°]. Formed from the chloride and KOPh in alcohol (Lellmann a. Benz, A. 24, 2108). Large orystals.

Nitro-phenyl ethers C,H,(NO2)A'. The o., m., and p. nitro-phenyl ethers melt at 110°, 105°, and 70° respectively. They yield on reduction the corresponding amido-phenyl ethers melting at 103°, 94°, and 104° respectively.

p-Tolyl ether C.H.MeA'. [62°].

PHENYL-MEETHYL-SEMI-CARBAZIDE

NPhMe.NH.CO.NH. [138°]. Formed from phenyl-methyl-hydrazine hydrochloride and potassium cyanate (Fischer, A. 190, 164). Orystalline mass m. sol. hot water. Yields a nitrosamine NPhMe.N(NO).CO.NH, [77°].

Phenyl-di-methyl-semi-carbazide NMe., NH. CO.NHPh. [108°]. Formed from trimethylene bromide (Hanssen, B. 20, 781). phenyl-cyanate and di-methyl-hydrazine (Renout, Thick brown liquid.—B"H, SO,. [156°]. Needles.

B. 13, 2172). Pyramids. Decomposed by HCl into the parent substances.

Di-phenyl-di-methyl-carbaside CS(NH.NPhMe)2. [c. 168°]. Got by heating

phenyl-methyl-hydrazine with CS, (Stahel, A. 258, 250).

PHENYL-METHYL-CYANIDE v. Nitrile of PHENYL-ACETIC ACID.

Di-phenyl-methyl-cyanide v. Nitrile of Di-PHENYL-ACETIC ACID.

Di-phenyl-methyl dicyanide C. H. N. i.c. N CMe.N CPh. [110°]. (227° at 15 mm.). Formed from benzonitrile, AcCl, and AlCl, (Krafft a. Hansen, B. 22, 803; 23, 2382). Needles, sol. alcohol and hyroin. Decomposed by diluted H.SQ, into benzoic acid, acetic acid, and NH. Oxidised by alkaline KMnO, to C₃N_xPh_xCO₂H [c. 192°] which on hesting yields C₄N_xPh_xH [75°] (205° at 9 mm.).

Salts.—B'HCl: needles.—B'₂H_xPtCl_s.
DI - PHENYL - METHYLENE - p - AMIDOBENZOIC ACID *CPh_x:N.C₂H_x:CO₂H. [240°]. Formed from Ph_xCCl_x and p-amido-benzoic acid

Formed from Ph₂CCl₂ and p-amido benzoic acid (Hantzsch a. Krafft, B. 24, 3522). Short prisms. PHENYL-METHYLENE-AMINE CH,;NPh

or CH2 NPh CH2? [140°]. Formed by adding aniline to a solution of formic aldehyde (Wellington a. Tollens, B. 18, 3809). Formed also from trioxymethylene and aniline (Kolotoff, J. 1885, 777). Long slender needles. Decomposed by water at 100° into trioxymethylene and aniline.

Phenyl-trimethylene-diamine NIIPh.C₂H_e.NH₂ (282° cor.). S.G. 2 1.0356. A product of the action of Na on an alcoholic solution of phenyl-pyrazole (Balbiano, G. 18, 354; 19, 688; Rend. Accad. Linc. [4] 4, ii. 44). Formed also by boiling phenyl-y-amido-propyl-phthalimide with HClAq (Goddenring, B. 23, 1169). Oil. Sulphide of carbon forms NHHA.C.,H.,NH.CS,SNH.Ph.C.,H.NH., crystallising from alcohol in white plates.—B"2HCl: tufts of needles, v. e. sol. water. When heated it gives off NH₃ and NPh:C₄H₄, which forms (C₄H₁₁,N)₂H₂PtCl₄·-C₄H₁₁N₂Q₄H₂N₂O₅. Greenish crystals, decomposing at 195°.—Succinate

[100°]. Phonyl-di-trimethylene-triamine NPh(CH_CH_CH_NH_)r Formed by heating its phthalyl derivative with HClAq at 240° (Goldenring, B. 23, 1170). — B'''8HCl. —

B,""3H2PtCl. Di-phthalyl derivative NPh(CH₂CH₂CH₂N:C₄H₄O₂)₂ [145°]. Formed from y-bromo-propyl-phthalimide and aniline.

Di-phenyl-methylene-amine CPh₂:NH.

Formed by heating CPh₂Cl₂ with carbamic ether at 130° (Hantzsch a. Krafft, B. 24, 3517). Colourless liquid.-B'HCl: snow-white powder.

Di-phenyl-methylene-diamine CH_(NHPh)2. [49°]. Formed hy mixing a large excess of an aqueous solution of aniline with formic aldehyde solution (Pratesi, G. 14, 351; cf. Lermontoff, B. 7, 1255). Four-sided tables, sol. alcohol. Its hydrochloride is unstable.—B"H₂PtCl₈.

Di-phenyl-trimethylene-diamine CH₂(CH₂NHPh)₂. Formed from aniline and trimethylene bromide (Hanssen, B. 20, 781). Nitrosamine CH2(CH2, NPh.NO)... | DI-PHENYL-METHYLENE-ANILINE

NPh:OPh. [109°]. (above 360°). Formed from CPh.Cl. and aniline (Pauly, A. 187, 199). Yellow tables (from ether). Split up by HClAq into aniline and benzophenone.

TETRA - PHENYL - DI - METHYLENE . TETRAZONE N₂(N:CPh₂)₂. Formed by shaking a bonzene solution of NH₂,N:CPh₂ with HgO (Curtius a. Rauterberg, J. pr. [2] 44, 200). Red needles. Decomposes readily into nitrogen and CPh.:N.N.CPh. Gaseous HBr ferms OPh.HBr

DI-PHENYL-TRIMETHYLENE DI-CARB. AMIC ACID.

Ethyl other OH (CH2. NPh. CO2Et), [560]. Formed from the chloride and NaOEt (Hanssen, B. 20, 783). Crystallines

Ohlowide CH,(CH,NPh.COCI)2. [102°]. Formed from CH2(CH2NPhH), and COCl2 in benzene. Needles.

PHENYL-TRIMETHYLENE DICARBOXYLIC ACID CHPh CH.CO.H. [175°]. Got by saponisying its ether. Prisms, m. sol. water, v. sol. alcohol and ether (Buchner a. Dessauer, B. 21, atonoi and etner (Duchner a. Debauci, S. Z., 2646; 25, 1152). When heated in vacco it yields an anhydride C, IH, O, [184°]. —NaHA": needles. Di-methyl ether Mc, A". [68°]. Ethyl ether Et, A" (257° at 120 mm.). NCHD,

Formed by distilling CO₂Et.CH N.CHPh N.CH.CO₂Et

in vacuo. Thick oil.

Phenyl-trimethylene-tri-carboxylic acid C3H2Ph(CO2H)3. [188°]. Got by saponifying its

whethy lether Me,A" [47°]. (210° at 20 mm.). Formed from NaOMe, methyl malonate, and methyl di-bromo-phenyl-propionate.

PHENYL METHYLENE ETHYL DIKETONE C.H.,CO.CH.,CO.C.H., Propionyl-acetophenone. (277°). S.G. 12 1-081. Formed from acetophenone, propionic ether, and NaOEt (Stylos, B. 20, 2181). Liquid.

DI-PHENYL-METHYLENE-HYDRAZINE CPh.;NNH. [98°]. (c. 227° at 55 mm.). Hydraside of benzophenone. Formed by heating benzophenone (5 g.) with hydrazine hydrate (18 g.) and Mcchol (1 g.) at 150° (Curtius a. Lauterberg, J. pr. [2] 44, 192). Prisms (from alcohol). Reduces alcoholic AgNO, forming a mirror. Reduces Fehling's solution on warming. Boiling dilute H₂SO, splits off hydrazine. Reacts readily with ketones. —B'HCl. [183°].

Acetyl derivative. [107°]. Prisms.
Bensoyl derivative. [116.6°]. Prisms.
Tetra-phenyl-di-methylene-hydrasine

Tetra-paenyl-at-metalytene-nyarasane CPh₂:N.N:CPh₂. Di-phenyl-ketazine. [162°]. Formed by boiling CPh₂:N.N:H₂ with iodine in alcohol. Yellow prisms, v. sl. sol. hot water, sol. alkalis. Decomposed by boiling dilute H₂SO, into benzoplenone and N₂H₄SO.

Phenyl - trimethylene - hydrasine C,H12N, [58°]. Got from phenyl-hydrazine and tri-methylene bromide (Marckwald, C. C. 1888, 1410). Converted by trimethylene bromide on further heating into (PhN_s),(C,H_s), [226°].

DI-PHENYL METHYLENE DIKETONE CH2(CO.C8H3)2. Benzoyl-acetophenone. benzoyl methane. [81°]. (over 200°).

Formation.—1. By boiling di-bensoyl-acetie acid with water (Baeyer a. Perkin, jun.; B. 16, 2134; C. J. 47, 240).—2. By the action of malonyl chloride and AlCl, upon benzene (Auger, A. Ch. [6] 22, 348).

Preparation.—By adding dry sodium ethylate to a mixture of acetophenone and benzoic ether, the reaction taking place with spontaneous heating. The crystalline mass is extracted with cold water, finally with dilute NaOH, and from the solution of the sodium salt the ketone is precipitated by means of CO₂; the yield is 0.50 p.c. of the acetophenone used (Claisen, B. 20, 655).

Properties.—Trimetric plates, v. sol. alkalis. C. Yields products of substitution by treatment with NaOEt and alkyl iodides.

Reactions .- 1. Bromine (1 mol.) in CHCl. forms Bz,CHBr [93°], which on heating with HOAc and KOAc yields Bz,CHOAc [94°], which on further bromination gives Bz, CIPr.OAc [102°] which is split up by heat into Ph.CO.CO.CO.Ph and AcBr.—2. Excess of bromine (2 mols.) in CHCl, forms Bz,CBr, [95°] whence HOAc and KOAc form di-phenyl triketone. - 3. Amyl nitrite and alcoholic HCl give Bz,C:NOH [146°], converted by nitrous acid into the triketone (Keufville a. Pechmann, B. 22, 852; 23, 3376).—4.
Phenyl-hydrazine forms tri-phenyl-pyrazole (Japp a. Klingemann, B. 22, 2886)

PHENYL METHYLENE METHYL DI-KETONE v. BENZOYL-ACETONE.

PHENYL METHYLENE METHYL SUL-PHONE-KETONE C.H., SO., CH., CO.CH., Acetonyl phenyl sulphone. [57]. Formed by oxidising PhS.CH Ac with KMnO, (Delisle, A. 260, Formed also from chloro-acetone and 262). Formed also from chloro-acetone and C₂H₂SO₂Na (Otto, B. 19, 1642; 21, 1871; 23, 756; J. pr. [2] 36, 402). Plates, sol. water and alcohol. Yields a phenyl-hydrazide [129°] and an oxim [148°]. Ammonia yields the compound NH:CMe.CH_SO_Ph [111°]. Phenyl mercaptan yields (PhS)₂CMe.CH₂SO₂Ph [104]. Potash yields (PhS)₂CMe.CH₂SO₂Ph [104]. Potash yields phenyl methyl sulphone. Br forms a hromo-derivative [96°] and a di-bromo-derivative bromo-derivative [96°] and a di-bromo-derivative

PHTHALIMIDINE C₁₃H₁₁NO s.e. O₄H₄CO NPh. [100°]. Formed by heating acetophenone o-carboxylic anilide at 230° (Mertens, B. 19, 2372). Prisms, v. sol. alcohol. An isomeride [265°], got by treating acctophenone o-carboxylic anilide with conc. H₂SO₂, is sl. sol. alcohol.

DI-PHENYL METHYLENE DISULPHONE CH_(SO,Ph). [119°]. Formed by oxidation of CH_(SPh), which is got by boiling CH,Cl, with NaSPh (Fromm, A. 253, 161). Needles, v. al. sol. boiling water.

DI. PHENYL. DI. METHYLENE DI. SUL. DI. PHENYI. DI. METHYLENE DI. 8UL. PHONE KETONE C., II, S.O., i.a. CO(CH.SO.Ph)., [150°]. Got from CHBr. CO.CH. SO.Ph and C.H., SO.Pha. Got also from CO(CHCl.), and O.H., SO.Pha (Otto, B. 19, 1542; 22, 1967). Small crystals (from HOAc). Yields an oxim [187°] and a phenyl-hydrazide [171°]. PhSH forms (PhS). C(CH. SO.Ph)., [191°].

DI. PHENYI. METHYLENE DI. THIO-GLY. COLLIC ACID CPP., (S.CH., CO.H)., [176°].

COLLIC ACID CPh.(S.CH.,CO.H). [176°]. Formed by heating benzophenone with thioglycollic acid and ZnCl. (Bongarts, S. 21, 488). Needles (from dilute HOAc), insol. hot water.

PHENYL-TRIMETHYLENE-THIO-UREA

OS NH .CH. CH. [215°]. Formed by boiling NHPh.C₂H_a.NH.CS.8NPhH_r-C₂H_a.NH_r with water (Goldenring, B. 23, 1172). White prisms. Di-phenyl-methylened-thio-urea C₁₁H₁₂N₂S

i.e. S

C(NPh)

NPh. [68°]. Formed from di-phenyl-thio-ures and CH,I. (Foerster, B. 21, 1872). Thin needles, v. c. sol. alcohol.— B',H,PtCl. Crystalline pp.
Di-phenyl-trimethylene-\psi-thio-urea

B<C(NPh)-NPh CH,CH,CH, . [123°]. Formed from diphenyl-thio-urea and trimethylene bromide (F.). Di-phenyl-trimethylene-di-thio-di-urea

CH,(CH,NH.CS.NPhH)2. Formed from phenylthiocarbimide. trimethylene-diamine, alcohol (Lellmann a. Würthner, A. 228, 236). Plates [115°] or nodules [60°], v. sol. alcohol.

Tri-phenyl-trimethylene-di-thio-di-urea NHPh.CS.NH.CH, CH, CH, NPh.CS.NHPh. [145°]. Formed by heating phenyl-trimethylene-diamine (1 g.7 with phenyl-thiocarbimide (2 g.) and alcohol (15 c.c.) (G.). Slender needles.

DPPHENYL-METHYLENE-p-TOLUIDINE C.H.MeN:CPh. (above 360°). Formed from Ph.CCl, and p-toluidine (Pauly, A. 187, 214). Oil, split up by acids into p-toluidine and benzophenone.

PHENYL-TRIMETHYLENE-UREA

 $CO < NPh.CH_2 > CH_2$. [215°]. Formed by heating phenyl-amido-propyl-urea at 240° (Goldenring. Yellowish plates, sl. sol. hot Aq. B. 23, 1173). Di-phenyl-trimethylene-urea

CO NPh.CH₂ CII₂. [156°]. Formed, together with CH₂(CH₂, NPh. COCl), [102°], from di-phenyl-trimethylene-diamine and COCl, in benzene (Hanssen, B. 20, 782). Plates.

Tetra-phenyl-trimethylene-di-urea
CH₂(CH₂,NPh.CO.NHPh). [153°]. Form
from CH₂(CH₂,NPh.COCI), and aniline (H.).
PHENYL TRIMETHYLENYL KETONE Formed

C.H., CO.CH C.H. or C.H.; CPh O. Benzoyl-trimethylene. Phenyl-furfurane dihydride (239°) at 720 mm. V.D. 5-27 (cafe. 5-04). Formed by heating its carboxylic acid at 200° (Porlkin, jun., B. 16, 2140; C. J. 47, 842). Oil with aromatic odour. Alcoholic hydroxylamine forms the oxim in the cold, but by heating the ketone with alcoholic hydroxylamine hydrochloride at 135' there are formed C₂₃H₁₇N₃O₃ (a red amorphous powder) and C₃₆H₂₈N₃O₂ (a black brittle mass which forms deep-blue B"H₂Cl₂ and B"H.PtCl.).

[87°]. Colourless plates.

TRIMETHYLENYL KETONE CARBOXYLIC ACID CH₂>CBz.CO₂H. [149°], Formed by saponification of the ether. Monoelinic prisms; a:b:c=2.380:1:2.132; $\beta=83^{\circ}4'$. M. sol. ether, \bullet sl. sol. water. Decomposed by water at 110° into phenyl oxypropyl ketone CH_OH_CH_CH_Bz which when extracted with ether and dried over K.CO, is found to have split off water, the resulting anhydride being possibly phesyl trimethylenyl ketone (Perkin, C. J. 31, 837). - AgA': flocculent pp.

Ethyl other Et.A". (282°) at 720 mm. Formed from benzoyl-acetic ether, ethylene bromide, and NaOEt (Perkin, B. 16, 2188; C. J. 47, 841). Oil.

Reference.-NITBO - PHENYL - TRIMETHYLENYL

METONE CARROXYLIC ACID.

PHENYL-METHYL-ETHYLENE-DIAMINE NH.CH.CH.NPhMe. (255°). Formed by the action of HCl on C.H.C.O...N.C.H.NPhMe (Newman, B. 24, 2200). Liquid, v. sol. water and alcohol.—B'C.H.(NO.),OH. [173°], Needles-

Di phonyl di-methyl-ethylene-diamine C,H,(NPhMe),. The methylo-bromide B"Me,Br, got by heating di-methyl-aniline with ethylene bromide (Hijbner, A. 224, 846), crystallies in deliquescent prisms and fields B"Me₁(OH), B"Me₂Cl₂, B"Me₂PtCl₄, B"Me₂Cl₃HgCl₃ [174°], B"Me₄L₅, B"Me₂Cr₂O₃, and B"Me₂(C₄L₃N₂O₃), [1240

PHENYL-METHYL-ETHYLENE Its carb-TONE v. Acerophenone-acerone. oxylic acid is described as ACETOPHENONZ-ACETO-

ACETIC ACID.

DI - PHENYL - DI - METHYL - v - ETHYLENE-DI-PYRROLE-DI-CARBOXYLIC ACID

CO, HC:CMe N.C, H, N CMe:C.CO, H HC:CPh N.C, H, N CPh:CH [1817]. Obtained by saponification of its ether, which is formed by mixing acetophenone-aceto-acetic cther with ethylene-diamine (Paal a. Schneider, B. 19, 3158). Crystalline solid. Sl. sol. alcohol, acetic acid, and conc. HCl, insol. other ordinary solvents. On heating above 180° it evolves CO, giving the free base.

Di-ethyl-ether Et,A": [1979]; plates; distillable under ordinary pressure; sol. alcohol, benzene, chloroform, and acetic acid, insol.

water and petroleum-spirit.

PHENYL-METHYL-ETHYL-080TRIAZOLE $NPh < N:CMe \atop N:CEt$. (270°). Formed by condensation of the oxim-phenyl-hydrazide of CH, CO.CO.C, H, (Pechmann, A. 262, 312). Needles. Yields a di-nitro-derivative [113°]. Oxidised by alkaline KMnO, to phenyl-methyltriazole carboxylic acid.

PHENYL - METHYL - ETHYL - PYRAZOLE $NPh < _{CEt;CMe}^{N=CH}$. (283°). S.G. 15 1.0476. Got by the action of phenyl-hydrazine C₂H₃.CO.CHMe.CHO (Claisen, B. 22, 3276).

Reference .- OXY - PHENYL - METHYL - ETHYL -

PYRAZOLE. TRI - PHENYL - METHYL - ETHYL - THIO-BIURET C.S., N., Ph., MeEt. [157°]. Formed from di-phenyl-ethyl-thio-urea and (Billeter a. Strohl, B. 21, 108). An isomeride [156°] is formed from di-phenyl-methyl-urea and NPhEt.CSCl. Both bodies crystallise in needles, sl. sol. alcohol.

PHENYL - METHYL - ETHYL - THIO - UREA CS(NHMe).NPhEt. Got from methyl thiocarbimide and ethvl-aniline (Gebhardt, B. 17, 8037). Crystalline solid.

Di-phenyl-methyl-ethyl-thio-urca CS(NPhMe).NPhEt. [49.50]. Formed from methyl-aniline and NPhEt.COCl (Billeter, B. 20, 2). Monoclinic crystals.
PHENYL-METHYL-FURFURANE C₁₁H₁₀O, 1632).

i.e. CH:CMe Or Oxyphenyl-pentamethenyl

hydride CH_aCH_aCO. [40°]. (c. 238°). Formed by heating phenythronic acid, and prepared by warming acetophenone-acetone with fuming HClAq, the yield being 65 p.c. (Paal, B. 17, 2769; Fittig, B. 21, 2134; A. 250, 222). Needles or prisms, insol. water and alkalis, volatile with steam. Br forms C₁₁H_aBr₃O [210°]. Phenylhydrazine forms a compound [165°-175°], crystallising from alcohol in golden panagles.

Tet†ahydride CHr. CHPh. O. (c. 230°).

Formed by reduction in alcoholic solution by
Na. Oil, miscible with alcohol and ether.

Na. Oil, miscible with account and central PHENYL METHYL-FURFURANE CARBOXYLIO ACID O. Ho. o. CO. H.C.CMe. HC.CPh. O. HC.C

Phenyl-methyl-furfurane carboxylic acid C₁₂H₁₀O₂ i.e. CO,H.C=CPh>O or

CO₂H.CH.CPh CH. Phenuvic acid. [145°].

Formed by heating phenythronic acid (Fittig, B. 21, 2134). Its ether is obtained from chloro-acetone and sodium benzoyl-acetic ether (Colefax, C. J. 59, 190). Long silky needles.—Cah', 2aq.—Bah', aq.—Agh': amorphous pp.

Phenyl-methyl-furfurane dicarboxylic acid

C₁₁H₁₀O₄ i.e. CO₂H.CH. CPh CC.CO₂H or

CO₂H.C:CMe O. Phenythronic acid [193°].

Formed by saponifying its ether with boiling baryta (Fittig, 4.250, 216). Silky needles, m. sol. hot water, v. sol. alcohol.—CaA" Saq. S. 5.—BaA" aq.—Ag₂A": crystalline pp.

Mono-ethyl ether EtHA". [112°].

Mono-ethyl ether EthA". [112].
Formed by the action of Ac₀O on a mixture of sodium succinate and benzoyl-acetic ether.—
Ca(EtA'); crystalline nodules (from alcohol).—
Ba(EtA''),—AgEtA''; white amorphous pp.
Diethyl ether EtA''. [44:52].

PHENYL-METHYL-GLYCOCOLL v. PHENYL-

PHENYL-METHYL-GLYOXALINE C₁₀H₁₀N₂
i.e. CMe≪N-C;H. [159°]. Formed by heating phenyl-methyl-oxazole with alcoholic NH, at 230° (Lewy, B. 22, 2195). Needles, v. sl. sol. alcohol. Salts.—B'HCl. [242°]. Needles.—B'₂H₂PtCl₂ 2aq. [212°]. Yellow prisms.
Phenyl-di-methyl-glyoxaline C₁₁H₁₂N₂ i.e.

Phenyl-di-methyl-glyoxaline $C_{11}H_{12}N_2$ i.e. $CPh \stackrel{N}{\sim} NHCMe$ [230°-234°]. Formed by heating diacetyl with benzoic aldehyde and alcoholic NH, (Wadsworth, C. J. 57, 8). Needles (from benzene).— $B'_2H_2PtCl_4$; needles. Di-phenyl-methyl-glyoxaline

OMe N—(Ph. [235°]. Formed by the action of aldehyde and NH, on benzil (Japp, C. J. 49, 466; 51, 557; C. J. Proc. 3, 34). Trimetric crystals; abic=1:207:1:1:920. Crystallises with diphenylglyoxaline (1 mol.), the compound melting at 218°.

PHENYL-METHYL-HYDANTOIC ACID C₄H,NH.CO.NH.CH(CH₃).CO₂H [170°]. Formed by the combination of phenyl cyanate with alanine and boiling the product with alcoholic KOH (Kühn, B. 17, 2884). Glistening scales.

PHENYL-METHYL-HYDANTOIN

CHPh CO. NMe [162°]. Formed from phenylhydantoin, KOMe, and MeI (Pinner, B. 21, 2325). Needles, sl. sol. cold alcohol.

*s-PHENYL-METHYL-HYDRAZINE

Och-NH.NHMe. Hydraso phenyl methyl.

Got by saponification of its dibenzoyl derivative, which is formed by heating NPhBz.NBzH with NaOMe and MeI (Intel, B. 18, 1740). Obtained also by the action of alkalis on nitroso-antipyrin (Knorr, A. 238, 137). Oil, oxidised by HgO to PhN:NMe. Reduces Fehling's solution and ammoniacal AgNO, in the cold.—B'₂H₂SO, [180°].—Oxalate: white needles.

Di-benzoyl derivative PhNBz.NMeBa. [145°]. Crystals, v. sol. alcohol and ether.

u-Phenyl-methyl-hydrazine NPhMe.NH₄. (227° i.V.) at 745 mm. Formed by converting methyl-aniline into phenyl-methyl-nitrosamine, and reducing this body (5 pts.) by zinc-dust. (20 pts.), HOAc (10 pts.), and water (35 pts.) at 0° (E. Fischer, A. 190, 152; 236, 199).

Properties.—Colourless oil, turning brown in air; m. sol. hot water, miscible with alcohol.

Reactions.—1. Nitrons acidyields NPIMe.NO, water, and N.O.—2. Diazobenzene nitrate solution forms PhN, and methyl-aniline nitrate.—3. HgO added to its solution in chloroform produces NPIMe.N.N.NPIMe [137°].—4. Reacts with aldehydes and ketones in the same way as phenyl-hydrazine, forming products of condensation; thus benzoic aldehyde forms NPIMe.N:CHIPh [104°] (Ebers, A. 227, 340), acctophenous forms NPIMe.N:CMePh [50°], acctone forms C₁H₁,N₂ (216°) (Degen, A. 236, 152), propionic aldehyde yields O₁,H₁,N₂ (198° at 170 mm), glucous yields C₂,H₁,O₂,N.NPIMe[171°], while benzil yields Ph.CO.CJPh.N.PIMe [56° and N.PhMe:CPh.CPh:N.PhMe[180°] (Kohlrausch, A. 253, 16; Fischer, B. 22, 87).—5. CS₂ at 100° forms CS(NH.NPIMO)₂ [c. 168°] (Stahel, A. 258, 250).—6. Nitroso-aniline forms C₁,H₁,N₂ O [151°], while nitroso-dimethylaniline gives C₁,H₁,N₂ O [141°] (O. Fischer, B. 22, 622).—7. With PhN:SO it forms PhNMe.N:SO [77°] crystallising from alcohol in yellow needles (Michaelis, A. 270, 120).

Salt.—B'.H.SO.: plates, v.e. sol. water. Actyl derivative NPhMe.NHAc. [93°]. Prisms, m. sol. hot water. Converted by Na and McI into NPhMe.NMcAc [68°], which is not decomposed by alkalis, but gives methylaniline when boiled with HOlAq.

Benzoyl derivative NPhMe.NHBz, [153°]. Formed by heating NPhH.NHBz with NaOMe and MeI. Needles (Tafel, B. 18, 1743).

NaoMe and Mel. Needles (Tafel, B. 18, 1743). Sulphonic acid SOJI C.H.NMe.NH.Formed by heating with fuming H.SO. (Pfülf, A. 239, 219). Plates.—NaA'aq: slender needles.

PHENYL-METHYL-IMESATIN v. Anilide of Methyl Isatin.

DI - PHENYL METHYLIMIDO - DI - ETHYL DISULPHONE NMe(C₂H, SO₂Ph)₂. Formed by heating NH(C₂H, SO₂Ph) with alcehol and MeI at 115° (Otto, J. pr. [2] 30, 335).—B'HCl²221°].

PHENYL-METHYL-INDOLE C,H,N ... C.H. CH CPh. [101°]. Formed by heating the phenyl-hydrazide of acetophenone with ZnCl, at 130° (Fischer, B. 19, 1565; Degen, A. 236, 155). Formed also by heating CH, Bz. NMePh with ZnCl, at 180° (Staedel, B. 21, 2196; Culmann, B. 21, 2596), and by heating the isomeric C.H. CPh OH with ZnCl₂ at 220° (Ince, A. 253, 40). Needles (from alcohol). Colours pinewood, moistened with HCl, dark-red.

C_•H_•<^{CAc}_{NMe}>CPh. Acetyl derivative [136°]. Formed by heating CH2Ac.CPh:N.NMcPh with ZnCl, at 150°. Needles (from dilute HOAc). C,H,<CPh NMeSCH. Phenyl-methyl-indole

[65°]. Formed from phenyl-acetic aldehyde and phenyl-methyl-hydrazine (Ince, A. 253, 38). Crystals, v. sol. benzene. Colours acidified pine-Crystals, v. soi. benzene.a. conours wood reddish-violet.—B'C₆H₄N₇O₇, [90].

Phenylemethyl-indole C₆H₄(CNH) CMe.

[60°]. Formed by heating the phenyl-hydrazide of benzyl methyl ketone with ZnCl₂ (Trenkler, A. 248, 110). Prisms (from ligroin).—Picrate: [142°]; v. sol. benzene.
PHENYL METHYL KETONE v. Aceto-

PHENONE.

Phenyl methyl diketone C₆H₃.CO.CO.CH₅. Acetyl-benzoyl. (217°). S.G. ¹⁴ 1·1041. S. ·26 at 20°. Formed by distilling its oxim Bz.C(NOH)Mo with dilute H₂SO₄ (Von Pechmann, B. 21, 2119; 22, 2129) or with isoamyl nitrite (Manasse, B. 21, 2177). Heavy oil, volatile with steam.

Oxim C.H. CO.C(NOH).CH. Nitroso-pro-piophenone. [114°]. Formed by the action of isoamyl nitrite and HCl or NaOEt on the ketone (Claimon a. Manasse, B. 22, 529). Prepared by the action of nitrous acid on hearzyl-propionic ether (1 mol.) and KOHAq (3 mols.) (P.; Gude-man, B. 22, 562). Needles (from hot water), forming a deep-yellow solution in albalis. SnCl. and HCl yield hydroxylamine and phenyl methyl diketone. Reduced by sedium-amalgam to a base which crystallises from alcohol in needles [108°].

Di-oxim Ph.C(NOH).C(NOH).Me. [236°]. Formed from the mono-oxim and hydroxylamine hydrochloride. Needles (from dilute alcohol).

Phenyl hydrazide C15H14N2O. [145°] Di-phenyl-di-hydrazide CMe(N₂HPh).CPh(N₂HPh). [1 [105°]. Yellow crystals, v. sol. ether.

Oxim-phenyl-hydrazide

CPh(N2HPĥ).CMe:NOH. [202°]. White needles. Phenyl methyl triketone. Mono-oxim C.H.,CO.C(NOH),CO.CH. [124°]. Formed by the action of nitrous acid on phenyl methylene methyl diketone (Ceresole, B. 17, 814). Needles,

v. sol. benzene, sol. alkalis.

Di-oxim C.H., C(NOH). C(NOH). CO.CH. [178°]. Formed by neating the mono- oxim with hydroxylamine hydrochloride. Needles, insol. cold water, sol. alkalis.

PHENYL METHYL-KETONE CARBOXYLIC ACID v. BENZOYL-ACETIC ACID and ACETOPHENONE CARBOXYLIC ACID.

PHENTL-METHYL-MALONIC ACID v. Ben-EXE-MALONIC ACID.

Tri-phenyl-methyl-malonic ether Formed CPh.CH(CO,Et)2 [133·5°]. CPh,Br and sodium malonic ether (Henderson, B. 20, 1014; C. J. Proc. 2, 251). Needles (from alcohol). Yields tri-phenyl-propionic acid when heated with alcoholic potash.-NaA'aq: needles. -BaA', aq. -AgA': minute white crystals.

PHENYL - DI - METHYL - NAPHTHALENE TETRAHYDRIDE v. METHBONOL.

BHENYL - METHYL - (β) -NAPHTHOTRIAZ-INE DIHYPRIDE C18H13N3 i.e. C18H4 N.NPh

Formed by adding aldehyde to a mixture of benzene-azo-(β)-naphthylamine and alcohol (Goldschmidt a. Poltzer, B. 24, 1004). Plates, v. sol. hot alcohol. Ph. 16. [252°].—B'_H_PtCl. Yellow needles.-B'MeI. [244°].-B'2Me2PtCl. [260°]. Yellow needles.

PHENYL - METHYL-(6)-NAPHTHYL-THIO-URDA C, H, N.Si.e. NPhMe.CS.NHC, H, [127°]. Formed from (3)-naphthyl thiocarbimide and methyl-aniline (Gebhardt, B. 17, 2091). Yellow needles.

PHENYL - METHYL - NITROSAMINE Nixosamine of Methyl-aniline, vol. iii. p. 285. PHENYL-METHYL-OSOTRIAZOLE

 $NPh <_{N:CM_0}^{N:CH}$ $(242^{\circ}).$ S.G. ¥. 1·1071. Formed by oxidising the diphenyl-hydrazide of pyruvic aldehyde and warming the resulting NPh.N:CMe. Formed also by the action of NaOH on CH, C(N, HPh). CH: NOAc (Pechmann, B. 21, 2751; A. 262, 279). Oil. Yields a trinitro-derivative [138°], and a sulphonic acid, of which the Na salt crystallises in hexagonal plates.

Phenyl-di-methyl-osotriazole

NPh N:CMe [35°]. (354°). Formed by heating the phenyl-hydrazide-oxim of diacetyl with Ac.O (P.). Crystalline, insol. water, sol. conc. HClAq, but reppd. by water. Yields a dinitro- derivative [1390] and a tri-nitro- derivative

PHENYL-METHYL-080TRIAZOLE CARB-NPh<N:C.CO.H. ACID Formed by oxidising phenyl-di-methyl-oso-

Needles, v. sl. sol. water. AgA': white pp.
PHENYL-METHYL-OXAMIDE C,H,s,N,2O,2 i.c. NHPh.C.O., NHMe. [180°]. Formed from NHMe.C.O., OEt and aniline (Wallach, A. 184, Needles.

PHENYL-METHYL-OXANTHRANOL

C21H18O2 i.e. C6H2Me CO CPh(OH) C6H4. [195]. Formed by oxidation of phenyl-methyl-anthranol with K₂Cr₂O₇ and HOAc (Hemilian, B. 16, 2366). Trimetric tables, v. sol. hot alcohol, insol. alkalis. Conc. H.SO, forms a purple solution.

Isomeride $\left[1:\frac{4}{5}\right]C_{\bullet}H_{\bullet}Me < \frac{CPh(OH)}{CO} > C_{\bullet}H_{\bullet}$ [213°]. Formed by oxidising di-phenyl-tolyl-methane o-carboxylic acid with K₂CrO₄ and conc. H.SO. (Hemilian, B. 19, 3064). Prisms, insol. alkalis. Reduced by zinc-dust to a phonyi-methyl-anthranol.

PHENTL-METHYL-OXAZOLE C., H, NO i.e. OCPh:CH [45°]. (242°). Formed by heating acetamide with bromo-acetophenone at 125° (Blümlein, B. 17, 2579; Lewy, B. 20, 2576; 21, 924). Needles (from sloohol). Yields benzoie acid on oxidation. Na and alcohol form an oily tetrahydride $C_{10}H_{13}NO$ (251°), which yields crystalline $C_{10}H_{13}NO$ (140°). HI and P give oily $C_{10}H_{18}$ (c. 275°). Conc. nitric acid forms $C_{10}H_{4}(NO_{2})NO$ (157°), which may be reduced to $C_{10}H_{4}(NH_{2})NO$ (115°). Hydroxylamine, phenylatic states of the state of the states hydrazine, and hot zinc-dust have no action. B'HCl.—B',H,PtCl, 2aq.—B'C,H,N,O, [134°].

Phenyl-methyl-omzole O CPh: CM: (240°).

Formed by boiling benzamids with chloro-acetone (Lewy, B. 21, 2193). Oil with fruity odour.—B₂H₂PtCl₂ 2aq. [170]. Yellow needles. Dihydride O<CPh=N₂ (244°). F6-med

by the action of KOH on bromo-propyl-benzamide in hot aqueous or alcoholic solution, the product being distilled with steam (Gabriel a. Heymann, B. 23, 2499). Liquid. Part'y converted, by evaporation with excess of HClAq (or HBrAq), into \$-chloro- (or bromo-) propyl-benz-amide [78°] (or [73°]). Boiling with an equiva-lent of HClAq yields \$-amido-propyl benzoate. B',H,PtCl,—B',H,Cr,O,—B'C,H,N,O,(167°). PHENYL-TRI-METHYL-PHENYL-CARBI.

NOL C, H18O i.e. CHPh(OH).C, H2Me, Phenylmesitylene carbinol. [34°]. (330°). Formed by reducing benzoyl-mesitylene with sodium-amalgam (Louise, Bl. [2] 45, 231; A. Ch. [6] 6,

209). Prisms. Boiling diluted H₂SO₄ (1:1) converts it into (C₁₀H₁)₁₀O [137°].

Ethyl ether O₁₀H₁EtO. [32°]. Prisms.

Acetyl derivative O₁₀H₁A,AcO. [52°].

Benzoyl derivative. [94°]. Crystals.

Benzoyt derivative. [947]. Crystals.
DIPHENYL TRIMETHYLPHENYLENE DIRETONE (C.H., CO), C.H.Me. [1177]. Formed
by heating C.H., CO.C.H.Me. with BzCl and
AlCl. (Louise, C. R. 98, 151; A. Ch. [6] 6, 236). Prisms, sol. alcohol and ether.

Di-phenyl tetramethylphenylene diketone C.Me.(CO.C.H.). [270°]. A product of the action of BzCl and AlCl, on durene (Friedel a. Crafts, C. R. 88, 880). Minute prisms, sol. benzene, almost insol. boiling alcohol. PHENYL METHYLPHENYL KETONE v.

PHENYL TOLYL RETONE.

Phenyl dimethylphenyl ketone v. PHENYL XYLYL RETONE.

Phenyl trimethylphenyl ketone

C₂T₄,CO₂CO₄H,Me₃[1:2:4:6]. Benzoyl-mesitylene, Phenyl mesityl ketone. [35°]. (319°). V.D. 8·18. Formed from BzOl, mesitylene, CS₂, and AlCl. (Elbs, J. pr. [2] 35, 485; cf. Louise, A. Ch. [6] 6, 200; C. R. 96, 499; Claus, B. 19, 2879). Prisms (from alcohol), sol. acetone and ligroin.

Does not react with hydroxylamine (Smith, B. 84, 4052).

Reactions .- 1. Conc. H2SO, or H2S2O, 100° gives benkoic acid and mesitylene sulphonic acid.—2. Conc. H,SO, at 50° forms phenyl-mesityl-ketone sulphonic acid C_{1s}H_{1s}O.SO_sH.—8. A mixture of fuming HNO_s and H,S₂O, forms two trinitro-derivatives [188°] and [145°]. 4. HNO, (S.G. 1.1) at 200° forms benzoyl-uvitic or phenyl-tolyl-ketone dicarboxylic acid.--5.

Potash-fusion gives mesitylene and KOBs .-- 6. HI reduces it to benzyl-mesitylene.-7. Sodiumamalgam yields the carbinol .- 8. Chromic acid oxidises it to C.H.CO.C.H.Me.CO.H.

Phenyl tetra-methyl-phenyl ketone C₄H, CO.C, HMe, [119⁴]. (343°) Formed by heating durene with BzCl and AlCl, at 120° (Friedel, Crafts, a. Ador, C. R. 88, 980). Crystalline. Decomposed by potach-fusion into benzoic acid and durene. Reduced by HIAq

and P at 240° to CH.Ph.C.HMe, [60.5°], (310°).

Romeride C.H., CO.C.HMe, [63°], (300°).

Formed from BzCl and isodurene (got from a toluene, McCl, and AlCl₂). Crystals (Essner a.

Gossin, Bl. [2] 42, 171) PHENYL TRIMETHYLPHENYL KETONE o-CARBOXYLIC ACID C.H.Me., CO.C.H., CO.H. [212°]. Formed from phthalic anhydride, mesitylene, and AlCl. (F. Meyer ac Gresly, B. 15, 639; A. 234, 234). Needles (from alcohol). Phenyl tetramethylehenyl ketone carboxylic

acid v. Tetra-methyl-benzoyl-benzoic acid.

PHENYL - TRIMETHYLPHENYL - THIO-UREA NHPh.CS.NHC, H.Me,. [193°]. Formed by heating methyl-thiocarbimide with an alcoholic solution of aniline (Eisenberg, B. 15, 1014). PHENYL-DI-METHYL-PHOSPHINE

PMe₂Ph. (192° cor.). S.G. ¹¹ 977. Formed from POl₂Ph and ZnMe₂ in benzene (Michaelis, A. 181, 359). Liquid, oxidised by air. Combines with CS₂ forming PMe₂PhCS₂ crystallising in red plates and yielding B'2H2PtCl4 (Czimatis, B. 15, 2017).

Salts.—B'HCl: crystalline, sl. sol. ether, v. e. sol. alcohol.—B'2HCl. Liquid.—B'2HLPtCl.

Methylo-iodide PMe, PhI. [205°]. Bromo-ethylo-bromide

PMe₂Ph(O₂H₄Br)Br. [173°]. Formed from PMe₂Ph and C₂H₄Br₂ (Gleichmann, B. 15, 199). PMe, In and c. II. pr. (criecumann, B. 10, 1891, Vicids (B'(C,H,Br)Br), PtCl, and the unstable B'C,H,Br. An alcohole solution of phenyl-di-methyl-phosphine forms (PMe,Ph),C,H,Br. [above 300], S. (alcohol) 2 at 21°, which gives unstable (FMe,Ph),C,H,Br. [171°].

Di-phenyl-methyl-phosphine PMePh. (284°).

S.C. 12 1°08. Formed from PCIPh, and ZnMe, Wichesies, Link 4 207 210). Liquid Vicids

S.G. 12 108. Formed from PGIFA, and ZnMo, (Michaelis a. Link, A. 207, 210). Liquid. Yields PMe,Ph.J. [241°], 4PMe,Ph.J.PtCl, [218°], and PMcPh.O [112°] (Michaelis a. La Coste, B. 18, 2116; A. 229, 316).

PHENYL-DI-METHYL-PHOSPHINE p-CARBOXYLIC ACID C₈H₄(CO,H).PMe,The methylo-chloride C₈H₄(CO,H).PMe,Cl, formed the cidelic of the methylo-chloride to a cidelic of the cidelic of the methylo-chloride to a cidelic of the cidelic of th by oxidation of the methylo-chloride of p-tolyldi-methyl-phosphine, crystallises in prisms di-metalyi-phosphine, crystallises in prisms (Michaelis, B. 15, 2018). It yields the compounds B'Me,PtCl₂, C,H₁(CO₂H).PMe₃OH 2aq, and C₄H₄(CO₂H).PMe₃SO₄H.

Oxide C₄H₄(CO₂H).POMe₂. [243°]. Formed

by oxidation of the ethyleno-bromide of tolyl-di-methyl-phosphine. Colourless prisms.

PHENYL METHYL PROPYLENE DI-

PHENYL MEHILL FROM LINES EXECUTED TO SERVICE CO.CH. (265°-270°). Formed from benzoyl-acetone, N., and Etl (Claisen a. Lowman, B. 21, 1152). Liquid. PHENYL - METHYL-PROPYLENE-y-THIO-

UREA CHMe.S CNPhMe. (c. 800°). Formed by heating methyl-aniline with allyl thiocarb-imide and HClAq at 100° (Prager, B, 22, 2096), —B',H,PtCl, [184°].—B'C,H,N,O, [125°].

TRI.PHENYL-METHYL.PROPYL-DI.THIO-BIURET C'S, N, Ph, MePr. [110°]. Formed from NPhMetCSCl and di-phenyl-propyl-thio-urea Rilleter a. Strohl, B. 21, 109). Small yellow pyramids. An isomeride [111°] is formed from NPhPr.CSCl and di-phenyl-methyl-thio-urea.

DI - PHENYL - METHYL - PROPYL - THIO-URBA NPhMe.CS.NPhPr. [56°]. Formed from CSCl., propyl-apiline, and MeCl or from CSCl., methyl-aniline, and PrCl (Billeter a. Strohl, B. 21, 103). Colourless prisms.

DI-PHENYL-DI-METHYL-PYRAZINE . $CMe \leqslant_{CPh,N}^{N:CPh} \geqslant_{CMe.} [124^{\circ}].$ Formed when phenyl amido-ethyl ketone is allowed to stand with NH, Aq (Schmidt, B. 22, 3253).—B'HCl: needles.—B',H,PtCl.

Di-phehyl methyl pyrazine-dihydride

N CPh.CPh N. [112°]. Formed from benzil and propylene-diamine (Strache, B. 21, 2363). Needles, v. sol. benzene; m. sol. alcohol.

Di-phenyl-tetra-methyl-pyrazine dihydride

C.,H.,N. i.e. NPh CMe:CMe NPh. (281°). Formed by heating \$\beta\$-bromo-\$-acetylpropionic acid (1 pt.) with aniline (3 pts.) at 95°; the yield being 70 p.c. of the theoretical amount (Wolff, B. 20, 429). Satiny plates, v. sol. ether and conc. HClAq.

References .- NITRO- and OXY-DI-PHENYL-METHYL-PYRAZINE.

PHENYL-METHYL-PYRAZOLE

NPh<\(\frac{N=CMe}{CH:CH}\). [37°]. (255°). S.G. 12 1 085.

Formation .- 1. By heating oxy-phenylmethyl-pyrazole NPh N=CMe with zinc-dust (Knorr, A. 238, 199).—2. From acetoacetic aldehyde, phenyl-hydrazine, and HOAs (Claisen, B. 21, 1147; 24, 1888).—3. By heating its carboxylic acid at 210° (Ach A. 253, 55).—4. From

oxy-phenyl-methyl-pyrazole dihydride and P₂S₂ (Knorr a. Duden, B₂S₂, 766).

Properties.—Needles, v. sol. alcohol and ether; volatile with steam. Oxidised by KMnO₄ to phenyl-pyrazole carboxylic acids [146°].

Salt .- B'H.PtCl : orange needles.

NPh CH2 CH2 [759]. Dihudrida Formed by reducing the base in alcoholic solution with Na. Flat needles, m. sol. alcohol.

Phenyl-methyl-pyrazole NPh CMe;CH (262°). Formed by distilling its dicarboxylic acid (Knorr a. Laubmann, B. 22, 178). Got also from acetone, oxalic acid, and phenylhydrazine (Claisen a. Roosen, B. 24, 1890). Yields phenyl-pyrazole carboxylic acid [183°] on oxidation by KMnO₄.—B'₂H_PtCl₂ 2aq. [147°].

Phenyl-di-methyl-pyrazole

NPh N= CM (273° i.V.). Formed by heating its carboxylic acid (Knorr, B. 20, 1103) and by warming acetyl-acetone with phenyl-hydrazine (K.; Combes, Bl. [2] 50, 145). Oil, volatile with steam. -B', H, PtCl, 4aq. Decomposes at 186°.

Methyle-iodide B'MeI. [190°]. Crystals, v. sol.swater.—B',Me,PtCl,. Decomposes at 220°.

Dihydride NPh CHMe.CH₂. (290° i.V.). Formed by adding Na to a boiling alcoholic solution of the base.

Phenyl-tri-methyl-pyrazole. Dihydride NPh CMe, CH2. Formed by heating mesityl oxide with phenyl hydrazine (Fischer a. Knoevenagel, A. 239, 203). Oil, v. e. sol. ether and alcohol, sl. sol. water. Its solution in dilute HCl gives a violet colour with K₂Cr₂O₁,—B'₂H₂PtCl₂: crystalline pp.

Di-phenyl-methyl-pyrazole CieH, Ne i.e. NPh CM x CH . [63°]. (335° or 355°). Formed by heating its carboaylic acid at 250°, and also by warming ben toyl-acetone with phenyl-hydraz-ine (Knorr, B. 18, 314; Fischer, B. 18, 2185). Insol. water, v. sol. alcohol. Weak base. Yields C_{1c}H₁ BrO₂ [75°]. — B'₂H₂PtCl_a aq. — B'MeI. [187'].—B'₂M₂PtCl_a. [241°]. Orange-red needles. Dihydride C₁₆H₁₆N₂. [109°]. Long prisms (from ether). Its acid solution is coloured in-

Di-phenyl-methyl-pyrazole C.H.N. NPh CH CPh:CMe. [47°]. (365°). Formed by heating its carboxylic acid, and also, together with its dihydride, by distilling the phenylhydraxide of benzylidene-acetone (Knorr, B. 18, 931; 20, 1100). Weak base.—B'_zH_PtCl_: red prisms.—B'MeI. [192°].—B'_Me_PtCl_. [229°].

Dihydride C_iH_iR_. [114°]. (c. 850°). Prisms. Its solutions fluoresce blue and give a blue colour with nitrous acid.

tensely red by nitrous acid.

Tri - phenyl - methyl-pyrazole. Tetrahydride NPh NMe CHPh. [110°]. Formed by the action of Na and boiling alcohol on triphenyl-pyrazole methylo-iodide (Knorr a. Laubmann, B. 21, 1205). Insol. water, v. sol. alcohol. Resinatied by conc. HNO.

References .- Oxy-AMIDO- and Oxy-PHENYL-

METHYL-PYRAZOLE:

PHENYL - METHYL . PYRAZOLE CARB-OXYLIC ACID NPh CMe:CH Formed from acetone, oxalic acid, and phenyl

hydrazine (Claisen a. Roosen, B. 24, 1891).

Methylether MeA'. (256° at 109 mm.). Amide. [146°].

Phenyl-methyl-pyrazole carboxylic acid

NPh

C(CO,H):CH

ing NPh

CO.C(OH)

CH

CO.C(OH)

CH

CO.C(OH)

CH with HClAq at 170°

(Ach, A. 253, 54). Needles, sol. hot alcohol.

Phenyl-methyl-pyrazole dicarboxylic acid C₁₂H₁₀N₂O₄ i.e. NPh < $\stackrel{N}{\sim}$ C.CO.H. Formed by oxidising phenyl-di-methyl-pyrazole carboxylic acid with alkaline KMnO. (Knorr a. Laubmann, B. 22, 177). Needles (from water).

Phenyl-di-methyl-pyrazole cartoxylic acid NPh N=CMe CMe: C.CO.H. [197°]. Got by saponify. ing its ether, which is obtained from ethylideneacetoacetic ether and phenyl-hydrazine (Knorr, B. 20, 1102). Needles, v. sl. sol. water.—KA'. Ethyl ether Eth'. [68°]. (286° at 260 mm.).

Di-phenyl-methyl-pyrazole carboxylic acid C₁,H₁,N₂O₂ i.e. NPh CMe:C.CO.H Got from its ether, which is obtained by the action of phenyl-hydrazine on benzoyl-acetoacetic ether (Knorr a. Blank, B. 18, 311). Sol. alkalis and conc. HClAq, insol. water.

Ethyl ether EtA'. [122°]. Di-phenyl-methyl-pyrazole carboxylic acid

NPh CPh: OMe [194°]. Formed from its ether, which is got by mixing benzylidene aceto-acetic ether with phenyl-hydrazine (Knorr a. Blank, B. 18, 931). Crystalline, v. sol. alkalis

Ethul ether Eth. [110]. References .- NITRO- and OXY-PHENYL-METHYL-

PYRAZOLE CARBOXYLIC ACINE

PHENUL-DI-METHYL-PYRIDAZINE. Di-

hydride NPh CMe; CH. [82°]. 176° at 730 mm.). Formed by heating the dicarboxylic acid at 220° (Knorr, B. 18, 304, 1568). Volatile with steam. Insol. water and alkalis, sol. conc. HClAq. Colours pinewood, dipped in HClAq, red. H₂SO₄ added to its solution in HOAc containing phenanthraquinone gives a deep-red colour.

Dicarboxylic acid of the dihydride

C1,H1,N2O4. Obtained from its other, which is formed by mixing acetic acid solutions of diacetyl-succinic ether and phenyl-hydrazine.

Needles (from HOAc).—BaA".

Ethyl ether Et₂A". [127°]. Prisms.

Reference .- OXY-PHENYL-METHYL-PYRIDAZINE. PHENYL-DI-METHYL-PYRIDINE

N € CMe: CH > CPh. [55°]. (287°) at 731 mm. Formed by distilling its dicarboxylic acid with lime (Bally, B. 20, 2591). Prisms (from ether).

B'HCl 3aq: needles.—B'₂H₁P'tCl_e 4aq: needles. -B'HNO₂, [177°]. Needles. -B'H_{*}Cr₂O₇.
Needles. -B'C_bH_{*}N₂O₇, [222°]. Needles. •

Methylo-todide B'MeI. Granules, sl. sol.
water. -B'₂M₂PtCl₂, [250°].

Hezahydride C₂NH₄M₂Pt. (274°) at 731

mm. Got by adding Na to an alcoholic solution of phenyl-di-methyl-pyridine. Liquid. Does not give a 2p. with pioric acid.—B'HCl.—B'HNO₂. [210°].—Il'₂H₂PtCl₄. [237°]. Flates.

References.—Nitro- and Oxy-Phenyl.-Di-

METHYL-PYRIDINE. PHENYL . METHYL . PYRIDINE DICARB.

OXYLIC ACID C_{1,1}H₁,NO₄ i.e. CO₂H₁C₄H₂CCHCH: CMe (CO₂H).C CO₂C(CO₂H):N [201°]. Formed by oxidising methyl·(β) -naphthoquinoline by KMnO₄ in acid solution (F. Scitz, B. 22, CO²C). No allow (contribing an incomplete contribing and contribution and contribut 257). Needles (containing aq) or anhydrous prisms. FeSO₄ colours its aqueous solution lemon-yellow. — Na₂A" 2aq. — ZnA" 1½aq. — CuA" 1 aq: minute bluish-green plates.

Phenyl-di-methyl-pyridine carboxylic acid N CMe:C(CO,H) CPh. [190°]. Got from its ether, which is formed by heating the mono-ethyl ether of the dicarboxylic acid (Hantzsch, B. 17, 2911). Small prisms (containing 2aq), v. Bol. hot water.—CuA'₂.—(HA'),H,PtCl, aq.

Ethyl ether EtA'. (316°-320°). Thick
liquid. Yields (EtA'),H,PtCl, [196°] and also

EtA'MeI [c. 206°], which is converted by alcoholic potash into C₁₅H₁₅NO, [161°], split up by HClAq at 180° into acetic acid and oxy-phenyldi-methyl-pyridine [112°].

Phenyl-di-methyl-pyridine dicarboxylic acid

 $N \leqslant_{CMe.C(CO_2H)}^{CMe.C(CO_2H)} \geqslant_{CPh}$.

Mono-ethyl HEtA". ether Formed by boiling the di-ethyl other with alcoholic KOH (1 mol.) (H.). Cubes (from alcohol). Di-ethyl ether Et.A". [67°]. Formed

by exidising its dihydride with nitrous acid. Dihydride of the di-ethyl ether

N CHMe. CH(CO,Et) CPh. [157°]. Formed by heating a mixture of benzoic aldehyde, acetoacetic ether, and alcoholic NH₃ (Schiff, a. Puliti, B. 16, 1607; Bally, B. 20, 2591). Formed also by mixing benzylidenc-acetoacetic ether with β imido-butyric ether (Beyer, B. 24, 1666). Colourless crystals, sol. acohol.

(β)-Phenyl-di-methyl-pyridine dicarboxylic

Formed by oxidising di-methyl-(\$)-naphthoquinoline with KMnO, (Recd, J. pr. [2] 35, 311). Syrup.—AgA'.

Reference. -- OXY-PHENYL-DI-METHYL-PYRIDINE CARBOXYLIC ACID.

PHENYLTRI METHYL PYRIDYL KETONE CARBOXYLIC ETHER

N < CMe.C(CO.Et) > CMe. Formed by the action of nitrous acid on its dihydride. - B'HNO: white plates. — B'HCl. [192°]. Prisms. — B'2H2PtCl8: needles.

Dihydride NH CMe:C(CO,Et) CHMe.

[187°]. Formed from ethylidene-acetoacetic ether and C.H., CO.CH., C(NH).CH, (Beyer, B. 24, 1667). Yellowish plates.

Methyl derwative of the dihydride NMe<CMe:C(CO.Et)>CHMb. [87°] Formed, in like manner, by the action of the methylimide of benzoyl-acetone on ethylidene-acetoacetic ether (B.). Yellowish-white needles, RHENYL-METHYL-PYRIMIDINE C11H16N2

i.e. CPh N.CMe CH. [74°-78°]. Formed by distilling the oxy-derivative (from benzamidine and acetoacetic ether) with zinc-dust (Pinner, B. 18, 2850). Colourless needles.—B'2H2Cl2PtCl4. [190°].

References .- OXY- and OXY-ANIDO-PHENYL-METHYL PYRIMIDINE.

PHENYL-METHYL-PYRROLE C,H,N i.e. NH CMe: CH. [101°]. Got by heating acetophenone-acetone CH_Bz.CH_Ac with alcoholic NH, at 150°; the yield being 30 p.c. of the theoretical (Paal, B. 18, 367). Plates, v. sol. alcohol. May be sublimed. Gives a purple-red colour with isatin and H.SO.

Phenyl-di-methyl-pyrrole C.H .. N i.e. NPh CMe.CH. [52°]. (252°). Formed by distilling its dicarboxylic acid at 2448 (Knorr, 4. 236, 306).

DI-PHENYL-METRYL-PYRROLE $C_{i_7}H_{i_8}N$ NPh CMe: OH. [84]. Formed by heating the broxylic acid [226°] to above its melting-point dederer a. Paal, B. 18, 2596). Large tables. Tetra-phenyl-methyl-pyrrole

Me CPh:CPh [214°]. Formed by heating idesyl C, H, O, [255°] with aqueous methylmine at 150° (Fehrlin, B. 22, 554). Groups of sinute needles, sol. hot alcohol and ether.

Reference. - OXY - TM - PHENYL - METHYL - PYR-OLE. PHENYL-METHYL-PYRROLE CARBOXY-

IC ACID NH CMe:C.CO.H. [c. 190°]. Got y saponification of its ether, which is formed allowing acctophenone acctoacetic ether to tand with excess of NH, Aq (Lederer a. Paal, B. 18, 2593). Flat needles (from HOAc).

Ethylether Eth'. [120°]. Needles. Phenyl-di-methyl-pyrrole carboxylic ether Ch:H17NO2 i.e. NMe CMe:C.CO2Et Formed from acetophenone acetoacetic ether and NMeHAq (L. a. P.). Plates (from alcohol-

other), v. e. sol. alcohol.

Phenyl-di-methyl-pyrrole m-carboxylic acid CO₂H.C₆H₄.N CMe:CH [135°]. Formed by heating acetonyl-acetone with m-amido-benzoic

seid and alcohol (Paal, B. 19, 558). Flat crystals, sl. sol. water, v. sol. alcohol. Phenyl-di-methyl-pyrrole di-carboxylic acid

CO₂H.CH₂N<CMc:C.CO₂H [152°]. Got by saponifying its ether. Small needles (from alcohol), sl. sol. water.

Ethyl ether Et. A". [131°]: Got by allowing acetophenone-acetoacetic ether to stand with Plycocoll and HOAc (Paal a. Schneider, B. 19, 3160). Needles (from HOAc), sl. sol. water.

Phenyl di methyl pyrrole dicarboxylic acid NPh CMe:C.CO.H Gotfrom its ether. Powder, CMc:CAU_II

decomposing at 224° into CO₂ and phenyl-dimethyl-pyrrole.—CaA".—CaII,A"₂: prisms.

Ethyl ether Et₂A". [38°]. (280°) at 500 mm. Formed by warming di-acetyl-succinic mathematical and the color of t ether with aniline and HOAc (Knorr, A. 236, 805). Crystals.

Di-phenyl-methyl-pyrrole carboxylic acid NPh CPh:CH CMe:C.CO₂H [226°]. Obtained saponification of its ether, which is formed by boiling acetophenone-aceto-acetic ether with an

acetic acid solution of aniline (Lederer a. Paal, B. 18. 2595). Small needles (from acetic acid).

Ethyl ether A'Et: [100°]; prisms.

Di-phenyl-methyl-pyrrole di-o-carboxylio acid NMe C(C,H,CO,H):CH [231°]. Formed from C,H,(CO,C,H,CO,H), and methylamine in legals at 1009 (Bangang P 90 1489). Doop alcohol at 100° (Baumann, B. 20, 1489). Deepyellow plates, insol. water, sl. sol. ether.

Di-phenyl-methyl-pyrrole dicarboxylic acid CO₂H.C₆H._NCCMe.C.CO₂H. [210°]. Formed by saponifying its ether, which is got from acetophemone-acetoacetic ether, m-amido-benzoic acid, and HOAc (Paal a. Schneider, B. 19. 8162). Needles (from dilute alcohol).

Ethyl ether EtA'. [160°]. Needles. Reference. - OXY . PHENYL . METHYL . PYRROLM CARBOXYLIC ACID.

PHENYL-METHYL-QUINAZOLINE DIHY-

DRIDE C₁₅H₁₄N₂ i.e. C₈H₄ < N - CMo Formed by reduction of the acetyl derivative of o-nitro-benzyl-aniline with tin and HClAq (Paul a. Krecke, B. 23, 2638). Rosettes of white needles, insol. water, m. sol. ligroin. The tin double chloride melts at 122°.—B'HCl 2aq. [257°].—B'₂H.PtCl₂. Flat orange needles. Decomposes at 223°.

Reference.—Oxy - PIERNYL - METHYL - QUINAZ-

OLINE.

(Py. 1,3) - Phenyl-Methyl-Quinoline C.H. CPh:CH [100°]. Formed by boiling an alcoholic solution of o-amido-benzophenone with acctone and KOHAq (Geigy a. Königs, B. 18, 2406; 19, 2428). Obtained also from paraldehyde, acetophenone, HCl, and aniline, and by heating benzoyl-acetone-anilide C₁H₁NO with H₁SO₄ on the water-bath (Beyer, *J. pr.* [2] 33, 420; *B.* 20, 1771). Tables (from ether).—B'ILSO₄. [236°].—B'₂H₂PtCl₃2aq. [225°]. Its acid solutions fluoresce blue. By heating with phthalic anhydride and ZnCl, at 150° it is converted into the phthalone C2,H1,NO, [270] which crystallises from alcohol or HOAc in spaningly-soluble orange-red crystals.

(Py. 3,1)-Phenyl-methyl-quinoline O, H, N i.e. C.H. CMe:CH Flavoline. [65°]. (374°). V.D. 7.7 (calc. 7.6). Formed by distilling flave-nol with zinc-dust. Prepared by adding a little dilute (10 p.c.) NaOHAq to a solution of equi-molecular quantities of o-amido-acetophenone and acctophenone, and then heating on the water-bath (Fischer, B. 15, 1503; 16, 68; 19, 1037). Thick tables. Yields flavaniline on nitration and reduction. Salts .- B'HCl 2aq.-B',H,PtCl,: reddish-yellow needles.-B'MeI. [1852] (Bernthsen a. Hess, B. 18, 34). Converted by KOHAq into a strongly alkaline solid 'methyl-flavolinium hydrate.'— B'₂Mc₂PtCl₂.

(Py. 3,2)-Phenyl-methyl-quinoline C.H. CH:CMe. [53°].. (above 300°). Formed by heating a mixture of CHPh:CMe.CHO, aniline, and conc. HClAq at 200° (Miller a. Kinkelin, B. 19, 527). Trimetric prisms, v. sol. alcohol and ether.—B',H,PtCl,: orange plates.-B'C,H,N,O,. [202°]. Large yellow plates.

(B. 2)-Phenyl-(Py. 4)-methyl-quinoline tetrahydride C16H1,N i.e. CPh:CH.C.CH2 .CH. CH.C.NMe.CH2 Formed by reducing (B. 2)-phenyl-quinoline methylo-chloride with tin and HClAq (La Coste a. Sorger, A. 230, 24. Amorphous powder, insol. cold water.—B'HCl.—B'HI.—B'G.H.N.O., [147°].—B'McI aq. [195°]. Yellow Pates. (Py. 3)-Phenyl-(B. 4)-methyl-quinoline CH:CH. (C.CH:CH.

CH:CMe.C.N=CPh. [50°]. Formed by distilling its (Py. 1)-carboxylic acid with soda-lime (Doebner a. Giesecke, A. 242, 299). Plates (from alcohol).—B'2H_PtCl_s. Brick-red needles. (Py. 3)-Phenyl (B. 2)-methyl-quinoline CMe:CH:CCH:CH [68°]. (above 360°). Got by distilling its carboxylic acid with soda-lime (D. a. C.). Small yellow needles (from cilute alcohol).—B'_H_PtCl_a: golden needles.

References.—Nitro-and Oxy-PHENYL-METHYL-

QUINOLINE.

(Py. 3)-PHENYL-(B. 4)-METHYL-QUINOL-INE (Py. 1)-CARBOXYLIO ACID C.H., NO., [245°]. Formed by heating equi-molecular proportions of o-toluidine, benzon aldehyde, and pyruvic acid in alcoholic solution on the waterbath (Doebner a. Giesecke, 4. 242, 298). Small yellow crystals (from alcohol), w. sl. sol. hot water.—CuA', aq.—AgAbaq: needles (from Aq).

bath (Doebner a. tiesecke, A. 222, 239). Smain yellow crystals (from alcohol), w. sl. sol. hot water.—CuA'₂aq.—AgAsaq: needles (from Aq). (Py. 3)-Phenyl. (B. 2)-methyl-quinoline (Py. 1)-carboxylic acid. [228°]. Formed in like manner from p-toluidine (D. a. G.). Yellow needles (from alcohol).—CuA'₂.—PbA'₃.—AgA'.
—H₂A'₂H.PtCl_n: golden needles, v. sl. sol. hot Aq. Reference.—Oxy-phenyl. Methyl. -Quinolyne

CARBOXYLIC ACID.

PHENYL (Py. 8)-METHYL-(B. 2)-QUIN-OLYL RETONE C₆H₄.CO.C₆H₃< $\stackrel{\text{CH:CH}}{N}$ = $\stackrel{\text{CM:CM}}{CM}$? [68°].

(above 300°). Formed from anido-benzophenone, paraldehyde, and HClAq at 100° (Hinz, A. 242, \$23). Needles (from water) or plates (from alcohol).—B'₂H₂PtCl₂ 2nq.—B'₂H₂Cr₂O,.—B'MeI. [220°]. Small dark-green needles; v. sol. water.

Phenyl (Py. 3)-methyl-(B. 4)-quinolyl ketone. [108]. Formed by boiling o-amido-benzophenone with dilute II,SO, and paraldelyde (Geigy a. Königs, B. 18, 2406). Matted needles (from dilute alcohol).

PHENYL DI - METHYL QUINOLYL THIO-UREA NHPh.CS.NH.C₁₁H₁₀N. [159°]. Formod by heating phenyl-thiocarbimide with amido-dimethyl-quinoline (Marckwald, B. 23, 1025). Prisms, v. sol. hot alcohol.—B'₂H₂PtCl₄: pp.

PHENYL-METHYL-QUINOXALINE
CM::CH.CN.CII· [79°]. Formed by reducing
C₂H,Me(NO₂).NH.CH₂Bz with SnCl₂ and HCl
(Lellmann a. Donner, B. 23, 171). Needles, v.
sol. alcohol.—B'HgCl₂. [223°]. White needles.
Phenyl-methyl-quinoxaline

CMe:CH. c.N:CH. [135°]. Formed, together with the preceding isomeride, by the action of chloroacetophenone on tolylene-o-diamine (Hinsberg, A. 237, 370). Formed also by warming phenylglyoxylic aldehyde C.H., CO.CHO with tolylene-o-diamine sulphate and NaOAc (Pechmann, B. 20, 2905). Needles, v. sol. hot alcohol and ether. Phenyl-di-methyl-quinoxaline

 $C_{\rm e}H_{\rm a}{\rm Me} < {
m N:CMe \over
m N:CPh}.$ [48°]. Formed by boiling phenyl methyl diketone with tolylene-o-diamine in ether (Müller a. Pechmann, B. 22, 2130). V. sol. most solvents.

Di-phenyl-methyl-quinoxaline $C_{n}H_{1k}N_{2}$ i.e. $C_{s}H_{s}Me < \stackrel{N:CPh}{N:CPh}$ [111°]. Formed by heating benzil with tolylene-o-diamine in alcoholic solution (Hinsberg, B. 17, 322). Silvery plates. May be distilled. Weak base. Nearly insol. Aq.

Di-phenyl-v-methyl-quinoxaline dihydride

OpH Ne. CPHh. [133°]. Formed by heating

phenylene-methyl-o-diamune with benzoln at 165° (Fischer a. Busch, B. 24, 2682). Yellow needles, m. sol. alcohol. Its solutions fluoresca greenish-yellow.

Reference. — OXY - PHENYL - METHYL - QUIN-

PHENYL-METHYL-ROSINDULINE

C₁₀H_s(NPh) \ll NPh C₄H₂Me $\left[\frac{1}{2}4\right]$. [232°]. Formed from benzene-azo-p-tolyl-(a)-naphthylathine (Fischer a. Hepp, A. 256, 243). Reddishbrown bronzed plates. Split up by conc. HClA₁ at 200° into an line and methyl-rosindone.

PHENYL-METHYL-SUCCINIC ACID

PHENYL-PYROTARTARIC ACID.

Phenyl-tri-methyl-succinic acid C₁₃H₁₆O, i.e. CH₂Ph.CH(CO₂H).CMe₂.CO₂H. [140°]. Formed from bramo-isgbutyric ether and sodium benzyl-malonic ether, the resulting ether (200°-220') being saponified (Bischoff, B. 24, 1060). Short needles (from water), v. sol. alcohol and ether.

needles (from watca), v. sol. alcohol and ether.
Di-phenyl-di-methyl-succinic acid. Nitrile
CPhMe(CN).CPhMe.CN. [227°]. Formed from
CITPhMe.CN by treatment with NaOEt and I
(Chalanay a. Knoevenagel, B. 25, 289). Insol.

benzene, sl. sol. alcohol.

PHENYL-METHYL-SULPHAMIC ACID

NPhMe.SO,H. Formed from CISO,H and methyl-aniline in chloroform (Traube, B. 24, 362).—NH,A'. Turns violet in air. Decomposed by boiling HClAq into methyl-aniline and H,SO,. The potassium salt is a crystalline powder, sl. sol. alcohol, v. sol. water.

PHENYL-DI.METHYL SULPHAMIDE SO₂(NMe₂)(NHPh). [85°]. Formed from NMe_SO₂(2 and aniline (Behrend, 4. 222, 128). Needles (from ether). Yields SO₂(NMe₂)(NPhNa)

crystallising in needles, v. sol. water and alcohol.

PHENYL METHYL SULPHIDE PhSMe.
(188°). Formed from Pb(SPh), and MoI at 100°

(Obermeyer, B. 20, 2926). Liquid.
PHENYL METHYL ESULPHONE C.H.SO. i.e.
C.H.SO.CH. [89]. Formed from benzene
sulphinic acid, NaOEt, and MeI at 100°, and
also by boiling C.H., SO.CH., CO.H with alcoholic potash (Michael a. Palmer, Am. 6, 251;
7, 65; Otto a. Bössing, B. 18, 156; 21, 652;
22, 1449, 1452, 23, 755). Plates (from hot water),
v. e. sol. alcohol and ether.

PHENYL METHYL SULPHONE ω-CARB-OXYLIC ACID υ. PHENYL-SULPHONO-ACETIC ACID.

PHENYL-METHYL-THIAZOLE C₁₀H₄NS i.e. NCMe:CH. (279° cor.). Formed from thiobenzamide and chloro-acctone in alcohol (Hubacher, A. 259, 236). Oil.

Phenyl-methyl-thiazole N CPh:CH. GMs.S [68:5°]. (284° cor.). Formed from thioacetamide and w-bromo-acetophenone (Hantzsch, B. 21, 913; A. 250, 269). Weak base. Not attacked in boiling alcoholic solution by sodium (Sohatzmann, A. 261, 7).—*B'HCl: sl. sol. Aq.

Phenyl-methyl-thiazole. Dihydride
NCH,CHMe. Formed by boiling propylene
bromide with thiobenzamide (Gabriel a. Heymann, B. 24, 785). Yellowish liquid.—Picrate
B'CeH,N₂O₁: crystalline.

Di-phenyl-methyl-thiasole N CPh:CPh

Pol. Formed from thioacetamide and bromooxybenzoin in alcohol (Hubacher, A. 259, 4). Stellate groups of needles, insol. water. Hydrochloride: [97°]; white crystals from dilute HClAq).

PHENYL-METHYL-THIAZOLE CARBOXY-FIC ACID N CMe;C.CO,H. [203°]. Formed

y saponifying its ether. Needles, sl. sol. ether. Ethyl ether Eth'. [43°]. Formed from hiobenzamide and chloro-acetic ether (Hubacher,

PHENYL (a) METHYL-THIENYL KETONE H., CO.C. H. MeS. [124°]. Formedby heating O,H,Me(HgCl)S with BzCl at 100° (Volhard, A. 267, 181; cf. Ernst, B. 19, 3280). Needles (fromligroin).

TRÍ - PHENYL - DI - METHYL - DI-THIO-BIURET C.,H.,N.S., i.e. NPh(CS.NPhMe), or CS(NPhMe).S.C(NPh)(NPhMe). [202°]. Formed from Cl.CS.NPhMe and aniline (Billeter a. Strohl, B. 21, 10s). Needles, v. sl. sol. cold alcohol.

PHENYLA METHYL . DI-THIO-CARBAMIC ACID NPhMe.CS.SMe. '882]. Formed by heating NPhMc.C(NMc).SMc or NPhMc.C(NH).SMc with CS at 160° (Bertram,

B. 25, 51). Plates.
PHENYL - METHYL - THIOCARBAMIC CHLORIDE NPhMe.CS.Cl. [35"]. Formed from methyl-aniline and CSCl₂ (Billeter, B. 20, 1631). Yellowish crystals. Converted by alco-· hol into (NPhMe.CS).O [116.5].

PHENYL . METHYL-THIO-SEMI-CARBAZ-IDE NHPh.NH.CS.NHMe. [89°]. Formed from methyl-thiocarbimide and phenyl-hydrazine (Dixon, C. J. 57, 262). Trimetric prisms, v. sl. sol. cold water. H2SO, forms an azure-blue solution. CuSO, gives a deep-blue colour, and FeCl, a greenish-blue.

Phenyl-methyl-thio-somi-carba#de

NHPh.CS.NII.NHMe. [143°]. Formed from methyl-hydrazine and phenyl-thiocarbimide (Brüning, A. 253, 11). Prisms (from alcohol).

Di-phensl-methyl-thio-semi-carbazide

NPhMe.NH.CS.NHPh. [154°]. Formed from phenyl-methyl-hydrazine and phenyl-thiocarb-imide (Fischer, A. 190, 166). V sol. hot alcohol. PHENYL-METHYL-THIOCARBIZINE

CS NPh. [123°]. Formed from phenyl-thiocarbizine and MeI at 100° (Fischer, A. 212, 330). Tables (from water). Not attacked by nitrous acid.

PHENYL-METHYL-THIOHYDANTOIC ACID NHPh.CS.NH.CHMe.CO.H. Formed alanine and phenyl-thiocarbinide in alcohol (Marckwald, B. 21, 3280; cf. Aschan, B. 17, 421).- KA': minute needles.

PHENYL-METHYL-THIOHYDANTOIN

CS<NPh,CO NH-CHMe. [184°]. Formed by treating phenyl-methyl-hiohydantoïc acid (v. supra) with HCl. Small prisms (from alcohol). Split up by HClAq at 150° into aniline, alanine, CO.,

Phenyl-di-methyl-thiohydantoin

CS NPh.CO [673]. Formed from phenylthiocarbimide and α-amido-isobutyric acid (Marckwald, B. 21, 3282) Crystals, sl. sol. Aq. Vol. IV.

PHENYL-METHYL-THIOPHENE C., II., S i.e. S CMe: CH. [51°]. (271° uncor.). Got by heating acetophenone-acetone with P.S. at 1250 the yield being 70 p.c. of the theoretical amount (Paal, B. 18, 367). Needles, volatile with steam. Gives the indophenine reaction.

S<CMe:CH :CPh. Phenyl-methyl-thiophene [73°]. Formed by heating CH.Ac.CHPh.CO.Na with P.S. or P.S. (Paul a. Püschel, B. 20, 2558). Piates, • sol. bot alcohol. Gives the indophenine reaction on warming. Br forms C, H, Br, S

s-PHENYL-METHYL-THIO-UREA C,II, N.S i.e. CS(NHPh)(NHMe). [133]. Formed from methyl-thiocarbimide and aniline (Gebhardt, B. 17, 3038). Six-sided tables. Yields NH, Me and CS(NHPh), on boiling with aniline.

u-Phenyl-methyl-thio-urea

CS(NIP)(NPhMo). [107°]. Formed from methylaniline hydrochloride and potassium sulphocyanide (Gebhardt, B. 17, 2094). Tables (from alcohol) or prisms (from hot water).

Phenyl-methyl-\psi-thio-urea
Mes.G(NII)(NIIPh). [71°]. Formed by warming phenyl-thio-urea with MeI and alcohol (Bertram, B. 25, 49). Colourless crystals, sl. sol. hot water. Converted by dilute H.SO, at 160° into MeS.CO.NHPh. - B'HI. [147°].— B'H.SO., [171°].—B'.H.SO., [171°].—B'.HNO., [113°].—B'.HO.do. [115°].—B'., H.PtCl., [184°].—B'.G.H.,(NO.),3OH. [175°]. Yellow plates. Phenyl-di-methyl-thio-urea

CS(NHMe)(NPhMe). [114°]. Formed from methyl-thiocarbimide and methyl-aniline (G.).

Phonyl-di-methyl-\psi-thio-urea MeS.C(NH)(NPhMe). Formed from phenylmethyl-\psi-thio-urea and methyl iodide (B.).
Oil. Converted by dilute H.SO, at 160° into [184°]. -MeS.CO.NPhMe [54°]. — BHI. B'C_sH_aN₃O₃. Small prisms.

Phenyl-tri-mothyl-4-thio-urea C. H. N.S i.e. MeS.C(NMe)(NPhMe). Methyl-imido-methylphenyl-carbamic thiic methyl ether. Formed by methylation of phenyl-di-methyl-+thio-urea (B.). -B'HI. [c. 184]. $-B'_2H_2PtCl_{g}$. [c. 174]. $-B'C_6H_3N_3O$. [126]. Lemon-yellow crystals.

Di-phenyl-methyl-thio-urca CS(NIIPh/(NPhMe), [87°], (205°). Formed from phenyl-thiocarbimide and methyl-aniline Prisms, v. sol. hot alcohol. Decomposed into the parent substances by distillation with steam. Boiling aniline yields CS(NHPh), and methyl-aniline.

Di-phenyl-methyl- ψ -thio-urea

MeS.C(NPh)(NHPh). [110°]. Formed from CS(NHPh), and MeI. Conc. HClAq at 150° Formed from yields aniline and methyl-mercaptan. -B'HI.

Di-phenyl-di-methyl-thio-urea CS(NPhMe), [72.5]. Formed from NPhMe.CS.Cl and methylaniline (Billeter, B. 20, 1631). Prisms (from ligroïn).

Di-phenyl-di-methyl-ψ-thio-ures MeS.C(NPh)(NPhMe). (above 300°). Formed from CS(NHPh)(NPhMe) and MeI (Bertram, B. 25, 57). CS, at 160° forms NPhMe.CS, Me.—B'HI. Crystalline meal, sl. sol. hot water.

Reference. - OKY - DI - PHENYL - METHYL- 4-THIO-UHRA.

PHENYL-METHYL-UREA C,H,ON,O CO(NH₂)(NPhMe). [82°]. Formed from methylandline hydrochloride and potassium cyanate (Gebhardt, B. 17, 2095). Thin crystals.

Phenyl-di-methyl-ures CO(NMe2)(NPhMe). Formed from NMe, COCl and aniline (Michler a. Escherich, B. 12, 1163). Crystal's (from alcohol).

Di-phenyl-methyl-urea CO(NPhMe)(NIIPh). [104°]. (204°). Formed from phenyl cyanate and methyl-aniline (G.). Small needles

Di - phenyl - di - methyl-urea CO(NPhMe). [121°]. (c. 350°). Formed from NPhMe.COCI and methyl-aniline (Michler a. Zimmermann, B. 12, 1165). Tables (from alcohol) PHENYL-(B)-NAPHTHACRIDINE

 $C_{10}H_{\text{s}} < \stackrel{CPh}{\sim} C_{10}H_{\text{s}}. \quad \text{[297°]}. \quad \text{S. (alcohol)} \quad 04.$ at 15°; S. (benzene) 29 at 18°. Formed by heating a mixture of di-(B)-naphthylamine with BzCl or with benzoic acid and P2O5 or ZnCl2 (Claus a. Richter, B. 17, 1595; Ris, B. 17, 2029) Klopsch, B. 18, 1586). Needles, v. sol. hot benzene. B'HCl. B'₂H₂PlCl_a: yellow needles.

Dihydride O10H6<NII C10H0. Got from benzoic aldehyde (1 mol.) and (3)-naphthylamine (2 mols.) in presence of condensing agents (Claisen, A. 237, 273). Oxidised to phenyl-naphthacridine.

enyl-naphthacridine.
(8)-PHENYL-NAPHTHALENE $C_{1a}H_{12}$ i.e. (calc. 7.05). C₁₀H,C₄H₅. [102°]. V.D. 7·12 (calc. 7·05). Formed by passing a mixture of naphthalene and bromo-benzene through a red-hot tube (Watson Smith, B. 12, 2049; C. J. 39, 546; ('. J. Proc. 5, 70). Formed also by the action of H₂SO₄ (80 g.) diluted with water (44 g.) on CHPh(OH).CH₂OH (Zincke a. Breuer, A. 226, 23; 240, 137). Fluorescent plates. May be sublimed. Gives rise on oxidation to a quinone $C_{10}H_{10}O_2$ [110°].

A hydrocarbon C₁₆H₁₂ [104°] got by distilling chrysoquinone with soda-lime is perhaps identical with the above (Graebe, B. 6, 66; 7, 792; Schmidt, J. pr. [2] 9, 285).

(α)-Phenyl-naphthalene dihydride v. Atron-

Reference.—OXY-AMIDO-FHENYL-NAPHTHALENE.
DI-PHEÑYL-NAPHTHAMIDINE C₂₃H₁,N₂
C_{0.}H₁,C(NPh).NHPh. [183·5°]. Formed i.e. C₁₀H₇.C(NPh).NHPh. [183:5°]. from (a)-naphthoic acid, aniline, and PCl₃ (Bössneck, B. 16, 642). Needles (from alcohol).

PHENYL-(β)-NAPHTHINDOLE C₁₃II₁₃N i.e. C₁₀H_eCH CPh. [130°]. Formed by heating the (B)-naphthyl-hydrazide of acetophenone with ZnCl, at 170° (Ince, A. 253, 42). Crystals, v. sol. alcohol and ether. Colours pinewood green.—B'C₆H₃N₃O₇. [166°]. Brown needles.

Phenyl-(β)-naphthindole $C_{10}H_{a} < {\rm CPh \atop NH} > CH$. [211°]. Formed by the action of alcoholic HCl on the (3)-naphthyl-hydrazide of phenyl-acetic aldehyde (I.). Needles, suddenly decomposed on fusion. Colours pinewood green. ZnCl. at 170° converts it into the preceding isomeride.

-B'C₂H,N₂O₇. [120°]. Reddish-brown needles.

PHENYL-NAPHTHOTRIAZINE. Dihy-

dride C1,H1,N, i.e. C10H4 N.CH2 [184°]. amine with formic paraldeliyde at 140° (Goldschmidt a. Poltzer, B. 24, 1002). Plates (containing ² aq).—B'HCl. [254°].—B'₂H₂PtCl₂.

Di-phenyl-(αβ)-naphthotriazine C₂H₁₇N, i.e. C₁₀H₈ N.CHPh? [194°]. Got by heating a solution of CHPh:N.C₁₀H₄·N₂Ph in HOAc (Meldola, C. J. 57, 330). White flattened needles. PHENYL NAPHTHOPHENANTHRAZINE

 $C_{_0}H_{_1}CH_{_1}N > C_{_{10}}H_{_6}.$ The phenylo-nitrate B'PhNO3, formed by boiling phenanthraquinone with phenyl-naphahylene-diamine in HOAc and then adding HNO, crystallises in dichroice needles or prisms (Witt, B. 20, 1185).

(Py.3)-PHENYL-(a)-NAPHTHOQUINOLINE

C₁₉H₁₂N i.e. C₁₀H₄ CH:CH N=CPh. [68°], Formed by heating its (Py. 1)-carboxylic acid with sodalime (Döbner, A. 249, 114). Yellow needles (from alcohol-ether). Yields a syrupy tetra-hydride. Salts. -B'₂H₂PtCl₆2aq. -B'H₆Cr₂O₃.
B'C₆H₃N₃O₇. (167°). Thin needles (from alcohol). (Py. 3) Phenyl-(β)-naphthoquinbline. [188°].

(Py. 3)-Pannyi-(B)-napathoquinoine. [100]. Formed by heating its carboxylic acid with sodaline (D.). Needles or plates, insol. water, v. sol. alcohol.—B'_2H_PtCl_aq.—B'C_2H_N_0O. • [250°]. Yellow plates, sl. sol. ether.—B'_2H_Cr_0.

Pthyloiodide. [233°]. Plates, inscl.

(Py. 3)-PHENYL-(a)-NAPHTHOQUINOLINE (Py. 1)-CARBOXYLIC ACID C₂₀H₁₃NO₂ i.e. $C_{10}H_6 < N - CPh$ [300°]. heating (a)-naphthylamine with pyruvic acid and benzoic aldehyde in alcoholic solution (D.). Yellow needles (from alcohol-acetone). May be reduced to a tetrahydride. Produces, on oxidation, di-phenyl-pyridine tri-carboxylic acid and CO₂H.C₅NHPh< C₀H₄ NaA' ½nq. — ChA'₂4aq.

-ZnA'..-PbA'. -AgA': insoluble powder. Ethylether EtA': [103]. Needles.

(Py. 3)-Phenyl- (β) -naphthoquinoline (Py. 1)-(17). - 3)- Γ neny1-(15)- naphthoquinoline (17). 1)-carboxylic acid C₂₀H₁₃NO₂. • [296°]. • Formed in like manner from (β)-naphthylamino (D). Needles, v. sl. sol. alcohol. – ΚΑ΄ 5aq. – NaΑ΄ 5aq. – CaΛ΄, 6aq. – ZpΑ΄, 2aq. – Cu₂Λ΄, aq (?). – AgΑ΄. PHENYL-NAPHTHOQUINOXALINE

C₁₀H_u<N:CH N:CPh. The phenylo-bromide B'PhBr formed from phenyl-napl.thylene-diamine and bromo-acetophenone, crystallises in yellow plates, and is converted by NaOH into B'PhOH [148°], which crystallises in prisms, and yields B'PhNO₃ (Fischer a. Busch, B. 24, 1873). Di-phenyl-naphthoquinoxaline

C₁₀H₀N:CPh [147²]. Formed by heating naphthylene-(1,2)-diamine hydrochloride with benzil in alcohol (Lawson, B. 18, 2426). Lightbrown plates, v. sol. alcohol and ether.

Phenylo-hydroxide $C_{16}H_6 < N = CPh$ [167°]. Formed by oxidation of C₁₀H₄ N=CPh NPh.GHPh [164°], which is got by heating phenyl-naphthylene-o-diamine with benzoin at 200° (Fischer, B. 24, 722, 1871). Formed also from naphthylene-phenyl-diamine Formed by heating benzene-azo-(6)-naphthyl- and benzil (Fischer, B. 24, 2679). Yellow

prisms, insol. water, v. sol. ether.—B'HNO_s.—B'HCl: dark-yellow needles, v. sol. alcohol.

Di-phenyl-naphthoquinoxaline dihydride

C₁₀H₄ NPh.CH₂. [165°]. Formed, together with a compound melting at 195°, from naphthylene-phenyl-diamine and benzoyl-carbinol at 155° (Fischer a. Busch, B. 24, 2680). Orange needles, v. sol. benzene, v. sl. sol. alcohol.

PHENYL-NAPHTHOROSINDULINE

 $\begin{array}{c} C_{a}H_{\bullet} \diagdown \overbrace{C(NPh).CH:C.NPh.C:CH} \searrow C_{a}H_{\bullet} \quad [256^{\circ}]. \\ Formed, together with naphthyl-rosinduline, from \end{array}$ •benzene-azo-di-(a)-naphthylamine, hydrochloride, aniline, and alcohol at 165 '(Fischer a. Hepp, A. 256, 247). Deep-red bronzed plates. Conc. HClAq forms aniline and naphthorosindone [295°

DI - PHENYL - (a) - NAPHTHYL-ACETAMID-INE C. H. CK. C(NPh).NHPh. [130°]. Formed from (a)-naphthyl-acetic acid (3 mols.), aniline (6 mols.), and PCl, (Boessneck, B. 16, 642).

Needles, sol. ether and benzene.

PHENYLe(a)-NAPHTHYL-AMINE C. H 13N i.e. C. H . NH. C10 H7. [60°]. Forms by heating (a)naphthylamine hydrochloride with aniline at 250° (Girard a. Vogt, Bl. [2] 18, 67; Streiff, B. 13, 1852). Prepared by heating a mixture of (a)-naphthol (15 pts.), aniline (19.4 pts.) and CaCl, (11.6 pts.) under pressure for 9 hours at 280°; the yield being 26 p.c. of the theoretical (Friedländer, B. 16, 2077). White plates or prisms, v. sol. alcohol. Its solutions show blue fluorescence. Yields a tri-bromo- derivative [137°] and a di-nitro- derivative [77°]. H.SO, at 100° forms a tetra-sulphonic acid.—B'HCl: prisms, decomposed by water. - B'CaHaNaOa.

Acetyl derivative C. II, NO. [1150].

Benzoyl derivative. [152°]. Nitrosamine. Cult. NPh.NO. Nitrosamine. C., H., NPh.NO. [92°]. Reddish-yellow crystals (Eischer a. Hepp, B. 20, 1247).

Phenyl- (β) -naphthylamine $C_{10}H_{13}N$. [108] (395°). Formed by heating (B)-naphthol with aniline and ZnCl, at 190° (Merz a. Weith, B.13, 1300), or with aniline hydrochloride (Merz a. Weith, B. 13, 1850).

Preparation. - A mixture of (B)-naphthol (15 pts.), aniline (19.4 pts.), and CaCl₂ (11.6 pts.) is heated under pressure at 280° for 9 hours; the yield is 98 p.c. of the theoretical (Friedlander,

B. 16, 2075).

Properties.-White needles, sol. McOII. Yields a tetra-bromo- derivative [198] and a nitro- derivative [87°]. With nitroso-di-methylaniline hydrochloride and HOAc it yields lustrous black crystals, which form a violet solution in H_SO₄ (Witt, B. 21, 723). Sulphur at 240° forms

SC₀H-NH [178°] (Kym, B. 23, 2466).

H_SO₄ at 100° forms a trisulphonic acid

Salts .- B'HCl: unstable crystalline powder. -B'C, H, N, O, Brownish needles, v. sol. CHCl,

Acetyl derivative. [93]. Crystals. Benzoyl derivative. [136] (Streiff, A. 209, 151); [143] (Claus a. Richter, B. 17, 1591).

Nitrosamine C10H,.NPh.NO. [93°]. Di-phenyl-naphthylamine C10H, NPh2. [142°]. (335°-340° at 85 mm.). Formed by adding abromo-napht Halene (20 g.) to a boiling solution of potassium (8.8 g.) in diphenylamine (20 g.)

mixed with aniline (15 c.c.) (Herz, B. 23, 2541). Silky needles (from dilute alcohol), insol. water.

References .- NITRO-AMIDO-, DI-NITRO-, and NITROSO- PHENYL-NAPHTHYL-AMINE.

PHENYL-(a)-NAPHTHYLAMINE BLUE v. TRI - NAPHTHYL - TRI - AMIDO-TRI-PHENYL-CARBINYL CHLORIDE

PHENYL . (A) - NAPHTHYL - CARBAMIC ACID.

Ethylether C, H. NPh.CO, Et. Formed by the action of NaOEt on the chloride (Paschkowezky, B. 24, 2919). Satiny needles.

Phenyl ether Co.H.NPh.CO.Ph. [149° Fren'y tether C₁₀(1,Nrh.Oz.Ph. [149]). S. (96 p.c. alcohol) 36 at 17°, S. (benzene) 23 at 17°. Formed from the chloride and NaOPh. Needles, v. 81. sol. cola alcohol. Chloride C₂(H.NPh.COC), [102°]. Formed from phenyl (β)-naph@lamine and COCl₂ in

toluene (Kym, B. 23, 425). White plates.

PHENYL-(a)-NAPHTHYL CARBINOL

Ph.CH(OH).C, H, [86.5°]. (above 360°). Formed from the ketone, zinc-dust, and KOH (Elbs, J. pr. [2] 35, 504; cf. Lehine, B. 13, 359; Beckmann, B. 22, 915). Crystals, v. sol. alcohol. Gives a giolet colour with H2SO.

Phenyl-di-(a)-naphthyl carbinol C2, H200 i.c. Ph.C(C₁₀H,).OH. [160°-170°]. Formed, together with benzoic aldehyde, by boiling phenyl-(a)-naphthyl-(β)-pinacolin (C₁₀H₁).CPhBz (got by reducing phenyl (a)-naphthyl ketone with zine and alcoholic HCl) with alcoholic KOH (Elbs, J. pr. [2] 35, 507). Grey crystalline crusts (from ether-alcohol), m. sol. alcohol, v. sol. ether.

PHENYL - (8) - NAPHTHYL - CARBINYL - THIO-UREA. Tetrahydride C₁₀H₁₀N₂S i.e. NHPh.CS.NH.CH₂C₁₀H₁₁. [140°]. Formed from C₁₀H₁₁.CH₂NH₂ and phenyl thiocarbimide (Bamberger a. Helwig, B. 22, 1913). Vitreous rosettes.

PHENYL-NAPHTHYL-CARBINYL-UREA. NJIPh.CO.NH.CH,C, HI Tetrahydride Formed from naphthyl-carbinylamine and pheny cyanate (Bamberger, B. 22, 1913). The (a)-compound melts at 126.5°, the (β)-isomeride at 141°. Both crystallise in needles.

PHENYL-(a)-NAPHTHYLENE-DIAMINE $\mathbf{C}_{10}\mathbf{H}_{11}\mathbf{N}_{2}$ *i.e.* $\hat{\mathbf{C}}_{10}\mathbf{H}_{6}(\mathbf{NH}_{2})(\mathbf{NHPh})$ [1:4]. [148°] Formed by reducing nitroso-phenyl-(a)-naphthylamine (Wacker, A. 243, 305). Needles (from

alcohol) or plates (from benzene). Phenyl-o-naphthylene-diamine

C₁₀H₆(NH₂)(NHC₆H₅) [1:2]. Amido (β)-naph-thyl-phenyl-amine. [140°]. Formed, together with aniline, by reduction of benzene-azo-(β) naphthyl-phenyl-amine with SuCl, (Zincke a. Lawson, B. 20, 1170; Witt, B. 20, 1184). Broad needles or plates. Nitrous acid passed into HOAc (11 pts.) containing the hydrochloride in suspension forms $C_{10}H_1N_1O_2$ or $C_{10}H_{10}N_1O_2$ [208°], whence SnCl₂ forms $C_{10}H_{12}N_4$ [194°], which yields B'HCl, $C_{10}H_{11}AcN_4$ [261°] and $C_{10}H_{10}Ac_2N_4$ [177°], and gives with benzoic aldehyde a compound C23H16N4 [15.0°] (Zincke a. Campbell, A. 255, 349).

Salts .- B'HCl: long colourless glistening needles, v. sl. sol. water, more readily in alcohol. -XB'H.SO.: needles, similar solubility.

Phenyl-dinaphthylene-amine C26H1,N i.e. C₁₀H_eNPh. [c. 144°]. Formed by heating (ββ)-di-oxy-dinaphthyl with aniline-zinc-chloride. at 800° (Walder, B. 15, 2175). needles, sol. alcohol.—B'2C₄H₄N₄O₇. Prisms or [169°].

Di-phenyl-naphthylene-diamine [2:2] C₁₉H₄(NHPh)₂ [168°]. Formed, together with C₁₀H₄(OH)(NHPh) [163°], by heating dioxynaphthalene with aniline and CaCl₂ (Annaheim, B. 20, 1372; Clausius, B. 23, 528). Silvery plates (from hot benzene).

Acetyl derivative C26H22N2O3. [198°].

Di-phenyl-naphthylene-p-diamine [1:4] C₁₀H_a(NHPh)₂. [144°]. Formed by reducing the di-anilide of (a) naphth quinone with zinc, HOAc, and alcohol (Fischer a. Hepp, A.

256, 255). Colourless prisms.

DI - PHENYL - NAPHTHYLENE - DI-THIOUREA C₁₆H₄(NH•CS.NH•Ph)... 1355°-380°1. UREA C₁₀H₆(NHCS.NHPh)₂, [355°-350°]. Formed from naphthylene (1,2) diamine and phenyl-thio-carbimide (Damberger a. Schieffeline B. 22, 1376). Needles.

DI-PHENYL-NAPHTHYLENE-UREA

C₁₀H_a(NH.CO.NHPh)₂. [335°]. Formed from naphthylene (1,2)-diamine and phenyl cyanate (Bamberger a. Schieffelin, B. 22, 1376). Crystalline granules, v. sl. sol, benzene.

PHENYL-NAPHTHYL-ETHANE CasHin i.c. C, H, CH, CH, Ph. Formed by heating nai hthyl benzyl ketone with HI and P at 155° (Graebe a. Bungener, B. 12, 1078). Yields chrysene on passing through a red-hot tube.

s-PHENYĽ- (β) -NAPHTHYL-ETHYLENE C₆H₃.C₂H₂.C₁₀H₃. [145°]. Formed by distilling (β)-naphthyl cinnamate, CO₂ being split off (Anschütz, B. 18, 1946). Silvery plates. Di-bromide. [192°].

PHENYL-NAPHTHYL-ETHYLENE-4-THIO-

UREA NPh:C< $^{N(C_{10}H,)}_{S,CH_2}>$ CH $_{\bf r}$ [185°]. Formed from phenyl-(a)-naphthyl-urea and ethylene bromide (Foerster, B. 21, 1870)

DI-PHENYL-NAPHTHYL-GUANIDINE $C_{22}H_{10}N_3CN_3H_2Ph_2(C_{10}H_1)$. [155°]. Formed by heating di-phenyl-thio-urea with (a)-naphthylamine, alcohol, and PbO (Tiemann, B. 3, 6; Z. [2] 6, 309). Crystalline, sol. alcohol.

PHENYL - (B) - NAPHTHYL - GUANIDINE CARBOXYLIC ACID

C, H, NH.C(NH).NH.C, H4.CO2H. Formed by heating cyan-carbimidamido-benzoic acid with (β)naphthylamine (Griess, B. 16, 338). sl. sol. hot alcohol.-B'HCl. Six-sided plates.

PHENYL (α)-NAPHTHYL-KETONE
C₁₇H₁₂O i.e. C₆H₃.CO.C₁₈H₇. Mol. w. 232. [75·5°]. (385°) (Schweizer, A. 261, 196). V.D. 119 (calc.

5). S. (alcohol) 2.5 at 12°.

Formation. — 1. Together with the isomeride, by heating naphthalene with HOBz and P₂O₃ at 210° (Merz, B. 6, 541, 966, 1238).- By heating (a)-naphthoic acid with benzene and P₂O₅ (M.).—3. Together with a smaller quantity of the (β)- isomeride, by the action of AlCl, on a mixture of naphthalene, CS₂, and BzCl. The two ketones are separated by crystallisation from alcohol-ether (Elbs, J. pr. [2] 35, 503; B. 19, 1965; Rospendowski, C. R. 102, 872) .- 4. By heating naphthalene with BzCl and ZuCl., or Zn (Roux, A. Ch. [6] 12, 338; Kegel, A. 247, 178).

Properties.-Trimetric prisms, very slightly

volatile with steam, Reactions.—1. Br forms C₁₇H₁₁BrO [98°] (E.); [100.5°] (Rospendowski), whence HNO.

gives C17HaBr(NO2)2O decomposing at 90° .- 2. Conc. H.SO, with a few drops of water forms at 100°-150° benzoic acid and naphthalene (\$)sulphonic acid.—3. Soda-lime at 350° forms naphthalene and NaOBz.—4. Chromic acid mixture forms C,H,.CO.C,H,(CO,H),[1:2:3]. [155°] .-- 5. Sodium acting on its ethereal solution forms a greenish-yellow compound CPh(C₁₀H₁,)₂CO.C₂H₃ and other bodies, while CO₂ acting on the Na compound forms a yellow powder, split up by water into ketone and C₆H₃, C(C₁₀H₁)(OH, CO₂H [148°] (Beckmann a. Paul, A. 266, 10).

Oxim C_aH_aC(NOH).C_{1a}H_r. [142°]. Groups of white needles (from dilute alcohol) (Kegel, A. 247, 181). Oxidised by CrO_a in HOAc to $C_6H_5.CO.C_6H_3 < \frac{CO.CH}{CO.CH}$ [152°], which yields an anilide CoH3Bz CO.C.NHPh [200°] and a ptoluide [197°] both converted by boiling NaOHAq

into C,H,Bz < CO.C.OH [222°].

Phenyl (β)-naphthyl ketone [82°]. S. 2 at 12. Formed, at the same time as the (of- isomeride, from naphthalene (v. supra). Formed also by heating (β) -naphthoic acid with benzene and P₂O₅ (Merz). Needles, v. sol. hot alcohol.

Oxim. [176°]. Needles. Oxidised by CrO₃

in HOAc to yellow C,H,Bz CO,CH, which is converted by heating with aniline into dark-red plates of $C_sH_3Bz < \stackrel{CO.C.NHPh}{<} [210^\circ].$

Reference. -- DI - OXY - PHENYL - NAPHTHYL -KETONE

PHENYL NAPHTHYL KETONE o-CARB-OXYLIC ACID C10 H7.CO.C0H1.CO.H. [174°]. The chloride is formed from naphthalene, phthalic armydride, and AlCl, (Ador a. Crafts, Bl. [2] 31, 531). Prisms (from dilute alcohol). PHENYL - NAPHTHYL - METHANE v.

BENZYL-NAPHTHALENE.

Phonyl-di-(a)-naphthyl methane C2, H20 i.e. C_bH₃CH(C₁₀H₂)₂. [c. 180°]. Formed from phenyl-(a) naphthyl-(b)-pinacolin by distilling with zinc-dust. Got also by heating phenyl-di-(a)-naphthyl-carbinol with zinc-dust (Elbs, J. pr. [2] 35, 508). Grey powder; cakes together at 100

Di-phenyl-naphthyl-methane C10H7.CHPh4. [134° and 149°]. Formed by heating di-phenylcarbinol with naphthalene and P₂O₂ at 140° (Lehne, B. 13, 358; Hemilian, Bl. [2] 34, 326). Needles, sol. benzene and ether, sl. sol. alcohol.

PHENYL - (a) - NAPHTHYL - METHYL-PYR -ROLE CH:CPh NC₁₀H₇. [74°]. (above 360°). Formed by heating the carboxylic acid [244°] (Lederer a. Paal, B. 18, 2598). Plates. sol. alcohol, benzene, and ligroin.

Phenyl-(3)-naphthyl-methy.-pyrrole CH:CPh NC₁₀H_r. [52°]. Formed by heating the carboxylic acid [249°] (L. a. P.). white concentric needles. V. sol. alcohol

PRENYL - (a) - NAPHTHYL - METHYL - PYR-ROLE CARBOXYLIC ACID

CO.H.C-CMe NC, H,. [244°]. Formed by

heating acctophenoneacetoacetic ether with (a)naphthylamine at 130°, and saponification of the product (Lederer a. Paal, B. 18, 2598). Needles. sol. alcohol, benzene, and acetic acid.

Phenyl-8-naphthyl-methyl-pyrrole oxylic acid. [249°]. Formed in like manner. using (β) -naphthylamine (L. a. P.). Small white needles, sol. alcohol and HOAc.

Ethyl ether EtA'. [115°]. Plates. PHENYL - (8)-NAPHTHYL-METHYL-THIO-

UREA C10H,NH.CS.NPhMe. [127°]. Got from (B)-naphthyl-thiocarbimide and methyl-aniline •(Gebhardt, B. 17, 2091). Long yellow needles.

Phenyl-(a)-naphthyl-methyl-\psi-thio-urea C₁₀H,N:C(SMe),NHPh. [96]. Formed from phenyl (a)-naphthyl-thio-urea and MeI (Foerster, B. 21, 1870). Small white needles. Yield (a)-naphthyl-thiocarbinnide on Reating with CS. Yields

PHENYI⁴ (a) - NAPHTHYL (b) PINACOLIN C_aH₂,C(C₁₆H₃),CO.C_cH₃, [e, 130°]. From phenyl-(a) naphthyl ketone by boiling with zine and HCl (Elbs, J. pr. [2] 35, 505). Pale greenishyellow crystalline crusts, v. sol. ether, sl. sol. alcohol, insol. water. Cakes together at 100°-110°. Boiling alcoholic KOH forms benzoic aldehyde and phenyl-di-naphthyl-carbinol.

PHENYL - (a) - NAPHTHYL - PINACONE C₁₆H,CPh(OH).ĈPh(OH).C₁₆H, [61°]. A product of the action of sodium-amalgani on an alcoholic solution of phenyl-(a)-naphthyl ketone (Lehne, B. 13, 1360). Needles (from ether).
DI - PHENYL - (a) - NAPHTHYL - PYRROLE

CH:CPh CH:CPh>NC₁₀H₁. [149]. Formed by heating its carboxylic acid with lime (Paul a. Braikoff,

B. 22, 3092). Needles, v. sol. hot alcohol.

Di-phonyl-(B)-naphthyl-pyrrole. [208°].

Formed in like manner (P. a. B.). Needles.
DI - PHENYL - (a) - NAPHTHYL - PYRROLE CARBOXYLIC ACID CD.H.C CH:CPh NC10 H,

[272]. Got by saponifying its other, which is obtained from phenacyl-benzoyl-acetic other and (a)-naphthylamine (Paul a. Braikoff, B. 22, 3091). Small white plates, sl. sol. hot alcohol .-Sl. sol. hot water.

Ethyl ether EtA'. [182]. Needles. Di-phenyl-(β)-naphthyl-pyrrole carboxylic

acid. [above 350°]. Got in like manner, using
 (β) naphthylamine. Plates.—KA'. Sl. sol. water.
 Ethyl other Eth'. [182°]. Needles.

PHENYL-(a)-NAPHTHYL SULPHIDE

 $C_{16}H_7$.SPh. [42°] (K. a. B.); [49°]. (c. 215° at 15 mm.). Formed from Pb(SPh)₂ and $C_{10}H$ Br (Krafft a. Bourgeois, B. 23, 3047). Formed also from (a)-diazonaphthalene chloride and NaSPh (Ziegler, B. 23, 2471). Prisms (from dil. alcohol).

Phenyl (β)-naphthyl sulphide. [52°]. (c. 221° at 14 mm.). Formed in like manner. Needles. PHENYL (a) - NAPHTHYL SULPHONE SULPHONE C₂H₂SO₂·C₁H₂, [100°]. Formed by oxidising phenyl (a)-naphthyl sulphide with CrO₂ and HOAc (Krafit a. Bourgeois, B. 23, 3047). Formed also, together with the (B)- isomeride, by heating benzene sulphonic acid with naphthalene and P₂O₅ at 175° (Michael a. Adair, B. 10, 585). Crystals (from alcohol).

Phenyl (β) - naphthyl sulphone. Formed in five manner, and also by heating naphtfialens (β)-sulphonic acid with benzene and P₂O₂ (M. s. A.), and by the action of zinc-

dust or AlCl, on a mixture of naphthalene and benzene sulphonie chloride (Grustschoff, B. 7, 1167; Otto a. Beckurts, B. 11, 2069). Needles. PHENYL-(a)-NAPHTHYL-THIO-SEMICARB. AZIDE NHPh.CS.NH.NIIC, H,. [135°]. Formed

from (a)-naphthyl-hydrazine and phenyl-thiocarbimide (Preund, B. 24, 4191). Needles.

Phenyl - (B) - naphthyl - thio - semicarbazide. [202°]. Formed in like manner from (\$)-naphthyl-hydrazine (P.). White plates.

PHENYL •(a) - NAPHTHYL - THIO - UREA NHPh.CS.NHC₁₀H₇. [163²]. Formed from (A)-naphthylamine and phenyl-thiocarbinide (Hofmann, Pr. 9, 274), and also from aniline and (a)-naphthyl-thiocarbinide (Mainzer, B, 15, 1414). Plates, y. sl. sol. alcohol. With ethylene bromide it gives two bases [185°] and [130°].

Tetra hydride MIPh.CS.HIC.

[1537]. Formed from phenyl-thiocarbimide and (a) na phthylamine tetrahydride (Bamberger, B. 21, 1794). Prisms, v. sol. benzene-alcohol.

Phenyl-(B)-naphthyl-thio-urea

NHPh.CS.NHC₁₀H., [165°]. Formed from (β) -maplythylamine and phenyl thiocarbinide (M.; •Freund a. Wolf, B. 25, 1468). Plates. Split up by HClAq at 150° into anilino, (β) naphthylamine, and phonyl and (β)-naphthyl thiocarbinides. COCl, in toluenc forms NPh:C \(\sigma_{10}^{\text{NC}_{10}\text{H}_{1}} \) CO [117°].

Tetrahydride NHPh.CS.NHC, Hu. [161°]. Formed from phenyl thiocarbimide and (B). naphthylamine tetrahydride (Bamberger a. Müller, B. 21, 858). Prisms (from alcohol). PHENYL-(a)-NAPHTHYL-UREA. Tetra

hydride NHPh.CO.NHC, H₁₁. [193°]. Formed from (a)-naphthylamine tetrahydride and phenyl cyanate (Bamberger, B. 21, 1794). Needles.

u-Phenyl-(β)-naphthyl-urea

NH ... CO.NPh.C in H .. [190"]. Formed by heating NPh(G₁₀H₂).COOl and alcoholic NH, at 130° (Kym, B. 23, 426). Needles, sl. sol. cold alcohol.

Phenyl-(β)-naphthyl-urea

NHPh.CO.NHC, II, [221°]. Formed from phenyl cyanate and (B)-naphthylamine (Gold-

schnidt, B. 21, 2567). Prisms (from alcohol).

Tetrahydride NHPh.CO.NHC, H₁, [166].

Formed from phenyl cyanato and the tetrahydride of (B)-naphthylamine (Bamberger a. Müller, B. 21, 859). Needles, v. e. sol. alcohol.

Phenyl-di-(B)-naphthyl-urea C_nH_{2n}N₂O i.c. NHPh.CO.N(C_nH₁). [182]. Formed from phenyl cyanate and di-(B)-naphthylamine (Gebhardt, B. 17, 3039). Formed also by heating N(C₁₀H₁)₂.COCl with aniline in CHCl₃ at 130° (Kym, B. 23, 429; Kühn a. Landau, B. 23, 811). Needles (from alcohol). By heating with aniline it is converted into CO(NHPh)2 and di-(B)naphthylamine.

Phenyl-tri-(B)-naphthyl-urea

CO(NPhC₁₀H₁).N(C₁₀H₁)₂, [168°]. S. (alcohol) 9 at 16°; S. (be zene) 4'54 at 16°. Formed from (C₁₀H₁)₂N.COCl and phenyl-(3)-naphthylamine at 260° (Paschkowezky, B. 24, 2924). Granular crystals, sl. sol. cold alcohol.

Di.phenyl. (8). naphthyl. urea NHPh.CO.NPhC, H., [133°]. Formed from NPh(C, H,). COCl and aniline (Kym, B. 23, 426). White plates, sl. sol. cold alcohol.

u-Di-phonyl-di-(β)-naphthyl-urea NPh. CO.N(C, H,), [104°]. Formed by heat

ing NPh2.COCl with (C10H2)2NH at 220° or by heating (C₀H_.)₂N.COCl with NPh_.H at 260° (Paschkowezky, B. 24, 2923). Crystalline powder, m. sol. cold alcehol.

s-Di-phenyl-di-(β)-naphthyl-urea

CO(NPh.C₁₀H₇)₂. [186°]. S. (alcohol) 1 at 18⁵°. S. (benzene) 59 at 18⁵°. Formed by heating C10H,NPh.COCl with C1eH,NPh.COCl at 2500 (P.). Polyhedral granules. Converted by HClAq at 250° into aniline, (β)-naphthol, and CO₂.

Tri-phenyl-(β)-naphthyl-ures

NPh₂CO.NPh.(C₁₀H₇). [128°]. Formed from C₁₀H₇NPh.COCl and NPh₂H at 240° (P.). Crys-

talline powder, v. sol. alcohol.

PHENYL o-NITRO-BENZYL KETONE C.H., CO.CH., C.H., NO. Nilso-dcoxybenzoin. Formed, together with the p-isomeride by nitrating phenyl benzyl ketone (Ney, B. 21, 2448). Sol. ether (difference from p-isomeride), p-isomeride yields a crystalline &xim [107°].

PHENYL p-NITRO BENZYL OXIDE C.H.,O.CH.,O.eH.,NO. [91°]. Formed from p-nitro-benzyl chloride and KOPh (Kumpf, B. 17, 1076). Plates (from alcohol).

Reference. - NITRO - PHENYL - NITRO - BENZYL

OXIDE.

PHENYL NITRODIPHENYLETHYL KE. TONE C.H. CO.CHPh.CH2.C.H4NO2. Formed from nitro-benzyl chloride, deoxybenzoïn, and NaOEt (Buddeberg, B. 23, 2071). The o-compound melts at 102' and yields diphenylquinoline [96°] (420°) on reduction. The p- isomerice melts at 112° and yields an amido-compound [141°] on reduction.

DI-PHENYL-DINITROSACYL. So-called. C₁₆H₁₆N₂O₄. [87°]. The chief product of the action of HNO₃ (S. G. 1·4) on acctophenone (Hollemann, B. 21, 860, 2835). It is accompanied by an isomeride [179°]. Crystals (from ether). Converted by acids and alkalis into benzoic and oxalic acids, NH3, and hydroxylamine. Ac₂O yields C₁₆H₁₀Ac₂N₂O₅ Aniline and benzanilide form compounds melting at 205° and 160° respectively.

DI-PHENYL-NITROSAMINE v. Nitrosamine of DI-PHENYL-AMINE.

PHENYL-NITRO-TOLYL-THIO-UREA NITRO-PHENYL-TOLYL-THIO-UREA.

DI-PHENYL-NITRO-p-TOLYL-UREA

 NPh_2 .CO.NHC₆H₃Me(NO_2) [1:4:3]. [139.59] Formed from nitro-p-toluidine and NPh COCI at 125° (Lellmann a. Bonhöffer, B. 20, 2121). Yellow needles, v. sol. chloroform and benzene.

 $\begin{array}{ccc} \textbf{PHENYL-OCTINOIC} & \textbf{ACID} & \textbf{C}_{11}\textbf{H}_{10}\textbf{O}_2 & \textit{i.e.} \\ \textbf{PhC(C_2H_2)(C_2H_2Et).CO_2H} & (310^\circ – 320^\circ). & \textbf{This} \end{array}$ appears to be one of the products of the action of CO at 170° on a mixture of NaOEt and PhCH₂.CO₂Na (M. Schroeder, A. 221, 46).

PHENYL-OCTOIC ACID. Nitrile. C.H. CHPh.CN. (2879). Formed from phenylacetonitrile, hexyl iodide, and NaOH (Rossolymo, B. 22, 1237). Oil.

DI-PHENYL-n-OCTYL TRICYANIDE C.H., C.N.Ph. [43°]. (285° at 15 mm.). Formed from C.H., COCI, benzonitrile, and AlCl, (Krafft a. Koenig, B. 23, 2384).

PHENYL-OCTYL-THIO-UREA C15H21N2S i.e. C.H., NH.CS.NHPh. [53°]. Formed from aniline and sec-octyl-thiocarbimide (Jahn, B. 8, 804).

v-PHENYL-OSUTRIAZOLE C.H.N. CH:N NPh. [224°]. Formed by warming the osotetrazone of glyoxal with FeCl, and HClAq (Pechmann, A. 262, 291). Sl. sol. water, v. sol. alcohol. HNO, yields C(NO,):N NPh [184°].

Tri-phenyl-osotriazole CPh:N NPh. [122]. Formed by heating the diphenyl-dihydrazide of beazil with alcohol at 210 (Auwers a. V. Meyer. B. 21, 2806). Wlate plates.

PHENYL-OSOTRIAZOLE CARBOXYLIC' ACID CO₂H.C=N NPh. [192°]. Formed by oxidising phenyl-methyl-osotriazole with KMnO. (Von Pechmann, B. 21, 2760). Formed also by boiling the phenyl-hydrazide of di-ni roso-acetone with NaOHAq (Pechmann, A. 262, 283). White needles, sol. alcohols not volatile with steam. Yields a nitro-compound [236°] which may be reduced to an amido-compound [252°]

Methyl ether Had. [90]. (286°).

Ethyl ether Eth. [59°]. (306°).

Mide C.N., IPP. CONH... [143.5°]. Formed

by boiling the phenyl-hydrazide of acetyl-di-nitroso-acetone with Na₂CO₄Aq (P.). Needles.

Nitrile C.HN, Ph.CN. [94 5]. (191° at 60 mm.). Formed by the action of NaOH on the phenyl-hydrazide of di-nitroso-acetone (Pechmann, A. 262, 297). Plates, v. sol. ether. H2S and alcoholic NH3 convert it into the thio-amide C2HN3Ph.CS.NH2 [1323].

Phenyl-osotriazole dicarboxylic acid

C(CO.H):N NPh. [256°]. Formed by oxidising: phenyl-di-methyl-osotriazole with KMnO, (Pechmann, A. 262, 311). Crystalline powder. After fusion it melts at 184°.—CaA": needles.—Ag.A".

PHENYL-OSOTRIAZOLE CARBOXYLIC ALDEHYDE C(CHO):N NPh. [70°]. Formed by boiling its oxim with dilute H.SO. (Peclimann, A. 262, 294). Insol. cold water.

Oxim C2HPhN3.CH:NOH. [115°]. A product of the action of alkalis on the compound! CH(NOH).C(N2HPh).CH(NOAc).

Phenyl-hydrozide C.HPhN, CH:N, HPh. [118°-140°]. Plates, v. sol. alcohol.

PHENYL-OSOTRIAZYL ALCOHOL

CH₂(OH).C=N>NPh. [67°]. Formed, together with the carboxylic acid, by warming the aldehyde with conc. NaOHAq (Pechmann, A. 262, 296). Prisms, v. e. sol. alcohol, sl. sol. cold Aq.

PHENYL-OSOTRIAZYL-AMINE C.H., N. i.e. CH₂(NH₂).C=N CH:N>NPh. (233° at 100 mm.).

Formed from C₂HPhN₂.CS.NH₂, by treatment in alcoholic solution with Zn and HCl (Pechmann, A. 262, 300). — B'HCl. [229]. Tables. — B'₂H₂PtCl₃. Prisms. — Di-thio-carbamate. [123°]. Tables.

PHENYL-OXALACETIC ETHER C, H16O, i.e. CO2Et.CO.CHPh.CO2Et. Formed by the action of Na on a mixture of oxalic ether and phenylacetic ether (Wislicenus, B. 20, 591; A. 248, 339). Oil, decomposed by distillation, v. sol. alkalis, FeCl, colours its alcoholic solution red. Boiling

dilute H2SO, gives CO, and phenyl-pyruvic acid [155°].

Phenyl-hydrazide CO.Et.C(N.HPh).CHPh.CO.Et. [70°]. Needles

(from dilute alcohol), v. sol. ether.

Ethyl ether of the semi-nitrile
CN.CHPh.CO.CO.Et. [130]. Formed from phenylacetonitrile, oxalic ether, and Na or NaOEt (Erleneneyer, jun., B. 22, 1483). Plates. FeCl, colours its alcoholic solution green.

PHENYL-OXAMIC ACID t. OXALIC ACID. PHENYL-OXAMIDE v. OXALIC ACID. PHENYL-OXAMIDE CARBOXYLIC ACID v.

OXALIC ACID.

PHENYL-OXANTHRANOL C20II,4O2 C.H. (CPh(OH) C.H. [2080]. Formed by oxidation of phenyl-anthranol with K.Cr.O. and HOAc (Bacyer, A. 202, 58). Colourless tables, insol. water, sol. alcohol. Conc. H.SO, forms a purple solution. Reduced by zinc-dust and HOAc to phenyl-anthranol. Benzene and II SO, form crystalline CaH, O.

Acetyl derivative C. H13AcO. [1960]. Reference. —DI-CHLORO- and OXY-PHUNYL-

OXANTHRANOL.

PHENYL-OXAZOLE C.II, NO i.e.

CPh ≪ N :CH. [6°]. (221°). Formed by heating bromo-acetophenone with formamide at 140° (Lewy, B. 20, 2578; Blümlein, B. 17, 2580).— B'HCl. [80'].— $B'_2H_2PtCl_2$ 2aq; yellow needles. Di-phenyl-oxazole $CPh \in \stackrel{GH,O}{N}$:CPh. [103'].

(339°). Formed by heating a-bromo-aceto-phenone with benzamide at 145° (B.; L.). Plates (from alcohol). –B'HCl. Needles.

Phenyl-iso-cxazole CII Formed from the oxim of benzeyl-acetic aldehyde and AcCl (Claiserfa, Stock, B, 24, 134).

PHENYL-OXAZOLE DIHYDRIDE C, II, NO.

i.e. CH₂ CH₂O_N (213°). Formed by warming bromo-ethyl-benzamide with alkalis (Gabriel a. Heymann, B. 23, 2495). Liquid, smelling like phenyl-thiazole dihydride. Miscible with alcohol and ether, sl. sol. water. IBrAq forms bromocthyl - benzamide and CH₂(OB₂),CH_NH_{...}
B'₂H₂PtCl₆.—B'₂H₂Cr_.O₇.—B'C₄H₄N₄O₇. [177].

DI-PHENYL OXIDE C₁.H₁₀O i.e. Ph₂O. Mol.

w. 170. [28°]. (253°). μ_{A} —15675 at 25°.

Formation.—1. By distilling cupric benzoate (List a. Limpricht, A. 90, 190).—2. By warming diazobenzene sulphate or chloride with phenol (Hofmeister, B. 3, 747; A. 159, 201; Hirsch, B. 23, 3709). -3. By heating phenol with ZnCl. at 350°, the yield being 6 p.c. (Merz a. Weith, B. 14, 187).-4. By heating phonol with AlCl, (M. a. W.) .- 5. Together with diphenylene ketone oxide and a body melting at 111°, by distilling sodium salicplate with phenyl phosphate (R. Richter, J. pr. [2] 28, 273).

Preparation .- By distilling Al(OI'h), (Glad-

stone a. Tribe, C. J. 41, 6).

Properties. Prisms (from cold alcohol), smelling like geraniums, almost insol. water and KOHAq. Conc. H₂SO, forms O(C₄H₄SO₂H)₂, which forms Na₂A" xaq, BaA", and Ag,A".

References .- DI-AMIDO-, DI-BROMO-, and DI-MITEO- and DI-OXY- DIAMENYL OXIDE.

PHENYL-OXY-ACETAMIDINE v. MANDEL-AMIDINE.

PHENYL-OXY-ACETIC ACID v. Manuelio ACID.

DI-PHENYL-OXY-ANGELIC ACID v. Dihydro-conviculatio acid

nyaro-connectant acid.

PHENYL p-OXY-BENZYL KETONE

Call, CO.CH., C.H., OH. [129°]. Formed from CII, Bz.C., H., NH. by the diazo-reaction (Ney, B. 21, 2419). White spangles (from water).

Acityl derivative. [87°]. Plates.

Isomeride v. Benzoin.

PHENYL-OXY-BENZYL-UREA C, H, N,O, i.e.[12]C₄H₄(OH),CH₂NH+CO,NHPh. Formed by warming C₄H₄(OH),CH₂NH, with phenyl synate and benzene. Needles, sdl. alcohol and ether.

Methyl derivative

Methyl Cervolive
[1:2]C_H_(OMe).CH_MH.CO.NHPh. [145°].
Formed from C_H_(OMe).CH_NH, and phenyl
cyanate (Goldschmidt a. Ernst, B. 23, 2743).
PHENYLOXY-BROMO-PROPIONIC ACID v.

Bromo-oxy-phenyl-propionic acid

PHENYL OXYBUTYL KETONE C,1H,1O, i.e. C.H.CO.CH...CH...CH...CH...OH.. [41°]. Formed by boiling the anhydride of its carboxylic acid with water (Perkin, jun., C. J. 51, 733; 57, 310). Iridescent plates, v. sol. alcohol. If left to stand over H.SO, it is converted into the anhydride.

Oxim C, H, C(NOH), C, H, OH. [57]. Minute

plates, sl. sol. ligroin.

Anhydride C₁₁H₁₂O i.e. CH CH₂CH₂>O. | (250° at 720 mm.). Formed by heating its carboxylic acid at 200° (Perkin, B. 16, 1792; 19, 2559; C. J. 51, 730). Oil. Converted by HBrAq into phenyl bromo-butyl ketone.

PHENYL OXY-BUTYL KETONE CARB. OXYLIC ACID. Anhydride C12H12O2 i.e. CH₂ $\stackrel{\text{C(CO_2H):CPh}}{\underset{\text{CH}_2}{\text{CH}_2}} = 0$. Benzoyl-tetramethylene carbocylic acid. Phonyl dehydrohexone carbocylic acid. [1412]. Formed by saponification of its ether, which is made by the action of trimethylene bromide on sodium benzoyl-acetic when the (Perkin, jun., C. J. 51, 726; B. 19, 2557). Monoclinic crystals, $a:b:c=2\cdot638:1:3\cdot398$; $\beta=74\cdot44'$. V. sol. alcohol and other. Converted by conc. IIBrAq in the cold into C.H., CO.C.H., Br. - CaA", -PbA": white pp. -AgA': white pp.

Ethyl ether EtA'. [60°]. Monoclinio prisms; a:b:c = 1.002:1:.591; $\beta = 68^{\circ} 34'$.

Reference .- NITRO-PHENYL OXY-BUTYL KETONE ANHYDRIDE CARBOXYLIC ACID.

PHENYL - OXY - BUTYRIC ACID v. Oxy-PHENYL-BUTYRIC ACID.

PHENYL OXY- \psi - CUMYL KETONE

C, H, CO.C, HMe, OH. [187°]. Formed by the action of nitrous acid on phenyl amido-\(\psi\)-cumyl ketone (Fröhlich, B. 17, 1806). Plates, v. sol. alcohol, sol. alkalis.

PHENYL OXYETHYL SULPHONE

C6H5.SO2.C2H4OH. Formed by heating glycolic chlorhydrin with sodium-benzene sulphinate and a little water at 120° (Otto, & pr. [2] 30, 186). Prepared by boiling C.H. (SO, C.H.) with KOHAq. Liquid, sl. sol. water, miscible with alcohol and ether. Reactions. - 1. Conc. H2SO, forms C_uH₅.SO₂.C₂H₄.O.SO₃H, which yields 3½BaA', aq, crystallising from water in needles .- 2. Sodiumamalgam reduces it to alcohol and Ph.SO.H or PhSH.-3. PCl, forms PhSO_C.H.Cl, crystallising from benzene in six-sided tablets [56°].-4. I'Cl, forms the sparingly soluble anhydride (Ph.SO, O,H), O [70°].—5. Aqueous NH, at 120° forms (Ph.SO, C,H,) NH.—6. Chromic acid

oxidises it to Ph.SO.CH.CO.H Acetyl derivative Co.H.SO. Oil. Benzoyl derivative Ph.SO.C.H.OBz

[125° PHENYL OXY . METHYL KETONE v.

BENZOVL-CARBINOL.

PHENYL - OXY - NAPHTHYL Ethyl derivative C₁₀H_a(DE).CO.C₁H₃. [75]. Formed from C₁₀H₁.OEt, BzCl, and AlCl₂ (Gattermann, B. 23, 1209). Needles.

Phenyl-di-oxy-naphthyl ketons $C_6H_5.CO.C_6H_3 < \stackrel{C(OH).CH}{C(OH).CH}$ [191°]. Formed by boiling (a)-benzoyl-naphtnoquinone with SnCl, and alcohol (Kegel, A. 247, 183). White plates.

Acetyl derivative. [155]. Plates. Isomeride v. DI-OXY-PHENY NAPHTHYL-KE-

PHENYL-OXYPHENYLBIAZYL-HYDRAZ. INE NPh.N C.NII.NHPh. [181°]. Formed by heating di-phenyl-carbazide with COCl, at 100° (Freund a. Kuh, B. 23, 2831). White crystals, insol. benzene. Oxidised by FeCl, to C,N,PhO,N:NPh [200°].

PHENYL - OXY - PHENYLTHIOBIAZYL -HYDRAZINE NPh.N C.NH.NHPh.

Formed by the action of COCl. on di-phenyl, thiocarbazide, the resulting C2N2PhSO.N:NPh [140°] being reduced by alcoholic ammonium sulphide (Freund a. Kuh, B. 23, 2827). Needles.

DI-PHENYL-DIOXYPHENYLENE KETONE v. DIOXYPHENYLENE DIPHENYL DI-

PHENYL-OXY-PIVALIC ACID v. p-oxy-PHENYL-VALERIC ACID.

PHENYL-OXY-PROPIONIC ACID v. Oxy-

PHENYL-PROPIONIC ACID.

DI-PHENYL OXYPROPYLENE DISUL-PHONE CH(OH)(CH., SO., C, H)... Formed by oxidation of the product of the action of NaSPh on dichlorhydrin (Otto a. Rössing, B. 23, 758).

Oil, v. sol. alcohol.

Benzoyl' derivative. [150]. Needles.

DI-PHENYL OXY-PROPYL SULPHONE. Anhydride (C,H,SO,CH,CH,CH,CH,)O. [85° Formed by heating di-phenyl trimethylene disulphone with alcoholic potash at 120° (Otto, B. 24, 1833). Hexagonal tables, insol. water.

PHENYL OXYTOLYL KETONE. Methyl derivative. C. II., CO.C., II., Me.OMc. [80°].
Formed from C., H., Me(OMc), BzCl, and AlCl., (Koenigs a. Carl, B. 24, 3897). Crystals.
PHENYL-OXY-VALERIC ACID v. OXY-

PHENYL-VALERIC ACID. Di-phenyl-oxy-valeric acid v. Tetrahydro-

CORNICULARIC ACID. PHENYL-PARABAMIC ACID v. PARABAMIC

PHENYL-PARACONIC ACID v. Anhydride of Oxy-BENZYL-SUCCINIC ACID and NITRO-PHENYL-PARACONIC ACID.

DI-PHENYL-PENTADECYL TRICYANIDE C₃N₃Ph₂(CH₂)₁₁CH₂. [64°]. (328° at 13 mm.). Formed by heating benzonitrile with palmityl chloride and AlCl, from 40° to 100° (Krafft a.

Hansen, B. 22, 809). Globular groups of needles (from isobutyl alcohol), v. sol. ether. PHENYL PENTADECYL KETONE

PHENYL FERMAN C₃H, CO.C₁, H₃₁. [59°]. (251° at 15 mm.). Formed from palmityl chloride, benzene, and AlCl₂ (Krafit, B. 19, 2982; 21, 2266). Plates " = lookell sol. ether. Yields benzoic and pentadecoic acids on oxidation.

Reference.—Oxy-phenyl pentadecyl ketone. PHENYL-PENTANE v. AMYL-BENZENE.

PHENYL-PENTANE DICARBOXYLIC ACID CO,H.C,H,CEt,CO,H. [198°]. Formed by the action of KOHAq upon its anhydride

CuHi CO O [53°], which is got by the action of alcoholic potash and EtI on di-oxyethyl-isoquinoline (Pulvermacher, B. 20, 2494).
Crystalline.—Ba\(\frac{1}{2}\)'.—Ag_A''; yellow powder.
Phenyl-pentane tricarboxylic \(\frac{1}{2}\)her

Thenyl-pentane tricarboxylic gher CHEt(CDL).C(CH_Ph)(CO_Et), (336° cor.), S.G. 40 1.0899. \(\text{\$\mu_n\$}\) 1.0897 at 20°. Formed from sodium butane tricarboxylic ether and benzyl chloride (Bischoff a. Mintz, B. 23, 654). Yields, on saponification, two benzyl-ethyl-succinic acids [157.5°] and [123.5°]

Phenyl-pentane tricarboxylic acid CMe₂(CO₂H), C(CH.Ph)(CO₂H)₂, [178°]. Ethyl ether Et₃A''', (337° cor.), S.G. $\frac{29}{100}$ 1 0950. $\mu_{\rm B} = 1.4831$ at 20°, Formed in like manner from isobutane tricarboxylic ether (B. a. M.). Yields, on saponification, the acid and also benzyl-di-methyl-succinic acid [155°].

Phenyl-peutane tri-carboxylic acid CHMe(CO2H).CH2.C(CH2Ph)(CO2H)2. One of the acids got by saponifying the product of the action of benzyl chloride on sodium isobutane tricarboxylic ether (Bischoff, B. 23, 1947). Plates (from water).

Di-phenyl-pentane tetra-carboxylic ether CH_(C(CO_Et)_CH_Ph),. (c. 240° at 20 mm.). Formed from disodium propane tetra-carboxylic ether and benzyl chloride (Dressel, A. 256, 191). Thick oil.

PHENYL-PENTENOIC ACID C, H, O2 i.c. H. Hydrocinnamenylacrylic Formed by reduction of phenyl-C₆H₅,C₄H₆,CO₂H₆ acid. [31°]. pentinoic acid by sodium-amalgam (Bacyer a. Jackson, B. 13, 122). Plates. Yields di-oxy-phenyl-valeric acid on oxidation by alkaline KMnO, (Fittig a. Mayer, A. 268, 51).

Dibromide. [109°]. Prisms. PHENYL-PENTINOIC ACID C11H10O2 i.e. C.H., CH:CH.CH:CH.CO.H. Styryl-acrylic acid. [166]. Formed from cinnamic aldehyde, Ac.O. and NaOAc (Perkin, C. J. 31, 403; Fittig, 268, 50). Prisms (from water). On oxidation by alkaline KMnO, it yields benzoic aldehyde and racemic and oxalic acids (Doebner, B. 23, 2374).—SrA'₂ 2aq. —Ag,A''.

Chloride C₁₂H₁₂OCl. [25°].

Amide. [186°]. Tables (from alcohol).

Di-phenyl-pentinoic acid

C.H.CH:CH:CPh.CN. [119°]. Formed from cinnamic aldehyde, phenyl-acetoritrile, and NaOEt (Freund a. Immerwahr, B. 23, 2856). Needles, v. sol. alcohol and ether.

Reference .- NIIRO- and OXY-PHENYL PEN-TINOIC ACID.

PHENYL-PHENTRIAZINE. Dihudride. $C_{\bullet}H_{\bullet} <_{CH,NPh}^{N=N}$ [128°], Formed by adding NaNO₂ to a solution of o-amido-benzyl-phenyl-hydrazine or o-amido-benzyl-aniline in HClAq at 0° (Busch, B. 25, 448). Plates, v. sol. alsohol. Salts.—B'HCl.—B'2H₂PtCl₆. [130°].—B'O₂H₁N₁O₂. [111°]. Orange-red needles. PHENYL-PHENTRIZZOLE C₁₂H₁N₁ i.s.

PHENYL-PHENTRIAZOLE C₁₂H_uN_s i.e. C_eH_i≪N_N NPh. [109°]. Occurs as a bypeoduct in the manufacture of amido-azo-benzene (Gattermann, B. 21, 1633). Formed by the action of phenyl-hydrazine on brono-di-nitro-benzene, the resulting nitro-phenyl-phentriazole [1:4:5]C_eH_z(NO_e):N_zPh being fiduced to amido-phenyl-phentriazole (183°) and NH_z then elimnated (Kehrmann a. Messinger, B. 25, 899).

Isomeride C.H. $\stackrel{\text{NPh}}{\sim}$ N. Phenyl-phenyl-ene-azimide. [90°]. Formed from o-amido-diphenylamine and nitrous acid (Schöpff, B. 23, 1843). Needles, sol. alcohol.

PHENYL-PHEN-(β)-NAPHTHACRIDINE

C_sH₄ $\stackrel{N}{\subset}_{CPh} \searrow C_{10}H_s$. [198° uncor.]. Formed by heating a mixture of phenyl-(β)-naphthylamine and benzoic acid with P₁O_s or ZnCl. (Chaus a. Richter, B. 17, 1595). Sublimes in white needles.—B'.H.2PCL: glittering vellow needles.

DI-PHENYL PHENYL ACETYLENE DI-KETONE v. Dehydro-acetofhenone-benzil, vol. i. p. 37.

Di-phenyl-diphenylacetylene diketone v. Oxylepiden, vol. iii. p. 137.

PHENYL-PHENYL-AMIDO-ACETIC ACID C₃H₁Ph.NII.CH_CO_11. Formed from p-amido-dipnenyl and chloro-accide acid (Zimmermann, B. 13, 1966). Plates (from hot water).—EtA'. [95°]. Needles (from dilute alcohol).

FHENYL PHENYL-AMIDO-ETHYL KE-TONE C,H,,CO.C,H,NHPh. [38*]. Formed from C,H,,COC.H,Br and amiline (Pampel a. Schmidt, B.19, 2896). Yellow crystals.

Acetyl derivative. [103°]. Needles.

PHENYL PHENYL-AMYL RETONE
C18H NO i.e. C. H. CO. CHPh. CH. Pr. [78?]. (330°
cor.). Formed from phenyl benyl ketone,
NaOEt, and isobutyl brounde (V. Meyer a.
Oelkers, B. 21, 1295). Needles. Yields an oxim

[118°] crystallising in prisms. • PHENYL-PHENYL-BENZAMIDINE

C₂₀H₁₆O i.e. C₃H₁Ph.CO.CH.Ph. [150²]: (above 360²). Formed from diphenyl, phenyl-acetic chloride, and AlCl₃ (Päpeke, B. 21, 1339). Plates (from alcohol). Converted by NaOEt and CSCl₂ into C₃H.Ph.CO.CPh.CS [above 220²].

PHENYL PHENYL-BUTYL KETONE

C. H. CO.CHPhBr. [33°]. (330°). Formed from sodium deoxybenzon and n-propyl bromide (Bischoff, B. 22, 346). Thread-like needles (from alcohol). Yields an oxim [100°].

Phenyl phenyl isobutyl ketone

C.H., CO.CHPhPr. [48°]. (325°). Yields an

oxim [70°] and a phenyl-hydrazide [72°].

DI.PHENYL-DI.PHENYL-OARBINOL

(C.H.Dh.,CH.OH. [151°]. S. (alcohol) 1.25; ether) 9; (ligroin) 5 at 65°. Got by reducing

the corresponding ketone with sodium-amalgam (Adam, A. Ch. [6] 15, 260; cf. Weiler, B. 7, 1189). Plates.

PHENYL-DI-PHENYL-CARBINYLAMINE
C_aH_b, C_aH_b, CHPh.NH_c... \$77°]. Got by reducing
the oxim C_aH_b, C_bH_b, C(NOH), C_aH_b by sodium
amalgam (Koller, M. 12, 518). Needles (from
ether), insol. water. Conc. ILSO, forms a deepviolet colour, becoming claret-red on warming.

-B'HQAc.[161°]. White needles (from water).

-B'HCl... [252°]. White needles.—B'HNO₃,
[211°].—B'₂HPCl_a'4aq. [191°]. Yellow needles.

-Phenyl-triphenylcarbinyl-amine

NHPh.CPh₂, [146°]. Formed from aniline and CPh Br (Elles, B. 17, 703; Hemilian a. Silberstein, B. 17, 746). Hevagonal prisms, v. sol. (Sz., Yields a enitrosamine [c. 156°] and a fetra sulphonic acid C₂, H₁₁(SO, H). N which yields easily soluble Ba₂A* and Cu₂A*.

PHENYL TRI-PHENYL-CARBINYL KE-TONE v. (β). ΒΕΝΣΡΙΝΑΡΟΙΙΝ.

• DI-PHENYL-DIPHENYLENE - DI-UREA. NHPh.CO.NH.C.H.,C.H.,NH.CO.NHPh. [above 300°]. Concentric needles (from aniline). Formed by adding phenyl cyanate (2 mols.) to an othereal solution of benzidine (Kühn, B. 18, 1478).

PHENYL PHENYL-ENNYL KETONE
C₆H₃,CO.CHPh.C₇H₁, [61°], (350°–355°),
Formed from deoxybenzoin (E. Bischoff, B. 22,
348). Yields an oxim [101°] crystallising in
long needles.

PHENYLPHENYL ETHYL ALCOHOL [1:3]C,H,Ph.CHMe.OH. [86]. Formed by reducing G,H,Ph.CO.CH, with sodium-amalgam (Adam, A. Ch. [6] 15, 257). Crystalline mass. Cannot be distilled.

DI-PHENYL DIPHENYLETHYLENE DI-KETONE CHIPhib. CHPhib.. Bidesyl. Hydrocarlepiden. [255°]. Formed as described in vol. ii, p. 139. Needles (from benzene), insol alcohol. On boiling for two hours with alcohol it changes to an isomeride [261°], sol. alcohol (Fehrlin, B. 22, 553).

Isomeride. [161]. Isobidesyl. Accompanies bidesyl when prepared from deoxybenzoïn, NaOEt, and I, or from BzCHBrPh_NaOEt, and deoxybenzeïn (Knövenagel, B.21, 1356). Prisms (from alcohol). Reacts with hydroxylamine forming C₂₀H₂N₂O₄ [110²-120"]. Cone. H₂SO₄ forms with bidesyl and isobidesyl a green solution, turning brown. NH₂ forms tetraphenyl-pytrole.

PHENYL PHENYL-ETHYL RETONE C.H., CO.CHMe.C.,H., [53?]. (318° cor.). Formel from C.H., CO.CHNa.C.,H., and MeI (V. Meyer a. Oelkers, B. 21, 1297). Needles (from alcohol). Forms an oxim [120°].

Phenyl phenyl-ethyl ketone C₅H₅,CO.CH.-CH₂-C₅H₃. [73°]. (above 360°). Formed by reducing phenyl styryl ketone with zinc-dust and HOAc (Schneidewind, B. 21, 1325). Plates (from alcohol). Yisids an oxin [87°]. Isoamyl nitrite and NaOEt form C₁₅H₁₅NO₂ [126°].

Phenyl diphenyl-ethyl ketone C.H.,CO.CHPh.CH.Ph. [120°]. Formed from phenyl benzyl ketone, NaOEt, and benzyl chloride (V. Meyer a. Oelkers, B. 21, 1300). Needles (from alcohol). Yields an oxim [208°].

PHENYL PHENYL-ETHYL KETONE CARBOXYLIC ACID C.H., CO.CHPh.CH., CO.H. [152°] (J. a. M.); [161°] (M. a. O.). Formed by oxidising dehydro-acetone-benzil with CrO, and HOAc (Japp a. Miller, B. 18, 184). Needles .--

BaA', 2aq.—AgA'. Ethyl ether Formed from Ph.CO.CHNaPh and ClCH2CO2Et (V. Meyer a. Oelkers, B. 21, 1305). When heated it yields an anhydride OCO CH₂ [152°], whence ammonia forms NH CO .CH₂ [189°]. Phenylhydrazine acting on desylacetic acid forms C₂M₁₈N₂O [110°] and (C₂M₁,N₂O)₂[243°]. The former, NHPh.N CO .CH₂? may be reduced by Na and isoamyl alcohol to NH CO—CH₂
CHPh.CHPh

[207°] Aniline converts the acid into NPh CO .CH. [190°] and

NPh CO .CH .CH .CO NPh not melted at 800°.

Phenyl phenyl-ethyl ketone carboxylic acid. Methyl other CoH_CO.CH(CO_Me).CH_Ph. C₆H₂CO.CH(ČO₂Me).CH₂Ph. (c. 253° at 50 mm.). Formed from methyl benzoyl-acetate, NaOEt, and benzyl chloride (Perkin a. Calman, C. J. 49, 155).

Phenyl di-phenyl-ethyl-ketone carboxylic acid C_{2.}H₁₆O₃ i.e. C₆H₃CO.CH_{2.}CPh_{2.}CO₄H₅ [183°]. Formed by heating the lactone of oxytri-phenyl-crotonic acid with alcoholic potash (Japp a. Klingemann, C. J. 57, 681). Plates. Reduced by boiling HIAq to tri-phenyl butyrolactone. Phenyl-hydrazine in alcoholic solution yields $C_{22}H_{21}N_{21}O$, which is reduced by Na and isoamyl alcohol to oxy-tri-phenyl-pyriole dihydride $C_{22}H_{18}NO$.—NH₄A'.—AgA'. On heating with alcohol and hydroxylamine hydrochloride it forms C₂₂H₁₇NO₂ [152°] and C₂₁H₁₇NO [143°].

Methylamide C₂₂H₁₇NO₂. [156°]. Formed

from tri-phenyl-crotolactone and methylamine.

Ethylamide. [130°]. Needles.

Phenyl tri-phenyl-ethyl ketone carboxylic

acid. Mathylamide CeH. CO.CHPh. CPh. CONHMe. [260°]. Formed by heating the lactone of oxy-tetra-phenyl-crotonic acid with alcoholic NH, Me at 100° to 200° (Klingemann a. Laycock, B. 24, 514). Plates, sl. sol. alcohol. Yields, on distillation,

NMe CO .CPh. [158°].

PHENYL PHENYL-HEPTYL KETONE C₆H₃.CO.CHPh.C₆H₃. [59°]. (345°). Needles or plates (from alcohol). Yields an oxim [89°] (Bischoff, B. 22, 347).

PHENYL-DI-PHENYL-HYDRAZINE

NHPh.NHC, H,Ph. [127°]. Formed by reducing C.H.N.C.H.Ph with ammonium sulphide (Locher, B. 21, 911). Needles or plates (from dilute alcohol). Yields a di-acetyl derivative [203°]

PHENYL-DI-PHENYL KETONE v. PHENYL-BENZOPHENONE.

PHENYL-PHENYL MERCAPTAN C12H108 i.e. C.H.Ph.SH. [111°]. Formed by educing C.H.Ph.SO.cl with tin and HCl (Gabriel a. Deutsch, B. 13, 386).—Pb(S.C.H.Ph), Reddish

brown pp.—C₁₂H₉SMe. [108°]. Needles (Obermayer, B. 20, 2927).

DI-PHENYL-DI-PHENYL-METHANE

(C₈H₄Ph)₂CH₂. [161°]. (360°). Formed from diphenyl, methylal, HOAc, and H₂SO₄ (Weiler, B. 7, 1188). Forned also from diphenyl, CH₂Cl₂, and AlCl₃; the yield being bad (Adam,

A. Ch. [6] 15, 254).
DI - PHENYL DI - PHENYL - METHYLENE DISULPHIDE CPh₂(SPh)₂. [139°]. Formed by passing dry HCl into a hot mixture of benzophenone, phenyl mercaptan, and ZnCl₂ (Baumann, B. 18, 889). Prisms (from ether).

PHENYL-PHENYL DI PHENYL ETHYL KETONE C, II, Ph.CO.CHPh.CH, Ph. [158°]. Formed from C.H.Ph.CO.CH.Ph, NaOEt, and

benzyl chloride (Papeke, B. 21, 1339). Needles (from alcohol). Yields an oxim [175°]. PHENYL PHENYL PROPINYL KETONE CARBOXYLIC ACID CPhiC.CHBz.CO.2II. [135°]. (c. 275° at 40 mm.) Formed from di-benzoylpropionic ether and alcoholic potash (Kapf a. Paal, B. 21, 1488). Yellow needles or plates, insol. water. Phenyl-hydrazine forms C.,IL,N,O [100°]. Boiling with alcohol and HClAq forms di-phenyl-furfurane carboxylic acid [217°]. Alcoholic NH, yields di-phenyl-pyrrole carboxylic

ether.—KA'2aq: yellow needles (from alcohol).
PHENYL a. PHENYL-PROPYL KETONE C₆H₅.CO.CHEtPh. [58°]. (324° cor.). Formed from phenyl benzyl ketone, NaOEt, and EtI (V. Meyer a. Oelkers, B. 21, 1299). Needles.

Yields an oxim [130°]. Phenyl phenyl-propyl ketone

C_bH₃CO.CH₂.CHPh.CH₃ or C_bH₃.CO.CMc₂Ph [70°]. (340°-345° i.V.). Formed by heating acetophenone with HI and P at 140° (Graebe, B. Plates (from alcohol), v. e. sol. other.
 PHENYL DI-PHENYL-PROPYL THIO-UREA NHPh.CS.NII.CH, CHFh.CH, 14. [129°]. Formed from di-phenyl-propyl-amine and phenyl

thiocarbimide (Freund a. Remse, B. 23, 2862). PHENYL PHENYL - PYRAZYL KETONE C₃H₂PhN₂CO.C₆H₃. [123°]. Formed by heating phenyl-pyrazole with BzCl at 245° (Balbiano, G. 19, 139). Needles (from dilute alcohol). Yields an oxim [154°] and a phenyl-hydrazide [140°].

DI-PHENYL-DI-PHENYL SULPHIDE

CaH, S i.e. (CaH, Ph) 28. [172°]. Formed by distilling Pb(S, CaH, Ph), (Gabriel a. Deutsch, B. 13, 386). Plates, sol. alcohol and ether.

Di-phenyl di-phenyl disulphide (C,H,Ph).S. [150°]. Formed by atmospheric oxidation of C_aH₄Ph.SH (G. a. D.). Needles, sol. alcohol and CS...

PHENYL-PHENYL SULPHOCYANIDE C_eH₄Ph.SCN. [84°]. Formed from Pb(SC_eH₄Ph)₂ and ICy (Gabriel a. Deutsch, B. 13, 389). White

crystals.

DI-PHENYL-DI-PHENYL SULPHONE

(C_aH₄Ph)₂SO₂. [216°]. Made by oxidising (C_aH₄Ph)₂S with KMnO₄ (Gabriel a. Deutsch, B. 13, 387). Plates, sl. sol. ether.

.PHENYL-PHENYL-SULPHONO-BENZAM-IDINE PhC(NPhH):NSO₂Ph. [139]. Formed by the action of aniline on the imido-chloride obtained from the anilide of benzene sulphonic acid by the action of PCl, (Wallach a. Gossmann, A. 214, 214). Narrow plates (from alcohol). Appears not to combine with HCl. On dry dis80, and phenyl sulphides.

PHENYL PHENYL THIOCARBIMIDE C.H.Ph.N:CS. [58°]. Formed by distilling (C.H.Ph.NH) CS with P.O. (Zimmermann, B.

13, 1964). Needles.
PHENYL PHENYL-THIO-GLYCOLLIC ACID C.H.Ph.S.CH..CO.H. [170°]. Formed from chloro-acctic acid and C.H.Ph.SNa (Gabriel a. Deutsch, B. 13, 389). Colourless crystals, sl. sol water.

Phenyl-phenyl-di-thio-di-glycollic acid C₁₂H₈(S.CH₂.CO₂H)₂. [252⁻]. Formed from C₁₂H₃S₂Pb and ClCH₂.CO₂H. Crystals.

DI PHENYL-DI PHENYL-THIO UREA $CS(NH.C_6H_4Ph)_2$ [228°]. Formed from p-amidodiphenyl and CS, (Zimmermann, B. 13, 1963). Plates.

PHENTL PHENYL DI-TOLYL CARBINYL

RETONE v. Phenyl-tolyl-pinacolin.
PHENYL-PHENYL-p. TOLYL-CARBINYLUREA NHPh.CO.NH.CHPh.C.H.Me. [206]. Formed from C₆II₁Me,CHPh.NH₂ and phenyl cyanate (Goldschmidt a. Stöker, B. 24, 2802).

PHENYL PHENYL-DI-XYLYL-CARBINYL KETONE v. PHENYL-XYLYL-PINACOLIN.

PHENYL PHOSPHATES.

Mono - phenyl di - hydrogen phosphate C.H.O.PO(OH)2. Phenyl-phosphoric acid. [982]. A product of the action of P.O. on phenol (Rembold, Z. 1866, 652; Jacobsen, B. 8, 1519; Rapp, A, 224, 157). Deliquescent needles. Partially decomposed by boiling water into phenol and phospheric acid. Yields phenol and HPO, on distillation. -CaA". -BaA": prisms.

Chloride C, H, O.POCl₂ (242°). A product of the action of POCl₃ on phenol. Formed also from Cail, O.PCl, and SO, (Anschütz a.

Emery, A. 253, 110).

Di-phenyl hydrogen phosphate (C₀H₂O)₂PO.OH. [56°] (R.). A product of the action of P₂O₂ on phenol. Formed also by boiling (PhO)₂PO (1 mol.) with aducous KOH (1 mol.) (Glutz = 143 *30°) and by January (1 mol.) (Glutz, d. 143, 193), and by decomposing the chloride with water. – BaA'₂, – AgA'. – NII₃PhA'. [c. 160°] (Wallach, B. 8, 1235).

Chloride (C.H.O).POCI. (315° at 272 mm.). Formed from phenol and POCI. Oil, slowly de-

composed by water.

Anilide (CaH5O)2PO.NHPh. [129]. Sixsided tables, v. sl. sol. water (W.).

Tri-phenyl phosphate $(C_0H_3O)_3PO$. [45°] (J.). (245° at 11 mm.) (A. a. E.) Formed, together with chlore-benzene, by the action of PCl, on phenol (Williamson a. Scrugham, C. J. 7, 240). Formed also from phenol and POCl, (Jacobsen), or PCl, (Glutz), followed by water. It is also a product of the action of water on C_oH₂O.PCl, (Auschütz a. Emery, A. 253, 110).

Preparation .- A mixture of phenol (280 pts.) and phosphorus oxychloride (150 pts.) is heated to boiling with an inverted condenser for 16 hours, the excess of phenol is removed by distillation or by shaking with dilute NaOH; the yield is 90 p.c. of the theoretical (Heim, B. 16, 1763).

Properties .- Needles, insol. water, sl. sol. alco-

hol, v. sol, ether.

Reactions. — By distillation with sodium acetate or benzoate it gives phenylacetate or benzoate. Heated with potassium sulphide it

tillation it gives di-phenylamine, benzonitrile, | yields tri-phenyl-thio-phosphate PS(OCaHa), together with phenol and some diphenyl and di-phenyl oxide. On distilling with MgO, PbO, ZnO, or CaO the chief product is phenyl, together with some diphenylere-oxide (Kreysler, B. 18, 1716). Chlorine passed into its cold ethereal solution forms (C₆H₅O)₃PCl₂ (A. a. E.).

Reference.—NTRO-PHENYL-PHOSPHATES.

PHENYL-PHOSPHINE C₈H₃PH₂. Mol. w. 110. (161°). S.G. 15 1.001. A product of the action of algohol on C₆H₅PI₃H and on C₆H₅PGl₂ (Michaelis, B. 7, 6; 10, 807; 12, 338; A. 181, 303). Pungent liquid.

Reactions. -- 1. Absorbs oxygen, forming CH₃PHCOH [70°]. --2. Sulphur at 100° forms liquid C.H.PH.S and solid (C.H.P), S [1380] .- 3.

CS, at 150° forms C II, P.S, Salts.—C, H, PH, I. Needles.—B', II, PtCl, Phenyl-di-chloro-phosphine C.H.PCl Phosphenyl chloride. Mol. w. 179. (225° cor.). S.G. § 13428 (Thorpe, C. J. 37, 347). Formed by passing benzene and PCl, through a red-hot tube. Formed also by heating HgPh2 with PCl2 at 180°, and by the action of AlCl, on a mixture of befizene and PCl₄ (Michaelis, B. 12, 1009; A. 181, 280). Pungent fuming liquid, decomposed by water into HCl and CaH PHO.OH [70°]. Chlorine forms CaH, PCl, [73°], which is split up at 180° into CaH, Cl and PCl, and is converted by water into C₆H₃PO(nH). SbCl₅ forms C₆H₄PCl₅SbCl₅, an unstable yellow crystalline powder. Br yields C₆H₄PCl₆H₇ (208°] and C₆H₄PCl₈Br₄. HI forms C₆H₄P'HI₅. H₈S yields oily (C₆H₆PS)₂ and crystalline C₂H₄m₈S₅ [198°]. S forms liquid C₆H₄PSCl₂ (270°) (Kë'iler, B. 13,

Phonyl-di-bromo-phosphine CallaPBr2. [257°]. Got from HgPh, and PBr, (Michaelis, B. 9, 519). Liquid. Br yields C, H, PBr, [207°] and

C.H.PBr.

Di-phenyl-phosphine (C,H,)2PH. (c. 280°). S.C. 10 1.07. Formed, together with the acid (C.H.) PO.OH by the action of dilute NaOHAq on (C.H.) PCl (Michaelis a. Gleichmann, B. 15, 801; Dörken, B. 21, 1508). Oil, v. sol. alcohol. Weak base. Yields (C.H.)2PO.OH on oxidation. CS, forms $(C_nH_n)_n^2H_nCS_n$ [167°]. — B'HCl. Crystalline. — B'_4H_P'LCl_6. — B'HL.

Di-phenyl-chloro-phosphine $(C_nH_n)_n^2PCl$.

(320°). S.G. 12 1 229. Formed from HgPh, and C₆H₃PCl₂ at 225° (Michaelis, B. 10, 627; 18, 2109; A. 207, 208). Formed also by heating C.H.P.Cl. in a scaled tube for 120 hours at 300° (Dörken, B. 21, 1505). Thick liquid, decomposed by water or Na.CO.Aq into (C.H.).PH and (C,H,),PO.OH. Absorbs oxygen from the air forming (C,H,)2POCl.

Tri-phenyl-phosphine P(C₆H₅)₄. [79°]. (abovo 360°) (Michaelis, B. 15, 802, 1610; A. 229, 297). Formed from C₈H₅PCl₂, bromobenzene and Na. Prepared by adding sodium to a mixture of Pol. (1 mol.) and C.H.Br (3 mols.) diluted with 4 volumes of dry ether and kept cool. The reaction is completed by boiling for 12 hours, and the ether is filtered off and evaporated to crystallisation.

Properties.—Large prisms or tables, sol. alcohol, ether, and benzene, insol. water.

weak base. Does not combine with CS₂.
Salts.—B'HI. [215°]. Prisms, sol. alcohol,
insol. water.—B'₂H₂PtCl₂.—B'HgCl₂.

by water.

Alkyto-halides .- B'Mel. [183°] .-B'MeClaq. [213°]. Crystals, v. e. sol. water and alcohol, insol. ether.—B'_Me_PtCl_. [238°]. B'Etl. [165°]. — B'PrI. [201°5°]. — B'PrI 261°1. [165°]. — B'PrI. [201°5°]. — B'PrI 261°1. [174°]. — B'CH.,Ph. [174°]. — B'CH.,Ph. [174°]. — B'CH.,Ph. [258°]. — B'CH.,Ph. [275°]. — B'CH.,Ph. [258°]. — B'CH.,Ph. [231°]. — B'2CH.,Ph. [258°]. — B'2CH.,Ph. [258°]. — B'2CH.,Ph. [258°]. — B'2CH.,Ph. [258°].

B',C,H,Sr. [aloove our].

Benzylo-nitrate B'C,H,NO. [203°]. S.

838 at 15°. Needles (from water).

Benzylo-picrate B'C,H,C,H,N,O., [448°].

Benzylo-bichromate (B'C,H,),Cr.O., Benzylo-sulphocyanide B'C,H,SCN.

[189°]. Prisms, v. sol. alcohol, sl. sol. water. Tri-phenyl-phosphine oxide (C,H,),R). [153.5°]. (c. 360°). Formed by oxidising triphenyl-phosphine with Brand NaOHAq or with conc. HClAq and KClO₂. Prisms (containing aq), sl. sol. water, v. e. sol. alcohol. Yields two trinitro-compounds [68°] and [242°], the latter of which yields a tri-amido-compound [258°], whence bromine water forms OP(C6H2Br2(NH2)), [206°]. -B'HNO. [75°]. Yellow needles, decomposed

Tri-phenyl-phosphine sulphide (C.P.,), PS. [157.5°]. Formed from Ph,P and S in CS,. Colourless needles, v. sol. alcohol, insol. water.

Tri-pkenyl-phosphine selenide (C_dH₅)₃PSe. [184°]. Formed from Ph₃P and Sc. Needles.

Tetra-phenyl-diphosphine P₂(C₃H₂), (67°), (400°). Formed from (C₃H₂)₂PCl and (C₃H₃)₂PH (Dörken, B. 21, 1509). With GS₂ at 138° it forms Ph₂PCS.8PH₂Ph₃ [157°], insol. ether. **PHENYL-PHOSPHINIC ACID** v. PHENYL-

PHOSPHITES.

Di-phenyl-phosphinic acid (C,H,)2PO.OH. [190°] (Michaelis, B. 8, 922; 11, 885; 15, 802; 18, 2113). Formed by oxidation of (CaHa) PCI or of di-phenyl-phosphine. Needles, sl. sol. cold

alcohol.—CaA', 3aq.—AgA': bulky pp.

Ethyl ether Eth'. [165°]. Need

Phenyl ether (CaH,),PO.OCaH,. Needles Phenyl ether (CaH.) PO.OCaH. [186°]. Formed by oxidising (CaH.) POCaH. (265°-270°), which is got by warming (CoHa), PCl with phenol.

Small needles, sol. hot alcohol, insol. water. PHENYL PHOSPHITES.

Mono-phenyl dihydrogen phosphite C.H.O.P(OH) Formed by adding water to C₆H₅O.PCl₂ (216°) which is got by the action of PCl₃ on phenol (Noack, A. 218, 90; Anschütz, A. 239, 310). Uncrystallisable syrup, decomposed by addition of more water into phenol and HaPOs

Isomeride C_cH,PO(OH)... Phenyl phosphinic acid. Phosphenylic acid. Benzene phosphunic acid. [158]. S. 23·5 at 15°. Formed by the action of water on C_oH,PCl, (Michaelis, A. 181, 321). Plates, sol. alcohol and ether. Yields, on

321). Plates, sol. alcohol and ether. Yields, on nitration, $C_bH_a(NO_2)PO(OH)_r$ [132°], which may be reduced to crystalline $C_bH_a(N\Pi_2).PO(OH)_r$.— NaHA"zaq. — Na,A" 12aq. — CaH,A", — CaA"2aq.—SrH,A.", 2aq.—CuA".—Fe,A", 23aq. Ethers.—Me,A.", (247°).—Et,A", (257°).
—EtHA".—Et&gA".—PhHA". [57°]. Formed from $C_bH_aPOCl_r$ by successive treatment with phenol and boiling water. Needles, sl. sol. water.—Ph.A". [63·5°]. Formed from phenol and C.H. POll.

and C.H.POl.

Chloride C₆H₂POCl₂. (258°). Formed from C₄H₄PCl₄ and water, and also from C₄H₄PCl₅ and O. Thick liquid.

Di-phenyl hydrogen phosphite (C,H,O).POH. Formed by adding a little water to the compound (C₈H₅O)₂PCl (295° at 731 mm.) which is got from phenol and PCl, (N.). Uncrystallisable. Decomposed by more water into H.PO. and phenol.

Tri-phenyl phosphite (C_aH₃O)_aP. (220° at 11 mm.). S.G. 73 1184. Formed by heating phenol (3 mols.) with PCl₃ (1 mol.) at 230° in a current of dry CO, (Noack, A. 218, 91; Anschütz a. Emery, A. 239, 311). Neutral liquid, v. sol. alcohol. Decomposed by water into phenol and $\Pi_a PO_3$. Dry bromine forms $(C_aH_aO)_aPBr_a$, which is converted by water into $(C_aH_aO)_aPO$.

PHENYL-PHTHALIDE v. Anhydride of Oxy-BENZYL-BENZOIC ACID.

Di-phenyl-phthalide i.e. $C_0H_4 < \frac{CPh_2}{CO} > 0$.

Phthalophenone. Tri-phenyl-carbinol carboxylic anhydride. [115°]. Formed by the action of AlCl, on a mixture of benzene and phthalyl chloride (Friedel a. Crafts, A. Ch. [6] 1, 523, Baeyer, B. 12, 612; A. 202, 50) or of benzene with [1:2]C, H, Bz.CO.OAc (Von Pechmann, B. 14, 1866). Got also by heating phthalyl chloride with HgPh, (Noelting, B. 17, 387). Plates (from alcohol). Insol. KOHAq, sol. boiling alcoholic potash, but reppd. by acids.

Reference. - DI-AMIDO-DI-PHENYL-PHTHALIDE.
DI-PHENYL-PHTHALIDE CARBOXYLIC ACID v. Anhydride of Tri-Phenyl-Carbinol Di-CARBOXYLIC ACID.

PHENYL-PHTHALIMIDE v. Phenyl-imide of PHTHALIC ACID.

PHENYL-PHTHALIMIDINE C, H, NO i.e. $\mathbf{c}_{_{6}}\mathbf{H}_{_{1}} < \stackrel{\mathrm{CH}_{2}}{\sim} \mathbf{NPh}$. [160°]. Got by heating phthalide with aniline at 210° (Hessert, B. 10, 1450; 11, 239; Racine, A. 239, 88). Formed also by reducing the phenylimide of phihalic acid with tin and HClAq (Graebe, A. 217, 305). Plates (from alcohol), v. 81. sol. hot water.

PHENYL-PIPERAZINE v. PHENYL-PYRAZINE HEXAHYDRIDE.

PHENYL-PIPERIDINE v. PHENYL-PYRIDINE HEXAHYDRIDE.

PHENYL-PROPANE v. CUMENE.

Di-phenyl-propane CH_((CH_Ph)₂. Di-benzyl-methane. (290°-300°). Formed by heating di-benzyl ketone with HlAq and P at 180° (Graebo B. 7, 1623). Got also from CH_Cl.CHCl.CH_Cl, benzene, and AlCl, (Claus, B. 18, 2935). Liquid.

Di-phenyl-propane CH₂Ph.CHPh.CH₃, (291°-295°). S.G. ² 996. Formed from benzene, AlCl₃, and propylene chloride or allyl chloride (Silva, C. R. 89, 606). Formed also by adding H.SO, to a cooled mixture of toluene and styrene (Kraemer, Spilker, a. Ebenhardt, B. 23,

3274). Oil, sol. alcohol and ether.
Di-phenyl-propane CMe₂Ph CMe,Ph, Formed by the action of benzene and AlCl, on CCl_Me₂ or CH₂:CCl.CH, (Silva, B. [2] 34, 674; 85, 289).

Tri-phenyl-propane C₂H₃(C₆H₃), (340°). Formed by the action of AlCl, upon a mixture of benzene and glyceryl tri-promide or tri-chloride (Claus a. Mercklin, B. 18, 2935). Oil.

PHENYL - PROPANE TRICARBOXYLIC ACID CH,Ph.C(CO,H),CH,CO,H. [168:5°]. Formed from benzyl-malonic ether, NaOEt, and chloro-acetic ether (Fittig, A. 256, 92).

Small prisms, m. sol. warm water. Vields benzyl-succinic acid [161°] when boiled with water.—Ca, Λ'', c b, aq.—Ba, Δ'', 2 l, aq.—Ag, Λ''.

Ethyl ether Et, Δ'''. (336° cor.). S.G.
19 1-1079. μ_D=1-481 at 20°. Formed from

sodium ethane tricarbexylic ether and benzyl chloride (Bischoff a. Mintz, B, 23, 653).

Di-phenyl-propane tetra-carboxylic acid. Di-nitrile of the di-ethyl ether (CO_Et)_C(CH_,C_6H_,CN)_. [86°]. Formed from sodium malonic ether and [1:2]C,H,(CN).CH,Cl (Hausmann, B. 22, 2019). Prisms.

Tri-phenyl-propane dRarboxylic Imids C₆H₄<C(C,H,) CO. [174°]. Formed from C,H, CH, CO,NH, benzyl chloride, and

NaOEt (Pulvermacher, B. 20, 210%). plates (from alcohol).

Benzyl-imide CanHanNO...

PHENYL PROPARGUL OXIDE Callato i.e. CaHa.O.CaHa. (210). S.G. 4 1.216. Formed AgA': plates (from hot water). by the action of alcoholic potash on the bromoallyl derivative of phenol (Henry, C. R. 96,

1233). Liquid.
PHENYL-PROPARGYL-UREA C, H, N, O i.e. CH:C.CH, NH.CO.NHPh. [133]. Formed from propargylamine oxalate, phonyl cyanate, and K.CO,Aq (Paal a. Hempel, B. 24, 3042). Needles.

PHENYL-PROPENYL-AMIDINE C.H. N. [58°]. Formed from propionitrile, HCl, and anilino (Michael a. Wing, 4m. 7, 72). Hexa-

gonal plates, sol. alcohol and ether. —B'.H.PtCl.,
PHENYL PROPENYL METHYL KETONE CARBOXYLIC ACID C. Higo, i.e.

CH, CO.C(CH, CO.H): CHPh. [125°]. S. 3 at 100°; 5 at 15°. Formed by boiling benzoic aldehyde with acetyl-propionic acid and NaOAc (Erdmann, A. 254, 187).—BaA', 5aq. - CdA', 2aq.

Methyl ether Med. (c. 215° at 35 mm.).

PHENYL PROPENYL SULPHIDE C.H. S.CMe:CH. (208°). Formed by heating phenyl-sulphydro-crotonic acid (Autenrieth, A. 254, 232). Yellowish oil, volatile with steam.

TRI-PHENYL PROPENYL TRISULPHONE C.H.(SO,Ph),. [226°]. Got from CHBr(CH,Br), and sodium benzene sulphinate (Stuffer, B. 23,

3). Needles, m. sol. hot alcohol. DI-PHENYL-PROPENYL-DI-UREA

CEt < N .CO.NHPh .CO.NHPh[170°]. Formed from propionamidine and phenyl cyanate (Pinner, B. 23, 2924). Needles, m. sol. alcohol. Yields diphenyl-urea [234°] when boiled for a long time with alcohol. Boiling dilute HOAc forms NHPh.CO.NH.CO.C.H., [137°].

PHENYL-PROPIOLIC ACID C, H.O. i.e.

C.H., C.C.CO.H. Mol. w. 146. [137].

Formation. -1. By the action of Na and CO. on ω -bromo-styrene (Glaser, Z. [2] 4, 328; A. 154, 140). -2. By choiling a 3-di-bromo-phenyl-propionic acid or its ether with alcoholic potash (G.; Perkin, un., C. J. 45, 173; Weger, A. 221, 70; Roser, A. 247, 138).—3. By boiling a bromocinnamic acid with alcoholic potash (G.; Bairisch, J. pr. [2] 20, 181).

Properties.—Trimetric twin crystals. Re-

duced by zinc and HOAc to cinnamic acid (Aronatein a. Hollemann, B. 22, 1181) and by sodium-amalgam to phonyl-propionic acid. Dry HCl passed through its solution in HOAc forms two chloro-cinnamic acids [142°] and [132°] (Michael, J. pr. [2] 40, 63).

Salts .- KA' .- BaA' aq: square tables .-BaA', 2aq: needles. - BaA', 3aq. - CuA', 4aq. -

AgA': sparingly soluble pp. Ethyl ether EtA'. (260°-270°).

References .-- AMIDO- and NITRO- PHENYL-PROPIOLIC ACID.

a-PHENYL-PROPIONIC ACID C,H10O2 i.e. CH₂,CHPh.CO.H. Hydratropic acid. (268°). Formed by reducing atropic acid (15 g.) with (5 p.c.) sodium-amalgam (90 g.) (Trinius, A. 227, 262; cf. Kraut, A. 148, 244; Fittig, A. 195, 165). Got also from acetophenone by treatment with HCy, the resulting CH₂-CPh(OH).CN being saponified and the oxy-phenyl-propionic acid reduced by HI and P (Janssen, A 250, 135).
Oil, with characteristic odour. Yields atrolaction acid GH_J.CPh(OH).CO₂H on oxidation by alkaline KMnO₄.—BaA'..2aq.—CaA'..3aq. — CaA'..2aq. —

Methyl ether MeA'. (221°). Ethyl ether Eth'. (230°) $(230^{\circ}).$

 $1.0147 * R_{\infty} = 83.3 \text{ (Brühl)}.$

[92°]. Plates. Formed by Amide CHMePh.CONH₂. [92° Nitrile CHMePh.CN. (232°). the action of PCl, on the amide, and from sodium phenyl-acetonitrile and McI (Oliveri, G. 18, 572).

B-Phenyl-propionic acid CII Ph.CH2.CO II. Hydrocinnamic acid. Mol. w. 150. [48.7]. (280° i.V.). H.C.v. 1,084,600. H.C.p. 1,085,500. 41.F. 105,500 (Stohmann, J. pr. [2] 40, 135). S. 6 at 20°. A product of the putrefaction of albumen, 20 g. being got from 5 kilos 61 ox-brain (Stöckly, J. pr. [2] 24, 17).

Formation.-1. By reduction of cinnamic acid by sodium-amalgam or III (Erlenmeyer, A. 121, 375; 137, 327; Popoff, Bl. [2] 4, 875; Giacosa, II. 8, 108).—2. By reducing αβ-dibromo-phenyl-propionic acid (Schmitt, A. 127, 319). 3. From ethyl-benzene vid CH_Ph.CH_Cl and CH.Ph.CH...CN (Fittig, Z. 1869, 166; A. 156, 249).- 4. By oxidising phenyl-propyl alcohol (W. von Miller, B. 9, 274).-5. By heating benzyl-malonic acid (Conrad, A. 204, 176).

Properties .- Needles (from water), sol. alcohol and other; volatile with seam. When taken internally it is secreted as hippuric acid

(E. a. H. Salkowski, B. 12, 663).

Salts. - NII₄A'. Plates, v. e. sol. water.—
CaA'₂ 1½aq.—CaA'₂2aq.—BaA'₂2aq.—PbA'₂aq.
ZnA'₄—AgA'. Phenyl-hydrazine salt: ZnA'₂.—AgA'. Phenyl-hydrazine salt [57°]; silky needles (Liebermann, B. 24, 1107).

[57°]; silky needles (Liebermann, 2. . . . , Methyl ether McA. (239° cor.). S.G. 2 1.0155. S.V. 196.0. Liquid, with peculiar odour. Ethyl ether Eth. (218° cor.). S.G. 2 S.V. 221.5 (Lossen, A. 254, 63).

n. Propyl ether PrA'. (262° oor.). S.G. 2 1.0152 (Weger, A. 221, 79). S.V. 246.

Isoamyl ether C.H., A'. (202°). S.G. 2

·981; 49 ·952 (E.,.

Benzyl ether C,H,A'. (c. 300°). S.G. 21 1 074. Formed by warming benzyl acetate with sodium (Conrad a. Hodgkinson, B. 10, 254; A. 193. 300).

Amide C.H., NO. [105°]. Formed by heating the ammonium salt at 230° (Hofmann, B. 18, 2740). Small needles.

Nitrile C.H.N. (261° cor.). S.G. 1 1.0014.

Occurs in the oil of Nasturtium officinale (Hofmann, B. 7, 520).

Di-a-phenyl-propionic acid CH, CPh, CO, H. [173°]. (above 300°). Made by oxidation of the (6)-pinacolin of acetophenone CPh.Me.CO.CH, [41°] with chromic acid mixture (Thörner a. Zincke, B. 11, 1993). Formed also by dissolving pyruvic acid and benzene in H,SO, at 0° (Böttinger, B. 14, 1595). White leaflets, sol. ether, alcohol, and hot water.—KA'—CaA'₂1½q—BaA' 2aq.—AgA': white pp.

αβ-Di-phenyl-propionic acid CH_Ph.CHPh.CO_H. [84°]. Formed by the action of sodium-amalgam on a mixture of benzylehloride and ClCO₂Et (Wurtz_BC. R. 70, 350). Got also by feducing phenyl-cinnanic acid (Oglialoro, J. 1878, 821). Needles, sl. soliling water.—CaA'₂.—PbA'₂. [146'].—AgA'. Nitrile CH₂Ph.CHPh.CN. [58°]. (c. 335°)

(Janssen, A. 250, 133).

Di-S-phenyl-propionic acid CHPh₂CH₂CO₂H. [145°]. Formed from allocinnamic acid, benzene, and H₂SO₄ (Liebermann a. Hartmann, B. 25, 960). Needles. - CaA'...

aaß-Tri-phenyl-propionic acid CH,Ph.CPh,CO₂H. [162°]. Formed by saponifying the nitrile with HOAc and fuming HClAq at 220° (Neure, A. 250, 147). White needles, v. sl. sol. water .- AgA': white insoluble powder.

8l. 80l. water.—Aga: white insolution powder.

Nitrile CH.Ph.CPh..CN. [1262]. Formed
from CHPh.CN, benzyl chloride, and NaOEL.

Tri.s-phenyl propionic acid Ph.C.CH..CO.H.

[177°]. Formed from Ph3C.CH(CO.Et)2 by boiling with alcoholic potash (Henderson, C. J. 51, 226; B. 20, 1014). Prisms (from alcohol), v. sl. sol. water.—KA'aq.—NaA'aq.—BaA'₂aq. -AgA'. Minute needles.

Ethyl ether EtA'. [81°].

References .- AMIDO-, AMIDO-SULPHO-, BROMO-, BROMO-SULPHO-, BROMO-AMIDO-, BROMO-NITO-, CHLORO-, IODO-, IODO-OXY-, NITRO-AMIDO-, NTRO-OXY-, NITRO-, OXY-AMIDO- and OXY- PHENYL-PROPIONIC ACID.

PHENYL-PROPIONIC ALDEHYDE

C.H. CH. CH. CHO. [208°]. Formed from and water (Etard, A. Ch. [5] 22, 254). Oil. Forms a crystalline compound with NaHSO₃.

Oxim. Oil. Yields a solid hydrochloride. Ac.O rapidly forms phenyl-propionitrile; hence it is a syn- oxim (Dollfus, B. 25, 1918).

PHENYL-PROPYL ALCOHOL C₉H₁₂O i.e.

CHPhEt.OH. Mol. w. 136. (216°). S.G. 1.016. Formed by reducing phenyl ethyl ketone with sodium-amalgam (Errera, G. 16, 322; cf. Barry, B. 6, 1007. Got also from benzoic aldehyde by successive treatment with ZnEt, and water (Wagner, Bl. [2] 42, 330). Yields CHPhEt.OAc (228° i.V.) and oily CHPhEtCl.

Phenyl-propyl alcohol CH_Ph.CH_CH_OH, (235° uncor.) (213° at 360 mm.). S.G. $^{\frac{30}{4}}$ 1 0079. $\mu_{\mathcal{B}}$ 1 5478. $R_{\infty} = 68.79^{\circ}$ (Brühl, A. 200, 191). Occurs in storax as phenyl-propyl cinnamate (Miller, A. 168, 202). Prepared by reducing cinnamyl alcohol with sodium-amalgam (Rüg-Heimer, B. 6, 214; A. 172, 123; Hatton a, Hodgkinson, C. J. 39, 319; Errera, G. 16, 310). Viscid oil. Heating with conc. HClAq yields CH_Ph_CH_CH_CI (219°), whence NaOEt forms CH.Ph.CH. CH.OEt (220°).

Acetyl derivative C.H.Ph.OAc. (245°).

Phenyl-isopropyl alcohol CH, Ph.CH(OH).CH3. Methyl-bensyl-carbinol. (215°). Got by reducing benzyl methyl ketone

(E.). Liquid, with pleasant odour.

Di-phenyl-propyl alcohol CH₂Ph.CHPh.CH₂OH. (301°). Formed by warming di-phenyl-propylamine nitrito (Freund a. Remse, B. 23, 2863). Oil, sol. alcohol.

PHENYL-PROPYL-AMINE $C_{\mu}H_{13}N$ CH_LPh.CH_,CH_,NH_, (222° i.V.). Formed by reducing the phenyl-hydrazide (20 g.) of cinnamic aldehyde dissolved in alcohol (300 g.) by (2) p.c.) sodium-amalgam (700 g.) and HOAc (700 g.) and hOAc (700 g.) and hOAc (700 g.) (70 g.) at about 30°, the yield being 30 p.c. of the theoretical (Tafel, B. 19, 1930; 22, 1857). Liquid, m. sol. water, miscible with alcohol and ether. Absorbs CO2 from air, forming a crystalline mass. The squeous solution is strongly alkaline B'HCl. [218°]. Plates B'H, SO. B'₂H₂C₂O₄. [156°]. Needles. — B'H₂C₂O₄.— B'₂H₂PtCl₆. Plates, sol. hot water.

Phenyl-isopropyl-amine CH2Ph.CHMe.NII2. (203°). Formed by the action of Br and KOHAq on the amide of phenyl-isobutyric acid (Edeleano, B. 20, 618). Liquid.—B',H,PtCl, Needles.

Isomeride v. CUMIDINE.

Di-phenyl-propyl-amine

CH_Ph.CHPh.CH_NH₂. (316°). Formed by reducing the nitrile (30 g.) of phenyl-cinnamic acid dissolved in alcohol by treatment with Na (75 g.) (Freund a. Remse, B. 23, 2860). Liquid, sol. alcohol. Forms with HgCl₂ a crystalline compound [107°].—B'HCl. [190°]. Needles.— Aurochloride [145°].

Di-acetyl derivative. [85°]. Needles.

PHENYL - n - PROPYL - TRIAZOLE CARB. OXYLIC ACID N.NPh C.CO2H.

Formed by sayonifying the nitrile which is made from phenyl-hydrazine dicyanide and butyric anhydride (Bladin, B. 425, 179). Cubes (from alcohol) or prisms (from benzene). -CuA', laq.-

AgA'. Bulky white pp.

A mide C₂N₃PhPr.CO.NH₂. [1225°]. The thio-amide C₂N₃PhPr.CS.NH₄ [130·5°] is got by the action of alcoholic ammonium sulphide on the nitrile.

Phenyl-isopropyl-triazole carboxylic acid N.NPh C.CO.H. [155°]. Formed in like manner (B.). Prisms. - HA'HCl. Needles. -

Thanher (D.). Trishis.—IA 170.

CuA', 2]aq.—AgA: minute tables.

Methyl ether McA'. [76°].

Amide. [128°]. Needles. The thio-amide

C.N.Ph.Pr.CS.NH. [148°], formed by the action

of alcoholic NH, and H, S on the crude nitrile,

crystallises in yellow needles. DI - PHENYL - DI-ISOPROPYL-TETRAZONE NPhPr.N:N.NPhPr. [79°]. Formed by oxidising phenyl-isopropyl-hydrazine with HgO (Michaelis a. Philips, A. 252, 281). Octahedra.

DI-PHENYL-PROPYL TRICYANIDE

CPh N:CPh N. [78.5°]. (239° at 15 mm.). Formed from benzonitrile, butyryl chloride, and AlCl, at 75° (Krafft a. Von Hansen, B. 22, 807). Decomposed by dilute H2SO, into NH2, butyric acid, and HOBz.—B',H,PtCl. Needles.

PHENYL-PROPYLENE v. ALLYL-BENZENE.

PHENYL PROPYLENE • ψ · THIO · UREA $_{\sim 10}^{10} H_{11}N_{12}S$ i.e. CHMe.S C.NHPh. [117°]. Formed from the isomeric phenyl-allyl-thio-urea [95°] and HClAq at 100° (Prager, B. 22, 2992). Oxidised by potassium chlorate and HClAq to $_{\sim}^{10} H_{\rm C} \times S_{\rm CM}$

CHMe.SO₃ C.NHPh [192°]. — B'_.H,l'tCl₈. — CH₁. — N B'C₈H,N₃O₅. [154°]. Yellow needles. D1 - PHENYL - ISOPROPYL - GLYOXALINE

TETRA - HYDBIDE GHPr NPh.QH2 [95°], Eormed from di-phenyl-ethylene-diannine and isobutyric aldehyde (Moos, B. 20, 734). Crystalline groups (from alcohol), sl. sol. water.

PHENYL-PROPYL-HYDRAZINE C, II, IN. i.e. C, II, NH. NHPr. [1582]. Formed by heating propionamide with phenyl-hydrogine (Freund, B. 21, 2461). • Plates (from chloroform).

Phenyl-isopropyl-hydrazine C₆H NPr.NH₂ (233²). Formed from sodic@n phenyl-hydrazine and isopropyl bromide (Michaelis a Philips, B. 20, 2485; A. 252, 278). B'HCl. [135²]. Crystalline. Yields a tetrazone [85²]. Phenyl-thiocarbimide forms NPhPr.NH.CS.NHPh. [416].

Acetyl derivative. [102]. Needles. DIPHENYL-PROPYLIDENE DISULPHIDE Mc.C(SPh). [56]. Formed from phenyl-mercaptan and acetone (E. Baumann, B. 19, 2804). Crystals, insol. water, v. sol. alcohol.

DI-PHENYL-PROPYLIDENE DISULPHONE Mc.C(SO,Ph)... [97-j(B.); [182°](F.). Formed by oxidising Mc.C(SPh), (Baumann, B. 19, 2810), and also by treating CH.(SPh), with NaOH and McI (Fromm, A. 253, 162). Crystals, almost insol. cold water.

PHENYL PROPYL KETONE C₁₆H₁₂O (.2. Ph.CO.Pr. Mol. w. 148. (221°). S.G. ¹² (992.

Formation. -1. By distilling calcium butyrate with calcium benzonte (Schmidt a. &ieberg, B. 6, 498). -2. By the action of AlCl, on a mixture of banzene and butyryl chbride (Burcker, Bl. 2) 37, 4). -3. By boiling benzoyl-acetic acid with dilute alcoholic potash (Bacyer a. Perkin, B. 16, 2131; C. J. 45, 181).

Properties. -- Oil. Does not unite with

Properties. — Oil. Does not unite with NaHSO₃. Oxidised by CrO₄ and H.SO₄ to benzoic and propionic acids (Pepoff, B. 6, 560), CrO Cl. forms C₁₀H₁₀O2CrO₂Cl., a brown powder. Phenyl isopropyl ketone Ph.CO.Pr. (200)—

Phenyl isopropyl ketone Ph.CO.Pr. (2009—217°). Formed by distilling calcium isobatyrate with calcium benzoate (Popoff, B. 6, 1255). Liquid. Yields benzoic acid, CO₂, and HOAc on oxidation.

Oxim.—Ph.C(NOH)Pr. [58°]. Plates (from ligroin) (Rattner, B. 20, 506).

PHENYL PROPYL KETONE CARBOXYLIC ACID v. Ethyl-benzoyl-acetic acid, vol. i. p. 482.

Phenyl isopropyl ketone o-carboxylic acid C.H.,O. i.e. Pr.CO.C.H.,CO.H. [121°]. Formed by boiling isopropylidene-phthalide with alcohol and KOHAu (Roser, B. 17, 2777). Crystals.

and KOHAq (Roser, B. 17, 2777). Crystals.

PHENYL: PROPYL METHYL KETONE
CARBOXYLIC*ACID CH.Ph.CHAc.CH...CO.7H.
[99°]. (235° at 40 mm.). Formed by reducing
benzylidene. \$\text{\text{Bacetyl-propionic acid with sodium-}}
manalgam in presence of H.SO.4 (Erdmann, A.
254, 203). Needles. It yields on oxidation

CHMe.O.CO.CO.

PHENYL METHYLENE PROPYL DI-METONE v. Butyryl-acetophenone.

PHENYL-PROPYL METHYL KETONE of CH., CO.CHMe.CH.,Ph. (239°). Formed by distilling calcium acetate with calcium phenylisobutyrate (Von Miller, B. 23, 1884). Oil.

PHENYL PROPYL METHYL KETONE CARBOXYLIC ACID r. BENZYL-METHYL-ACETO-ACETIC ACID, vol. i. p. 25.

Di-phenyl-isopropyl methyl ketone trioarboxylic acid. Ethyl ether of the dinitrile CO_E(C(CII__C_II__CN)__CO_CII__(120^3). Formed from sodium acctoacetic ether and the nitrile I1:2 CH_ClC_H_CN (Gabriel a. Hausmann, B. 22, 2018). Trisms (from alcohol).

Hexa-phonyl-isopropyl methyl ketone carboxylic acid C_eH₁₀O_ei.e. (GPh₂) C(CO.H).CO.CH₂, [160³]. Formed from sodium acetoacetic other and BrCPh₃ (Allen a. Kölliker, A. 227, 111). Crystals (from cher).

PHENYL-PROPYL-PYRAZOLE G₁₂H₁₁N₂ i.e. NPh C(G₃H₁); CH (280°). S.G. ¹⁵ 1 0435. Formed from butyryl-acetic aldehyde and phenylhydrazine (Claisen a. Stylos, B. 21, 1148).

Liquid.

PHENYL PROPYL SULPHONE Ph.SO...Pr. [44°]. Formed by the action of KOHAq at 100° on Ph.SO...CHELCO...H [124°], which is made from a-bromo-butyric acid and sodium benzene sulphinate (Michael a. Palmer, Am. 7, 67; cf. Otto, B. 21, 988). Pearly plates, v. sol. alcohol.

TRI - PHENYL - DI - PROPYL - DI - THIO-BIURET C.S.N.Ph.Pr. [154°]. Formed by the action of aniline (1 mol.) on NPhPr. CSCI (2 mols.) (Pilleter a. Strohl, B. 21, 109). Yollow needles.

PHENYL - PROPYL - THIO - CARBAMIC CHLORIDE NPhPr.CS.Cl. [36°]. Formed from propyl-aniline and CSCl, (Billeter a. Strohl, B 21, 102). Prisms (from ligroin).

DI - PHENYL - ISOPROPYL - THIO - SEMI-CARBAZIDE NHPh.CS.NH.NPhPr. [1169]. Formed from phepyl-thiocarbimide and phonylisopropyl-hydrazine (Michaelis a. Philips, A. 252, 280). Crystalline.

PHENYL-PROPYL-THIO-UBEA C₁₀H_AN_AS i.e. NHPh.CS.NHC₃H_r. [63°]. Formed from aniline and propyl-thio-carbinide and also from propyl-anine and phenyl thiocarbinide (O. Hecht, B. 23, 286). Pearly plates (from dilute alcohol).

Di-phenyl-propyl-thio-urea CSN,HPh,Pr. [1042]. Formed by heating propyl-aniline with phenyl-thio-carbimide on (Billeter a. Stroll, B. 21, 109). Needles.

Di-phenyl-di-propyl-thio-urea CS(NPhPr), [103°]. Formed from propyl-aniline and CSCL (B. a. S.). Large plates.

DI-PHENYL-PROPYL-UREA C, H, N,O i.e. NH_CO.NH.CH_CHPh.CH,Ph. [1122]. Formed from di-phenyl-propylamine hydrochloride and potassium cyanate solution (Freund a. Remse, B. 23, 2861). Needles, sol. alcohol and ether. PHENYL-PYRAZINE. Hexahydride

PHENYL-PYRAZINE. Hexahydride

NPh CH₂CH NH. Formed by heating
bromo-benzene (8 pts.) with pyrazine hexahydride (8 pts.) at 270° (Schmidt a. Wichmann,

B. 24, 8239). Thick liquid, v. sol. water.

Di-phenyl-pyrazine C16H12N2, i.e.

N≪CH:CPh CPh.CH≫N. Iso-indole. [196° cor.]. V.D. 7.95 (Treadwell a. Meyer, B. 16, 342). Formed by the action of cold alcoholic NH. on w-bromo-acetophenoneor on amido-acetophenone (Staedel a. Kleinschmidt, B. 11, 1744; 13, 837; Möhlau, B. 18, 163; Wolff a. Röders, B. 20, 432; Goodeckeneyer, B. 21, 2637). Broad yellow needles (from alcohol). — B'_4H_PtCl_e. Bronzed plates (from HClAq) quickly decomposed by water.

Hexahydride C₁₆H₁₈N₂. [109°] and [123°]. Formed by reducing di-phenyl-pyrazine with Na and isoamyl alcohol. Occurs in two forms. The (a)-variety [123°] crystallises from ligroin in white needles, and yields Bέ 2HCl [c. 310°], B'H,PtCl₂ laq, and a hitrosamine C_h.H_{1c}N_cO_s [143°]. The (β)-variety [109°] crystallises from alcohol in white needles and yields B" 2HCl [c. 295°] and B"H2PtCl, 2aq.

Di-phenyl-pyrazine N CPh.CPh N. [119]. (c. 340°). Formed by distilling the dihydride (M.). Needles (from ligroin), ppd. by adding water to its solution in HClAq. B',H,PtClo

Dihydride N\left\(\frac{CPh.CPh}{CH_2.CH_2}\right\)N. [181°]. Formed by boiling benzil with ethylene-diamine and alcohol (Mason, B. 20, 268; C. J. 55, 97). Prisms (from alcohol), insol. water. Split up by HClAq into the parent substances.

Di-phenyl-pyrazine. Hexahydride .v. DI-PHENYL-DI-ETHYLENE-DIAMINE.

Tetra - phenyl - pyrazine $N \leqslant_{\mathrm{CPh,CPh}}^{\mathrm{CPh;CPh}} N$. Di - tolane - azotide. [241°] (P.); [247°] (G.). Formed by heating benzoïn with ammonium acetate (vol. i. p. 477). Formed also by reducing the di-oxim of di-phenyl-glyoxal in alcoholic solution by sodium-amalgam (Polonowska, B. 21, 489), and by heating benzoic aldehyde with CPhH(NH.).CPhH(NH.) (Grossmann, B. 22, 2302). White needles (from HOAc), v. sl. sol. alcohol. Conc. H.SO, gives a blood-red colour

PHENYL-PYRAZOLE C,H,N, i.e. NPh.CH N-4-CH CH. [11°]. (247° cor.). 1.113. Formed by boiling epichlorhydrin with phenyl-hydrazine and benzene (Balbiano, G. 17, 176; 18, 354). Got also by distilling its tricarboxylic acid (Knorr a Laubmann, B. 22, 180). Oil, sol. alcohol and ether. - B'aH PtCl 2aq: needles, decomposing at 175°.

Ethylo-iodide B'Etl. [117°]. Prisms.

Dihydride NPh.CH₂ CH₂ [52°]. (274° at 754 mm.). Formed from phenyl-hydrazine (120 g.) dissolved in ether (600 g.) by addition of arcolein (50 g.) in ether (100 g.) (Fischer a. Knoevenagel, A. 239, 196). Sl. sol. hot water, Knoevenagel, A. 239, 196). Sl. sol. hot water, v. sol. alcohol, ether, and benzene. Sl. sol. dilute acids, sol. conc. HCl. May be distilled with steam: K.Cr.O, colours its solution in dilute H.SO, reddish violet, or, in very dilute solutions, blue. Gives no indole derivative when fused with ZnCl,.

Reference. — DI-BROMO-PHENYL-PYRAZOLE DI-

165 mm.). Formed from tri-methylene bromide, sodium phenyl-hydrazine, and benzene (Michaelis a. Lampe, B. 24, 3738). Liquid. -B'C, H, N,O, Short yellow needles.

Di-phenyl-pyrazole C, H,2N, i.e.

CH :CH NPh or CH:CPh NPh. [56°]. (336°). Formed by distilling its carboxylic acids (Beyer a. Claisen, B. 20, 2187; Knorr a. Laubmann, B.

21, 1212; 22, 176). White crystals.

**Dihydride ClaHaNa, [136]. Formed by reducing the base. Small needles. An isomeric or identical body [138], got by distilling the state of the control of the contr phenyl-hydrazide of cinnamic aldehyde; differs by fluorescing slightly in alcoholic solution.

Tri-phenyl-pyrazole C₂₁H₁₆N₂. [206²]. A product of the action of phenyl-hydrazine on anhydro - acetophenone-benzil (Japp a. Klinge-mann, C. J. 57, 709). Stellate groups of needles.

Tri-phenyl-pyrazole CH : CPh NPh. [138°]. Got by warming CH Bz, with phenyl-hydrazine (Knorr a, Laubmann, B. 21, 1205). Plates (from ether). Weak base.

Methylo-iodide B'MeI. [176°].

Dihydride CH NNPh. [135°]. Got by reduction or by warming benzylidene-acetophone with phonyl - hydrazine and alcohol. Yields C., H., Br., N., [179°].

PHENYL-PYRAZOLE CARBOXYLIC ACID C₁₀H₈N₂O₂. [220°]. Formed by distilling the tricarboxylic acid (Knorr a. Laubmann, B. 22, 180). Needles (from Aq), v. sol. alcohol, sl. sol. ether. May be sublimed. AgA': amorphous pp. Phenyl-pyrazole dicarboxylic acid

^{V(CO₂H);N} NPh. [256°] (B.); [266°] (C. ▲ R.). Formed by oxidising phenyl-di-methyl-pyrazole or phenyl-methyl-pyrazole carboxylic acid with alkaline KMaO, (Balbiano, R. 23, 1449; Claisen a. Roosen, / 21, 1892). Small white plates in spherical groups (from alcohol).—
(NH₁)A". [212"].—PbA".—AgA".

Methyl ether McA". [128"].

Amide Can HPh(CO.NH.). [190°] Phenyl-pyrazole tri-carboxylic acid

CO.H.C. N. NPh. [184°]. Formed by oxidising phenyl-methyl-pyrazole dicarboxylic acid with alkaline kMnO4 (K. a. L.). White needles (containing aq) (from ether), sol. water and alcohol.—BaHA" aq: plates.

Di-phenyl-pyrazole carboxylic acid CPh NNPh C16H12N2O2

CO.H.C.—NNPh. Got by saponification of its ether, which is obtained by boiling benzoylpyruvic ether CH2Bz.CO.CO2Et (20 pts.) with HOAc (100 pts.) and phenyl-hydrazine (10 pts.) (Beyer a. Claisen, B. 20, 2185). Crystals (containing EtOH), which melt at 185°, v. sol. acctone.

Ethyl ether Eth. [90°] (c. 400°).
Di-phenyl-pyrazole dicarboxylic acid

C₁,H₁₂N₂O₄ i.s. CO₁H.C.C(CO₁H) NPh. [218°]. Got by oxidation of di-phenyl-methyl-pyrazole carboxylic acid (Knorr a. Laubmann, B. 22, 175). Tetra-hydride NPh.CH, CH, (210° at NH,HA". [c. 270°]. Bad" aq. —CaA" 2aq.

References .- OXY- and OXY-AMIDO- PHENYL-PYRAZOLE CARBOXYLIC ACID.

DJ-PRENYL-PYRAZOLONE Oxy-Di-PHENYL-PYRAZOLE PHENYL PYRAZYL METHYL C,N,H,Ph.CO.CH, [122° cor.]. KETONE Formed by heating v-phenyl-pyrazole with AcCl at 150° (Balbiano, G. 19, 136). Small needles. Vields an oxim [131°] and a phenyl-hydrazide [144°].

TETRA - PHENYL - PYRIDAZINE DIHY. DRIDE C22H22N2 i.e. CH.:CPh:NPh ? Formed from desyl-acetophenone, phenyl-hydrazine, and HOAc (Smith, C. J. 57, 649). Yellow needles (from alcohol), v. sol. hot HOAc. According to Klingemann (A. 269, 106), this body is probably phenyl-amido-tri-phenyl-pyrrole, since on boiling with HOAc A yields tetra-

phenyl-pyrrole.

(a)-PHENYL-PYRIDINE $N < \stackrel{CPh.CH}{\leftarrow} CH$: (270°). A product of the distillation of its dicarboxylic acid with lime (Skraup a. Cobenzl, M. 4, 472). Heavy oil. Yields picolinic acid on oxidation.—B'.H.PtCl, 2aq. -Pi crate [c. 170°].

 $N \!\! < \!\! \stackrel{\mathrm{CH.CPh}}{<\!\! \mathrm{CH:CH}} \!\! > \!\! \mathrm{CH}.$ (B)-Phenyl-pyridine (270°). Formed by distilling its carboxylic acid with lime (Skraup a. Cobenzl, M. 4, 453). Got also by heating pyrrole with henzylidene chloride and NaOEt (Ciamician a. Silber, B. 20, 191). Heavy oil. Yields nicotinic acid on oxidation. — B'_II_PICI_3tq. — B'C_II_N_O, [163°]. Groups of yellow needles.

 $N \leqslant_{\mathrm{CH:CH}}^{\mathrm{CH.CH}} \geqslant_{\mathrm{CPh.}}$ (γ)-Phenyl-pyridine [78°]. (275° uncor.). Formed by distilling its tetra-carboxylic acid with lime (Hantzsch, B. 17, 1518). Plates (from water). Yields iso. 17, 1310. Tates (from water). Helds 180 micotinic acid [304°] on oxidation.—3k'_4H_PtCl_.

B'_4H_PtCl_.

Picrate. [196°]. Yellow needles.—
Picrate. [196°]. Yellow needles.

127 mm. Got by reducing the lower (Relly R.

727 mm.). Got by reducing the base (Bally, B. 20, 2590). Strong base, almost insol. water.—B'HCl. Needles.—B'₂H₂PtCl₂. [204°-207].

v-Phenyl-pyridine hexahydride

NPh CH₂CH₂CH₂ Phenyl-piperidine. (249°). Formed by heating piperidine with iodobenzene or bromo-benzene at 260° (Lellmann, B. 20, 680; 21, 2279. Alkaline oil, v. sol. alcohol and ether. -B'2H.PtCl, 2aq: needles or plates. -B'H, Cr, O,: plates.

References .- AMIDO- and NITRO- PHENYL-

Di-(α)-phenyl-pyridine C₁₇H₁₃N i.e.

N CPh.CH CH. [82°] (P. a. S.); [73°] (D.). Formed by distilling its carboxylic acids with Formed by distilling its carboxylic acids with soda-lime (Panl a. Strasser, B. 20, 2764; Doebner, A. 243, 121). Yellow needles, v. sol. alcohol. Yields an oily hexahydride.— B',H,PtCl. [205°].— B'HAuCl. [202°].— B',H,Cr,O₁₁. Orange-red needles.

Methylo-iodide B'MeI. [203°]. Tri-phenyl-pyridine O₂H₁₁N. [135°]. Formed by passing NH, through acetophenone, and adding P.O. (Engler, B. 6, 639; 19, 40; A. 238, 27).— B, H,PtCl.

Reference.—Oxy-Phenyl-Pyriding.

Vol. IV.

PHENYL-PYRIDINE o-CARBOXYLIC ACID

C₁₂H₀NO₂ i.e. N CH:C(C₀H₄·OO₂H) CH.CH f185%. Formed by heating the dicarboxylic acid at 185° (Skraup a. Cobenzi, M. 4, 450). Needles, sl. sol. cold water. Yields nicotinic acid on oxidation, -CaA', 2aq: long needles, v. sol. cold water.

(a)-Phenyl-pyridine dicarboxylic acid $C_{13}H_{p}NQ_{4}$ i.e. $N \leqslant \begin{array}{c} C(C_{0}H_{4},CO_{3}H);C,CO_{2}H \\ CH \end{array}$ [280°-235°]. Formed by oxidation of (a)-naphtho-quinoline (Skraup a. Cohenzl, M. 4, 463). Minute crystals, gives off indigo-blue vapours when heated. When distilled with CaO it yields (a)-pkenyl-pyridine and the compound C, H, NO [140-142] (315°), which crystallises from alrohol in yellow plate and yields P'_H_PtCl_

Yields a di-bromo-derivative $|205^\circ|$. Salts. — CaA" 2aq. — CuA" 4aq: violet crystalline pp. — Ag.A" 1\[\]aq. — H.A" HCl. — (I\[\]A")_2\[\]_1\[\]P(C\[\]_3\]aq.

(B)-Phenyl-pyridine dicarboxylic acid

 $N \leqslant \stackrel{C(CO,H):C.C_6H_4,CO_2H[1:2]}{CH}$, [207°]. Formed

by oxidation of (B) naphthoquinoline (Skraup a. Cohenzl, M. 4, 442). Prisms (containing aq), sl. sol. cold water. Salts. — HA'HCl. sl. sol. cold water. Salts. — HA'HCl. (HA'), H.PtCl. $2\frac{1}{2}nq.$ — $K_2A''3aq.$ — KHA''2aq.— CaA" 3aq. BaA" 4]aq. - CuA" 4aq. - Cu₂H₂A"₄.

-AgH₄A"₂.

Sulphonic acid C, H, NSO, i.e. $N \leqslant C(CO,H):C.C_0H_3(SO_3H)(CO_2H)[1:2:6]$ CH . CH :CH

Formed, as well as C₁₂H₆(SO₂H)NO aq, by *xidation of (s)-naphtho-quinoline sulphonic acid with alkaline KMnO₄ (Immerheiser, B. 22, 405). Crystals (from water). - K_aA''', - Ba₂H₃A'''₄, - Pb₄A'''₂(OH)₂- Ag₃A''' (dried at 100'). The by-product C₁₂H₄(SO₃H)NO aq yields KA'aq, BaA'₂2aq, PbA'₂3aq, AgA'aq, an oxim [290'] and a phenyl-hydrazide [c. 295°].

Phenyl-pyridine dicarboxylic acid

 $N \leqslant_{CH,C(CO_2H_1)}^{CH;C(CO_2H_1)} \geqslant_{CPh,[230^\circ] \text{ (hydrated); [246^\circ]}}$ (anhydrous). Formed by heating the tetra-carboxylic acid at 170° (Weber, A. 241, 13). Greenish-yellow plates (containing aq. — CuA" 2nq ; blue pp.

 (γ) -Phenyl-pyridine tetra-carboxylic acid $N \leqslant \stackrel{C(CO_1H).C(CO_2H)}{C(CO_2H).C(CO_2H)} \geqslant CPh.$ [207°]. Formed by oxidation of the phenyl-di-methyl-pyridine dicarboxylic acid, which is got from acetoacetic ether, NH3, and benzoic aldehyde (Hantzsch, B. 17, 1515). Crystals (containing 3aq), v. sol. water. KH A aq: small prisms or pyramids, sl. sol. cold water. -Ba, (NH4)2A'v2 Gaq: minute tables. -Cu_zA'v 7aq.

Di-phenyl-pyridine (γ)-carboxylic acid N < CPh.CH > C.CO.H. [275°]. Formed by

heating (CH₂Bz)₂C(CO₂H)₂ with alcoholic NH, at 120° (Paal a. Strasser, B. 20, 2761). Needles (from alcohol). -- AgA': pp., sl. sol. hot water. Dihydride C18H13NO2 i.e.

NH CPh:CH CH.CO.H. Crystalline flakes. -NH,A'. [270°]. Formed from (CH,Bz) CH,CO,H and alcoholic NH, in the cold. Needles, v. sol. . water.

Hexahydride NH CHPh.CH CH.CO2H. [889°]. Formed,

in small quantity, when di-benzoyl-di-methylmalonic acid is heated with alcoholic NH, at 120° (P. a. S.). Crystals, v. sl. sol. water. Yields a nitrosamine [159°].

Di-phenyl-pyridine tricarboxylic acid

 $N \leqslant \frac{C(C_eH_+,CO_2H):C.CO_2H}{CPh.CH}$ [250°]. Formed by oxidising phenyl-naphthoquinoline carboxylic acid with alkaline KMnO, below 50° (Doebner, A. 249, 120). Needles (from dilute alcohol).-Ag.A'": white flocculent pp.

At 100° the chief product is phenylene phenylyridylene ketone carboxylic acid C, 11, NO [226°], which on distillation with soda-lime yields CO C.H. PhN [68°], which forms an oxim [84°]

and B'2CrO3.

Reference. - OXY-PHENYL-PYRIDINE CARBOXYLIC

PHENYL PYRIDYL KETONE C_{1.}H_nNO i.e. C_{2.}H_{5.}CO.C₅H₁N. (307°). Formed by heating its carboxylic acid (Bernthsen a, Mettegang, B.

18 carboxyno acid (Derminen a. metergeng, γ. 20, 1209). Liquid. Yields a phenyl-hydrazide [143·5°].—Β'₂H₂PtCl₂.

PHENYL (β)-PYRIDYL KETONE CARBOXYLIC ACID 0₂H₂, CO.2, H. [147°]. Formed from quinolinic anhydride, benzene, and AlCl, (Bernthsen a. Mettegang, B. 20, 1209). Prisms, v. e. sol. hot water.

DI-PHENYL-PYRONE co<ch:CPh>o.

[139.5°]. Formed by heating its carboxylic acid (Feist, B. 23, 8734). Got also by heating dehydro-benzoyl-acetic acid with HClAq at 245°. Needles resembling asbestos (from benzene). Its solution in conc. H.SO, exhibits violet fluorescence. Alcoholic NH, converts it, on heating, into oxy-di-phenyl-pyridine.
DI-PHENYL-PYRONE CARBOXYLIC ACID

CO C(CO₂H):CPh O. [201°]. Formed by

warming chloro-dehydro-benzoyl-acetio acid (1 pt.) in H.SO. (3 pts.) at 140° (Feist, B. 23, 8730). Small crystals (from benzene), v. sol. chloroforr. NH, A. [135°].—BaA', 6aq.— Ag₂A'₂AgNO₂: curdy pp.
Di-phenyl-pyrone dicarboxylic ether

CO C(CO,Et):CPh O. [140°]. Formed by allowing a mixture of cupric benzoyl-acetic ether (24 g.), COCl. (10 g.), and toluene (40 g.) to stand for six weeks (F.). Got also from acetone dicarboxylic ether, Et,O, Na, and BzCl (Dünschmann a. Pechmann, A. 261, 189). Plates, v. sol. most solvents.

PHENYL-PYROTARTARIC ACID

C.H. CH, CH (CO.H) CH .CO.H. Benzyl-succinic acid. [161°]. Got by heating phenyl-propane tricarboxylic acid and by reducing phenyl-ita-conic acid (Bischoff, B. 23, 653; Fittig a. Roeders, A. 256, 87; cf. Baeyer a. Perkin, B. 17, 449). White plates, sl. sol. cold water. hydride (102°).—BaA" laq.—CaA".—Ag₂A".

Phenyl-pyrotartaric acid
CO,H.C.H.Ph.C.H.M. CO.

CO.H.CHPh.CHMe.CO.H. Two varieties [171°] and [198°] are formed by saponifying the product of the reaction of NaOEt on a mixture of a-cyano-propionic acid and a-bromo-phenyl-

acetic ether (Zelinsky a. Buchstab, B. 24, 1877). At 320° it forms an anhydride which on treatment with water yields a mixture of the two isomeric phenyl-methyl-succinic acids.

Reference. -- Oxy-amido-phenyl-pyrotartario

PHENYL-PYROXIMIDINE DIHYDRIDE

CH₂<CH₂·O CPh. Formed from γ-bromopropyl-benzamide by shaking with hot water (Gabriel, B. 24, 3214). Liquid, sl. sol. cold water.—B'₂H₂PtCl_e. [185°].—B'C_eH₄N₃O₇. [151°].

NH CPh:CH DI-PHENYL-PYRROLE

[143°]. Formed by the action of alcoholic potash on its carboxylic ether (Paal, B. 21, 3061). Got also by heating the dicarboxylic acid C,NH,(C,H,CQ,H)2 with lime (Baumann, B. 20, 1490). Plates (from HOAc or dilute alcohol). Forms a red solution in H.SO.. Colours pinewood, moistened with HClAq, red.

Tri-phenyl-pyrrole NPh CPh.CH Formed by heating its carboxylic acid or its dicarboxylic acid $C_1NH_2Ph(C_2H_1,CO_2H)_2$ with lime (P.; B.). Needles, sl. sol. ether and alcohol.

Tri-phenyl-pyrrole NH<CPh:CPh Formed by heating desyl-acetophenone with alcoholic NH, at 150° (Smith, C. J. 57, 645). Slender needles with violet fluorescence.

Tetra-phenyl-pyrrole C28II21N i.e.

NH CPh: (Ph [214·5°]. Formed from both bidesyls by heating with alcoholic NH, at 150° (Garrett, B. 21, 3107; Fehrlin, B. 22, 553; Magnanini a. Angeli, B. 22, 855). Got also by distilling its phenyl-v-amido- derivative (Klingemann, A. 269, 122). Needles or plates.

Acety derivative. [226°]. Needles.
Tetra-phenyl-pyrole NPh CPh:CH:

[197°]. Formed by boiling desyl-acctophenone with aniline and HOAc (Smith, C. J. 57, 646). White silky needles, v. sl. sol. cold alcohol. DI-PHENYL-PYRROLE CARBOXYLIC ACID

NH<CPh:C.CO₂H [261°]. Formed by saponifring the ether, which is got by the action of alcoholic NH, or of boiling NH,OAc and HOAc on di- β -benzoyl-propionic ether (Kapf a. Paal, B. 21, 1491, 3061). Orange needles, sl. sol. alcohol.

Ethyl ether EtA'. [159°]. Needles. Amide C₁₇H₁₁N₂O. [2170]

A mude C₁,H₁,N₂O. [217].

Di-phenyl-pyrole dio-osrboxylie acid dio-osrboxylie acid dio-osrboxylie acid the constant of t tallising from HOAc.

Tri-phenyl-pyrrole carboxylic acid
NPh CPh:C.CO.H. [273°]. Formed by saponifying the ether, which is got by boiling dibenzoyl-propionic ether with aniline and HOAc (Paal, B. 21, 3061). Needles (from HOAc). Ethyl ether Eth. [170°]. Needles.

Tri-phenyl-pyrrole di-earboxydic acid

NPh C(C,H,CO,H);CH
C(C,H,CO,H);OH
[295°]. Formed ty

parming C.H.(CO.C.H.CO.H), with aniline Baumann, B. 20, 1487). Crystals, insol. water.

ig A": bulky pp. Ethyl ether Et.A". [122°]. Needles. DI - a - PHENYL - 6 - PYRROYL - PROPIONIC CID C,H,N.CO.CH, CPh, CO.H. [216°]. Formed by saponification of di-phenyl-pyrrylerotolactone CH:C(C,H,N) O [184°] which is got by warming (a)-pyrryl methyl ketone with benzil and conc. KOHAq (Angeli, B. 23, 1356). Colourless crystals, almost insol. water. - KA'. -AA': light-yellow pp.

PHENYL PYRRYL KETONE C,H,NO i.e. NC,H,.CO.C,H,. [78°]. Formed by heating pyrrole with NaOBz and Bz,O (Ciamician a. Dennstedt, B. 17, 2955). Yields Ci, H, AgNO.
PHENYL-PYRUVIC ACID v. PHENYL-GLY-

CIDIC ACID.

PHENYL-QUINAZOLINE C.H. CH:N

[101°]. Got by distilling o-amido-benzyl-benzamide (Gabriel a. Jansen, B. 23, 2810). Yellow needles. Weak base.

Phenyl-quinazoline. Dihydride.

C₁₁H₁₂N₂ i.e. C₄H₄CH NPh [95°]. Formed by reducing [1:2]C.H.(NO.).CH. NPh.CHO with zine and HClAq (Paal a. Busch, B. 22, 2686; Donner, Ph. [3] 20, 43). Six-sided tables (from ether-ligroin), almost insol. water and alkalis. Split up into aniline and benzonitrile by heating with zinc-dust .- B'HCl 2aq. [80°] when hydrawith zinc-dust.—BEG 24d, [60] when hydrated; [221°] when anhydrous. Concentrion needles, sol. water.—B'HSnOl, [130°-134°]. White crystals.—B'₂H₂PtCl_e. [208°]. Yellow crystals.—B'₂H₂SO₄2aq. [79°]. Melts at 140°-143° when anhydrous.

Methylo-iodide B'MeI. [1570°] and [180°]. -B'MeI2. [157°]. Golden plates.

Tetrahydride C.H. NIh. (117°). Got by reduction. Needles. Yields a crystal-line acetyl derivative and a brick-red nitros-

Di-phenyl-quinazoline. Dihydride. C. H. N. i.e. C. H. C. N. Ph. [115°]. Formed by reduction of the benzoyl derivative of o-nitrobenzyl-aniline in HOAc with tin and HCl (Lellmann a. Stickel, B. 18, 1608). Small needles, v. sol. alcohol. - B'HCl : silky needles.

Reference .- OXY-PHENYL-QUINAZOLINE. (B. 2)-PHENYL-QUINOLINE

ÇPĥ:CH.Ç.CH:ÇH OH :CH.C.N = CH. p-Phenyl-quinoline. [111°]. [260° at 77 mm.). S.G. 22 1.1945. Prepared by heating p-amido-diphenyl with glycerin, nitro-penzene, and H.SO, (La Coste, B. 15, 562; A. 230, 8). Trimetric plates (from ether). B'_H_Ptcl. Orange crystalline powder. — B'_H_Cr_O, [136°]. — Tartrate B'C,H_O, 3aq. 153°]. Needles

Methylo-iodide B'MeI 2aq. [194°]. Ethylo-iodide B'Etl 2aq. [169°].

Tetrahydride C.H., PhN. Got by reduction. Unstable pp. Yields a nitrosamine Z.H., Ph(NO)N [112°], an acetyl derivative [100°], and a lenzoyl derivative [137°].—B'HCl llag. 204°].—B'C., H.N., O., [165°].

(B. 4)-Phenyl-quinoline CH:CH .C.CH:CH CH:CH o Phenyl-quinoline. (273° at 80 mm.). Got in . like manner, using o-amido-diphenyl (C.). Oil, with yellowish-green fluorescence. B',H,PtCl. -B.H.Cr.O., [126°]. Orange plates.

Methylo-iodide B'Mel. [163°]. Crystals,

v. sol. water. - B'_Me_PtCl, [193°].

(Py. 1)-Phenyl-quinoline $C_vH_i < CPh:CH_N = CH$ [62°]. Got by heating its carboxylic acid (Königs a. Nef. B. 19, 2430). Needles (from ether or ligroin). Solutions of its sulphate and hydrochloride fluoresce blue. BH, CrO.: needles.-B'2122PtCl6: yellow four-sided tables.

(Py. 2) - Phenyl quinoline CaH CH: CPh Formed by adding a little NaOH to a solution of o-amido-benzoic aldehyde and phenyl-acetic aldehyde in dilute aicohol (Friedländer a. Gohring, B. 16, 4836). Oil, sparingly volatile with steam. - B'HCl. [93°]. - B'2H,PtCl.

(Py. 3) - Phenyl - quinoline CoH: CH: NCPh. [86°]. (above 360°)

Formation .- 1. By heating cinnamic aldehyde (30 pts.) with aniline (20 pts.) and conc. HClAq (20 pts.) for two hours at 210° (Grimaux, C. R. 96, 584; Doebner a. Miller, B. 16, 1665; 19, 1194). -- 2. By warming o amido - benzoic aldehyde with acetophenone, dilute alcohol, and a little NaOH (Friedländer a. Gohring, B. 16, 1835).-3. By distilling m-oxy-phenyl-quinoline or di-oxy-phenyl-quinoline with zinc-dust (Miller a. Kinkelin, B. 18, 1908; Weidel, M. 9, 151,... 4. By distilling its carboxylic acid with soda-lime (Deebner, B. 20, 280; A. 242, 294; Pfitzinger, J. pr. [2] 38, 583).

Properties. - Silky needles (from dilute alcohol), sol. ether, sl. sol. water. Yields NHB&C,H,CO2H [1:2] [182°] on oxidation by KMnO, in acid solution.

KMnO, in acid solution.

Salts.—B'.H.PiCl₀ 2aq.—B'HAuCl, [160°].

—(B'HCl).AuCl, [204°]. Needles.—B'H.Cr.O,; stable golden plates.—B'C.H.N.O, [188°].

Alkylo-todides B'McI. [197°].—B'ELI. [195°].—B'ELI. [195°].—B'ELI. [195°].—B'ELI. [197°].—God and the stable of the

reducing the base with tin and HClAq (Dochner, B. 19, 1198). Oil, yielding an oily nitrosamine. --BHCl. Needles (from alcohol), v. sl. sol. water. (Py. 1,3)-Di-phenyl-quinoline

 $C_aH_i < N - CPh$. [112°]. Formed by heating the anilide of CH₁Bz₂ with H₂SO₄ (Beyer, B. 20, 1772). Mass of white crystals. -B'₂H₂PtCl₄ 2aq. - B'H.SO. Needles, v. sl. sol. dilute H.SO. (Py. 2,3)-Di-phenyl-quinoline

 $C_sH_i < N - CPh$. [96°]. (c. 420°). Formed by reducing [1:2] CaH4(NO2).CH2.CHPh.CO.CaH4 with iron and HOAc Buddeberg, B. 23, 2075). Large crystals, sol. alcohol.—B'.H.PtCl.

(Py. 2)-PHENYL-ISOQUINÖLINI

C₁₃H₁₁N i.e. C₆H₄ CH:ÇPh. [105°]. Obtained by reduction of the (Py. 4)-chloro-derivative by heating it with HI and P at 170° for three hours; also by distilling phthalimide with zinc-dust (Gabriel, B. 18, 3477). Rhombic plates. Slightly volatile with steam.—B',H,Cl,PtCl,: needles. Tetrahydride C.H. CH. CHPh.

•48°]. Formed by reduction of an alcoholic solution of the (Py.)-mono- or di- chloro-derivatives by boiling with (3 p.c.) sodium-amalgam (Gabriel, B. 18, 3479). Crystals, v. sol. alcohol.

References. - AMIDO-, CHLORO-, CHLORO-NITRO-, NITRO-, OXY-AMIDO-, and OXY- PHENYL-OHINGLINE.

(Py. 1) - PHENYL - QUINOLINE (Py. 3)CARBOXYLIC ACID C16H11NO i.e. .

C.H. CPh:CH [171°]. Got by oxidation of phenyl - methyl - quinoline - phthalone with chromic acid mixture (Kænigs a. Nef, B. 19, 2428). Yellow needles (from dilute alcohol), sol. acids and alkalis.

acids and alkalis. (Py. 3)-Phenyl-quincline (Py. 1)-carboxylic acid $C_0H_1 < C_0(C_0 H_1) : CH = OPh$. [207°]. Formed by warming pyruvic acid with Benzoic aldehyde, aniline, and alcohol (Doebner, B. 20, 280; A. 142, 291). Formed also by heating isatin with acetophenone and alcoholic potash (Pfitzinger, J. pr. [2] 83, 538). Needles, m. sol. cold_alcohol. Yields phenyl-quinoline [84°] on distillation with soda-lime. — (HA')_H_2HCl₀. — PbA'₂aq.— $\operatorname{CuA'_2aq}$.— $\operatorname{ZnA'_2aq}$.— $\operatorname{AgA'}$: white pp. **Phenyl** - quinoline - o - di - carboxylic acid

 $C_9H_4(C_9H_8)N(CO_2H)_2$ i.e. $C_8H_4 < CPh:C.CO_2H = C.CO_2H$ Formed by oxidation of phenyl-acridine with

Salts .- BaA"4aq : glistening needles (Claus a. Nicolaysen, B. 18, 2706).

(Py. 2,3) - Di-phenyl-quinoline carboxylic acid C_sH₄ C(CO₂H):CPh . [191°]. Formed by the action of isatin and alcoholic potash on deoxybenzoïn (Pfitzinger, J. pr. [2] 38, 583). Needles, insol. water, v. sol. hot alcohol.

(Py. 3)-PHENYL-QUINOLINE (B. 2)-SUL-PHONIC ACID SO, H.C.CH.C.CH.;CH HC:CH.C.N=CPh together with the more soluble (B. 3)-sulphonic acid, by heating (Py. 3)-phenyl-quinoline with HSO₄ and SO₄ at 100° (Murmann, M. 13, 60).— H₂SO, and SO₂ at 100 (Murmann, Plates, sk-sol, water, almost insol. alcohol. Gives oxy-phenyl-quinoline [238°] when fused with potash at 250°.—BaA'2: plates.—NII,A': plates. -AgA': granules.

(Py. 3) - Phenyl - quinoline (B. 3) - sulphonic acid. Formed as above (M.). Granules. Yields oxy - phenyl - quinoline [156°] on fusion with potash. - KA'aq. - BaA', 11aq: needles. -

AgA' 1 aq: needles.

(B. 2) - Phenyl - quinoline p-sulphonic acid C13H11NSO3 i.e. [1:4]SO3H.C6H1.C:CH.C.CH:CH HC:CH.C.N=CH

Formed, together with the following more soluble isomeride, by sulphonation of p-phenyl-quinoline (La Coste a. Sorger, A. 230, 30). Needles (containing 2aq). Turns brown, without fusion, at 300°. Alkaline KMnO, gives quinolinic aoid and p-sulpl o-benzoic acid.—NH, A'. [above 310°].—

NaA'aq.— $\operatorname{HgA'}_2$: white pp.
(B. 9) - Phenyl - quinoline (β) - sulphonic acid. Formed as above. Plates (containing aq), not melted at 300°.—NH,A': small scales.

PHENYL-DIQUINOLYL-METHANE. Octohydride CHPh(CoH10N) [153°]. Formed from quinoline tetrahydride, benzoic aldehyde, and ZnCl₂ in alcohol (Einhorn, B. 19, 1243). Its

Di-phenyl-(B. 1)-quinolyl-methane
CHPh_C:CH.C.CH:CH
HC:CH.C.N=CH
104°]. Formed [104°]. Formed by Skraup's method from amido-tri-phenyl-methane (Fischer a. Fränkel, B. 19, 749; A. 241, 364). Prisms, v. sol. alcohol. Yields a nitro-derivative [213°]. -B'2H_PtCl, (dried at 100°).

DI-PHENYL-(Py. 3) QUINOLYL-UREA C,H,NNPh.CO,NHPh. [150°]. Formed by heating carbostyril with phenyl isocyanate and benzene at 220° (Goldschmidt a. Meissler, B. 23, 276). Needles (from benzene), sol. HClAq and re-ppd. by NH,.

DI-PHENYL-QUINONE C18H12O2 i.e.

CPh CO.CH CPh. [214°]. Formed by heating phenyl methyl diketone with NaOHAq and a little K_3 FeCy₈ at 100° (Müller a. Pechmunn, B. 22, 2130). Orange-yellow plates, m. sol. benzene. Zinc-dust and HOAc reduce it to di-phenylhydroquinone [219°].

DI-PHENYL-QUINOXALINE C.H. N:CPh [126°]. Formed by heating benzoin with ophenylene-diamine in the air at 165° (Fischer. B. 24, 720). Needles.

Dihydride C.H. NH.CHPh [149°]. Formed by heating benzoin with o-phonylenediamine at 165° with exclusion of air. Prisms. Its solutions in ether and benzene fluoresce yellowish-green.

Phenylo-hydroxide $C_{i}H_{4} < NPh(OH):CPh \\ CPh$ [135°].

Formed from benzil and o-phenylese-phenyldiamine (Kehrmann a. Messinger, B. 24, 1239). - C₂₈H₁₀N₂ClFeCl₃. r Golden prisms, m. sol. cold water, insol, ether. — (C₈₅H₁₉N₂Cl)₂PtCl₄. — C₂₅H₁₉N₂HgCl₃. Yellow scales.

Tri-phenyl-quinoxaline. Dileydride

C_eH₄ NPh.(HPh. [117°]. Got by heating

benzoin with a-phenylene-phenyl-diamine in a sealed tube at 175° (Kehrmann a. Messinger, B. 24, 1875). Crystalline, v. sol. ether. Its solutions fluoresce bluish-green.

Tetra-phenyl-diquinoxaline, so-called. CPh:N.C.CH:C.N:CPh CPh:N.C.CH:C.N:CPh [289°]. Formed from tetra-amido-benzene and benzil (Nietzki a Müller, B. 22, 446). V. sol. hot HOAc. Forms a blue solution in conc. H.SO.

DI-PHENYL-QUINOXALINE CARBOXYLIC **ACID** $C_{21}H_{14}N_2O_2$, i.e. $\left[4\frac{2}{1}\right]C_9H_3(CO_2H) < N:CPh$ [288°]. Formed by mixing benzil and di-amidobenzoic acid, both dissolved in hot HOAc (Zehra, B. 23, 3627). Yellow plates or needles. - BaA'₂3aq: needles, sl. sol. hot vater.

· Ethyl ether EtA'. [151°]. Needles. TETRA-PHENYL-DIQUINOXALYL C., H., N., i.e. CPh:N C.H. C.H. N:CPh. [above 270°]. Formed by mixing acetic acid solutions of benzil and tetra-amido-diphenyl {0,H₂(NH₂);[1:8:4]}, (Brunner a. Witt, #: 20, 1026). Crystals (from phenol-HOAc). Forms a bright-red solution in conc. H₂SO

16. H₂50. PHENYL SELENIDE v. Organic compounds of SELENIUM.

TETRA - PHENYL - SILICANE v. Organic compounds of Silicon

PHENYL SILICATE Si(OPh), [48°]. (420°). Prepared by heating phenol with SiCl,; the yield being 78 p.c. of the theoretical amount (Hertkorn, B. 18, 1679). Long colourless prisms, r. sol. alcohol. Decomposed by hot water into phenol and silicic acid. Boiling alcohol forms ethyl silicates and phenol.

TRI-PHENYL-STIBINE v. vol. i. p. 294 PHENYL-STYRYL-HYDRAZINE C, H16N, i.c. CHPh:CH.CH., NPh.NH₂. [54°]. Formed from styryl bromide and sodium phenyl-hydrazide (Michaelis a. Claessen, B. 22, 2239). Crystals, y. sol. alcohol and ether.

PHENYL-STYRYL KETONE v. BENZYLIDENE-ACETOPHENONE. Its carboxylic other is described as Benzylidene-benzoyl-acetic ether, vol. i. p. 481.

PHENYL - SUCCINIC ACID C10H10O4, i.e. CO_H.CHPh.CH_.CO_H. [167°].

Formation. - 1. By saponification of the nitrile which is got from ω-chloro-styrene and KCy (Rügheimer, B. 14, 428). - 2. By saponitication of the product of the action of a-bromophenyl-acetic ether on sodium acetoacetic ether (R.). - 3. At 191° from CO.H.CHPh.CH(CO.H)., got from a-chloro-phenyl-acetic ether and sodium malonic ether (Spiegel, B. 14, 873, 1693; A. 219, 32; Alexander, A. 258, 74).—4. From hydro-

cornicularic acid by potash-fusion (S.).

Properties. Needles, sol. hot water and alcohel, sl. sol. chloroform. Br and PBr, yield a bromo- derivative [119"] converted by hot water into phenyl-maleic acid.

mo pnenyi-nate and. Sulty-CaN', $Anhydride\ C_{10}\Pi_1Q_3$ [c. 54°]. (a)-Di-phenyl-succinic acid $C_{11}\Pi_1Q_4$ i.e. (C.)-H.CHPh.CHPh.CO.H. [222°] (when dry); [183°] (when hydrated). H.C. 1,848,300 (Ossipofi, C, R, 149, 223). (S. (alcohol) 41 at 21°.

Formation -1. By heating a bromo-phenylacetic acid with KCy (Franchimont, B. 5, 1048). Together with the isomeric (β) acid, by reduction of di-phenyl-maleic anhydride with sodium-amalgam or Zn and HCl. Separated through the sparing solubility of the Ba salt (Reimer, B. 14, 1802; Anschütz, A. 259, 67). 8. By heating the (B)-isomeride with barytawater at 200° (R.).

Properties. - Prisms (containing aq) or needles (from dilute HOAc). Yields di-phenyl-ethane and di-phenyl-ethylene when distilled with lime.

HClAq at 200° converts it into the (β) acid. Salts.—BaA" 2aq. S. 32 at 18°.—BaA" 4aq. -Ag₂A": white pp.

Mono-ethyl ether HEtA". [140].

Di-ethyl ether Et.A". [81]. Needles. Anhydride $C_{10}H_{12}O_3$. [116]. (240° at 11 mm.). Formed when either of the two s-diphenyl-succinic acids is heated. Got also by

heating the (a)-acid with AcCl at 120° (Till-manns, A. 258, 87). Trimetric crystals; a:b:c = 508:1: 546. V. sol. chloroform. Yields the (a) acid on boiling with water, and a mixture of (a)- acid (80 p.c.) and (β)- acid (14 p.c.) when treated with KOHAq.

Nitrile CN.CHPh.CHPh.CN. (160°1. Formed, together with the (β) - isomeride by heating phenyl-acetonitrile with mandelic nitrile and alcoholic KCy at 55° (Chalanay a. Knoevena-gel, B. 25, 289). V. e. sol. alcohol. Converted into the (B)- isomeride by boiling with HOAc.

Phenylimide C., H., NO. [231°]. Got by heating either the (a)- or the (b)- anhydride with aniline.

Phenyl - amic acid C₂H₁₀NO₄ i.e. CO.H.CNPh.CHPh.CO.NHPh. [220°]. Got by boiling the pheuylimide with baryta (Anschütz a. Bendix, A. 259, 92).

(B)-Di-phenyl-succinic acid CO.H.CHPh.CHPh.CO.H. [230°]. H.C. 1,822,900. S. (aleohol) 1924 at 215.

Formation.-1. By heating its nitrile with HelAq at 200°.-2. By reduction of di-phenylmaleic anhydride. 3. By heating the a-isomeride with HCAq at 200°.

Properties.—Needles, sol. alcohol, sl. sol. bergene, insol. water. On distillation in vacuo at 250° it yields a mixture of the (a)-anhydride (89 p.c.) and the (β)- anhydride (11 p.c.).

Reactions. 1. Yields s-di-phenyl-ethane and di-phenyl-ethylene on distillation with lime (Reimer, B. 14, 1802). 2. Baryta-water at 200° converts it into the (a)- isomeride.

Salts.--BaA" 7aq. S. 21 at c. 18°, --AgA". Ethyl ether Et, A". [141°]. Noedles.

Anhydride CHPh.CO O. Formed by heating the (B)- acid with AcCl at 100°, and also by the action of AcCl on its salts. When boiled with water it yields the (a)- acid (75 p.c.) and some (3)- acid (25 p.c.). Cold KOHAq forms only the (β) -acid. On heating with aniline

Diphensuccindone

Formed by heating the acid (5 g.) with conc. H.SO₄ (8 g.) until dissolved, and then pouring n₂, N₂ to 8.7 mm dissoived, and then pouring into water (Roser, A. 247, 153). White crystals, insol. water, sol. alcohol. Yields a dioxim C₁₀H₁₀(NOH)₂ [254°] and a phenyl-hydrazide C₁₆H₁₀(N.HPh)₂ [c. 265°]. Reduced by HI and P to C₁₀H₁₁ [100°].

Nitrile CN.CHPh.CHPh.CN. [280°], Accompanies the (a)- isomeride (v. supra). Colour-

less needles, sol. hot alcohol.

Tetra-phenyl-succinic acid CO₂H.CPh₂.CPh₂.CO₂H. [262°]. Formed by heating a chloro-di-phenyl acetic ether with finely-divided silver at 125° (Bickel, B. 22, 1538). Insol. water, v. sol. alcohol and ether.

Ethyl ether Et.A". [89°]. Nitrile CN.CPh. CPh. CN. [c. 230°]. Formed by the action of NaOEt and I on diphenyl-acetonitrile (Auwers a. V. Meyer, B. 22, 1227; cf. Anschütz a. Romig, A. 238, 849). Formed also by the action of nitrous acid on diphenyl-acetonitrile (Neure, A. 250, 148). Flat needles (from HOAc), v. sl. sol. hot alcohol. Liquefied by heating for a long time at 180°.

Phenyl-isosuccinic acid v. Benzyl-malonic

References. -- NITEO. and OXY. PHENYL-SUCCINIC ACIDS.

DI-PHENYL-SUCCINIMIDINE C, HIN, i.s. C.H. C(NH) NPh. Formed from ethylene

cyanide and aniline hydrochloride at 154° (Blochmann, B. 20, 1856). Greyish-yellow crystals, insol. water. Yields the phenylimide of succinic acid when boiled with HClAq.—B'H.PiCl.,—B'H.SO.,—B'HBr.—B'HI.

PHENYL-SULPHAMIC ACID C.H. NSO, i.e. C.H.NH.SO.H. Formed as a salt from ClSO.H (1 mol.), aniline (3 mols.) and chloroform in the cold. Got also by the action of solid fuming sulphuric acid on aniline in CHCl, at allow temperature (Wagner, B. 19, 1157; Traube, B. 23, 1655; 24, 360).—NaA'.—KA': leathets, sol. hot alcohol.—BaA', 2aq: leaflets or needles, sol. hot water. Decomposed by acids into aniline and H.SO. - NH.PhHA'. [192°]. Plates.

PHENYL SULPHATE.

Hydrogen phenyk sulphate C.H.O.SO.OH. Phenyl-sulphuric acid. Occurs in urine of horses, men, and dogs (Baumann, B. 9, 55; 11, 1907; H. 2, 335), the quantity being generally increased by administration of phenol. The K salt is formed by adding K.S.O. (125 pts.) to a solution of phenol (100 pts.) and KOH (60 pts.) in water (90 pts.) at 65°. The free seid quickly splits up, in aqueous or alcoholic solution, into phenol and H.SO. - KA'. S. 14 at 15°. Plates (from alcohol). Not attacked by potash. The dry salt changes at 150°-160° into phenol psulphonic acid.—BaA', 3aq: needles.
DI-PHENYL SULPHAZIDE v. Phenyl-

hydraside of Benzene sulphonic acid.

DI-PHENYL SULPHIDE C12H10S i.e. Ph2S.

Mol. w. 186. (293°). S.G. 1·119.

Formation.—1. By the dry distillation of

sodium benzene sulphonate (Stenhouse, Pr. 14, 351; A. 140, 288). 2. From S(C, H, NH.), by elimination of NH₂ by the diazo-reaction (Krafft, B. 7, 384, 1164).—3. By distilling Pb(Sl'h)₂ (Kekulé a. Szuch, C. R. 64, 752).—4. By the action of Na on SO(C, H₅), (Colby a. McLoughlin, Am. 9, 67) .- 5. By the action of NaSPh on C.H.N.Cl in molecular proportions (Ziegler, B. 23, 2471) .- 6. By heating benzene with S and AlCl, at 80° (Friedel a. Crafts, A. Ch. [6] 14, 438).

Preparation .- Ammonium sulphide is slowly adled to an acid solution of diazobenzene, cooled with ice, the oil which separates is cohobated for 2 or 3 hours to decompose the disulphide, and finally distilled; the yield is good (Grache a. Mann, B. 15, 1683).

Properties .- Oil, with slightly alliaceous odour, v. sol. hot alcohol, miscible with ether. Its alcoholic solution is not ppd. by AgNO, or HgCl. Yields di-phenyl-sulphone on oxidation.

Di-phenyl disulphide Ph.S. Mol. w. 218.

[61°]. (310).

Formation.—1. By oxidising phenyl mer-naptan with dilute HNO₃ (Vogt, A. 119, 142; Otto, A. 143, 213), with chromic acid mixture (Kekulé, Z. 1867, 194), and by exposure of its ammoniacal solution to air. -2. From NaSPh and CyCl (Clemm, J. pr. [2] 1, 147). -3. Together with mercury by distilling Hg(Sl^hh)₂ (Dreher a. Otto, A. 154, 178).—4. From NaSl^h and I (Hübner a. Alsberg, A. 156, 330).—5. In small quantity by adding zinc-dust to a mixture of S.Cl., and benzene (Schmidt, B. 11, 1173) .- 6.

solution of phenyl-hydrazine in benzene, and heating to boiling (Michaelis a. Ruhl, B. 23,

Properties .- Needles, with faint odour, insol. water, v. sol. alcohol and ether.

Reactions. -1. Reduced by zinc and dilute H.SO, to C.H.SH.-2. Oxidised by nitric acid to benzene sulphonic acid .- 3. Split up by long boiling into Ph.S and S (Graebe, A. 174, 189). 4 Alcoholic potash forms KSPh and C.H.SO.K. 5. Alcoholic K.S forms KSPh.-6. Bromine forms crystalline Ph.SBr.

Di-phenyl tetra-sulphide (C₆H₃)₂S₄. S.G. 145 1-297. Formed by the action of H₂S on a conc. alcoholic solution of benzene sulphinic acid (Otto, J. pr. [2] 37, 208). Formed also by the action of S₂Cl₂ on phenyl mercaptan. Thick yellow oil, m. sol. alcohol, v. sol. ether,

Di-phenyl hexasulphide (CaH,),S amorphous solid formed by heating benzene (20 g.) with S.Cl. (10 g.) and iodine (1 g.) for 100 hours at 120° (Onufrovitch, B. 23, 3368).

References .-- AMIDO-, AMIDO-IMIDO-, BROMO-, CHLORO-, CHLORO-NITRO-, IODO-, NITRO-, and OXY-DI-PHENYL SCLPHIDES. V. also DI-PHENYL-DI-PHENYL SULPHIDE.

DI-PHENYL SULPHIDE o-CARBOXYLIC ACID Calla. S.CaHa. COaH. Formed by the action of alkalis on the product of the action of NaSPh on diazotised o-amido-benzoic acid (Ziegler, B. 23, 2471). Plates (from benzene), insol. water.

PHENYL SULPHINIC ACID is BENZENE SHEDWING ACTO.

Diphenyl sulphinic acid CaH.Ph.SO.H. Got by reducing C12H2.SO.Cl in ether with sodiumamalgam (Gabriel a. Deutsch, B. 13, 388). Crys talline powder, decomposing at about 70%.

PHENYL SULPHITE (Schall, B. 25, 1490, 1875). The salt NaSO, OPh is formed from NaOPh and SO, and exhibits the following reactions :- 1. Alkyl i dides convert it into phenyl ethers of the sulphonic acids R.SO, OH. 2. Benzyl ether forms phenyl benzyl oxide, SO., and NaCl at 180° (yield 16 p.c.).—3, COCl. forms CO(OPh)., SO₂, and NaCl at 180°.—4. Ioloform (1 mol.) heated with NaSO.OPh (3 mols.) at 180° forms MeI, CH₃.SO₂.OPh, and 'rubbadin.' Rubbadin C₄₄H₃₂S₄O₃, mol. w. 830 (by Racult's

Inethod, calc. 806). Rub. crystallises from dilute alcohol in minute brownish-red plates, S. (alcohol) 43 at 20°, and forms a claret-coloured solution in alkalis. Its solution in NH, Aq dyes silk and wool pale-claret colour, and cotton yellowish-violet.

Reactions .- 1. Reduced by zinc dust and NaOHAq to C₄₄H₃₄S₃O₅.—2. Conc. HNO₃, free from nitrous fumes, at 0° forms C₄₄H₃₆(NO₂),S₃O₆, a red crystalline powder, m. sol. hot alcohol, which may be reduced to C₁₄H_{2.}(NO₂)₁(NH₂)₂S₂O₆, a glittering black crystalline powder (from ethera glittering black crystalline powder (from etherphenol) which yields a black crystalline di-acetyl
derivative.—3. HClAq at 200° forms phenol
(2 mols.), H.S (2 mols.), and C₂H₂₀S₂O₈, a
reddish-brown crystalline powder which yields
the derivatives C₂H₁₈Ac₂S₂O₈, C₂H₁₈Mc₂S₂O₈,
and C₂H₁₈Pr₄Ac₈S₂O₈.—4. Fusion with NaOH
forms SO(C₂H₄OH)₂ [96°] and salicylic acid.

Di-acetyl derivative C₄H₂₈Ac₈S₂O₈.

Der brown powder decouppessed by heat with.

Dark brown powder, decomposed by heat without previous fusion. Split up by long boiling with alcohol into O_mH_aS₁O_p, sol. alcohol

and C₂₁H₂₂S₂O₄, insol. alcohol. Br in chloro-form converts the di-acetyl derivative into C₄₄H₂₁Br₄Ac₃S₄O₅. Di-methyl-rubbadin C₄₄H₃₀Me₂S₄O₄. Got from rubbadin, KOHAq, and MeI. Dark reddish-

brown powder.

SULPHOCYANIDE C.H. SCN. PHÈNYL (231° cor.). S.G. 17.5 1.155. Formed from Pb(SPh)2 and CvCl. Prepared by adding cuprous sulphocyanide to a solution of diazobenzene sulphate and potassium sulphocyanide (Billeter, B. 7, 1753; Gattermann & Haussknecht, B. 23, 738). Liquid. Yields phenyl mercaptan when heated with alcoholic potash.

[97°]. Got from Polymeride (Ph.SCy)_s. [97°]. Got from PhSNa and cyanuric chloride (Klason, J. pr. [2]

33, 120). Prisms (from HOAc).

Reference. -- NITRO-PHENYL SULPHOCYANIDE.
PHENYL SULPHOCYANO-ETHYL KETONE C₁₀H₂NSO i.e. C₆H₅.CO.C₂H₄.SCy. Get from C.H. CO.C.H.Br and KSCr in alcohol (Pampel a. Schmidt, B. 19, 2897). Liquid.

DI-PHENYL BULPHONE (C, H,)2SO2 Sulphobenzide. Mol. w. 218. [1286]. (376°) at

722 mm.

Formation. — 1. From benzene and SO, (Mitscherlich, P. 31, 628; Freund, A. 120, 76; Otto, A. 136, 160), furning H.SO, (Berthelot, B. 9, 349), or HSO Cl (Knapp. Z. (2) 5, 41). - 2. By oxidation of Ph.S (Stenhouse, A. 140, 290; Kekulė a. Szuch, Bl. (2) 8, 204). - 3. By distilling benzene sulphonic acid (F.). - 4. From benzene, C.H.SO,Cl, and AlCl; the yield being 80 p.c. of the theoretical amount (Beckurts a. Otto, B. 11, 2066).—5. By heating benzene (200 c.c.) with conc. H2SO4 (300 c.c.), the yield being 6 p.c. of the benzene employed (Istrati, Bl. [3] 1, 492) .-6. By heating C. H. SO. Cl with HgPh, (Otto, B. 18, 248) .- 7. By oxidation of di-phenyl sulphoxide with KMnO, and HOAc (Colby a. McLoughlin, Am. 9, 67).

Properties .- Monoclinic prisms (from benzene) or plates (from alcohol), y. sol, ether. PCl, at 160° forms C₄H₃SO₂Cl and chloro-benzene. Converted by potash-fusion into phenol, diphenyl, Ph.S. PhSII, and other boules (Otto, B. 19, 2425). Hot fuming H.SO, forms benzene sul-

phonic acid.

Вкомо-, Ситоко-, References. - AMIDO-, NITRO-, OXY-AMIDO-, and OXY- DI-PHENYL SUL-

PHENYL SULPHONE ACETIC ACID v. PHENYL-SULPHONO-ACETIC ACID.

DI-PHENYL SULPHONE o-CARBOXYLIC ACID C₁₁H₁₀SO₄ i.e. C₀H₁,SO₂C₀H₁,CO₂H₂ [152°]. Formed by oxidising PhS.C₀H₁,CO₂H with 11NO₄ (Graebe a. Schultess, A. 263, 7). Needles (con-'aining aq). Melts at 99° when hydrated.

Di-phenyl sulphone p-carboxylic acid. [above 300°]. Got by oxidation of phenyl tolyl sulphone with KMnO, (Michael a. Adair, B. 11, 119). Prisms (from alcohol), sl. sol. hot water. - AgA'.

Di-phenyl sulphone di-carboxylic acid SO₂(C₂H₂,CO₂H₃)₂. [above 300°]. Got by oxidising di-p-tolyl sulphone (M. a. A.). Small prisms, sol. nitrobenzene.

DI-PHENYL SULPHONE m-SULPHONIC ACID C.H., SO. C.H., SO.H. Got by heating diphenyl sulphone (1 mol.) with HO.SO₂Cl (1 mol.) at 450° (Otto, B. 11, 2075; 19, 2417). Fibrous orystalline mass, v. sol. water. - KA'aq.

NaA' 3aq. - CaA', 7aq. - BaA', 41aq. - PbA', 31aq. -CuA'. 7 laq. Chloride.

[99°]. White needles. Amide Ph.SO. C. H. SO. NH. [154°]. Anilide. [131²]. Hard nodules. Ethers.—Eth. [89°]. -PhA. [106°]. Di-phenyl sulphone di-sulphonic acid

SO.(C.H.,SO.H). Formed from di-phenyl sulphone (1 mol.) and HO.SO.Cl (2 mols.) at Formed from di-phenyl 155° (Otto, B. 19, 3124). Deliquescent mass.

155° (Otto, B. 19, 3124). Deliquescent mass.— K_A" aq.—Na,A" 3aq.—CaA" 6'aq.—BaA" 5aq.—PbA* 3aq.—CuA" 3'aq.
—PhA* 3aq.—CuA" 3'aq.
Chloride C_{1-H}_{2-S},O_cCl.—[176°]. Plates.
Anide. [242°]. Nearly insol. ether.
Anilde. (212°]. Lustrous plates.
Ether* Et.A". [82°].—Ph_A". [195°].
DIPHENYL SULPHONIC ACID C₁₂H₁₈SO₂

E.e. C₃H₁Ph.SO₂fi. Forened, together with the disubbonic axid by heating diphenyl with 4 SO. sulphonic acid, by heating diphenyl with H SO. (Engelhardt a. Latschinoff, B. 4, 561; 6, 193). -KA aq. Crystals (from 40 p.c. alcohol).-BaA',.-CuA', baq.

Ethyl ether EtA'. [74°]. Needles. Chloride C_{1,1}H_oSO₂Cl. [115°]. Amide C_{1,1}H_oSO₂NH_o [227°-230°]. Slender needes (Gabriel a. Deutsch, B. 13, 386).

Diphenyl di-o-sulphonic acid C12H1082Oa i.e. SO, H.C. H., C. H., SO, H. Formed by elimination of NII, from benzidine disulphonic acid (Limpricht, A. 261, 327). Viscid mass. Yields dioxy-diphenyl [99°] by potash-fusion. BaA"6½aq. -PbA" 5aq: needles, v. e. sol. water.

Chloride C₁₂H₈(SO₂Cl)₂. [138°]. Prisms. Amide C₁₂H₈(SO₂NH₂), 2aq. Prisms. Anilde C₁₂H₈(SO₂NHPh)₂. [157°].

Anilide C₁₂H₃(SO,NHPh). [157°].

Diphenyl di.p.-sulphonic acid C₁₂H₃(SO₂H)₂.

[72·5°]. Formed by sulphonating diphenyl (Fittig, A. 132, 209; Engehardt, Z. 1871, 260). Deliquescent prisms. - K A" 21aq. CaA". BaA

Chloride. [203°] (G. a. D.). Prisms. Amide. [above 300°]. Needles.

References. - NITRO-, OXY-AMIDO-, and OXY-DIPHENYL SULPHONIC ACID.

PHENYL-SULPHONO-ACETIC ACID C_uH₂SO₄ i.e. C_uH₃.SO₂.CH₂.CO₂H. [112°].

Formation. -1. From sodium benzene sulphinate and chloro-acetic acid (Gabriel, R. 14. 834) .- 2. By saponifying its ether which is got by boiling sodium benzene sulphinate with chloro-aceto-acetic ether (Otto a. Rössing, B. 23, 755).-3. By oxidising phenyl-thio-glycollic acid (Claesson; Blomstrand, B. 4, 712; 8, 120; Otto, B. 19, 3138).-4. By warming phenyl oxyethyl sulphone (1 vol.) with H₂SO₄ (1 vol.) diluted with water (2 vols.), and extracting with ether (Otto, J. pr. [2] 30, 340).

Properties.—Monoclinic crystals, m. sol. water, but separated by addition of NaCl. Sol. alcohol and ether.

Reactions.-1. Reduced by sodium amalgam to benzene sulphinic and acetic acids.-2. Gives off CO₂ above 160°, forming phenyl methyl sulphone.—3. Chlorine, passed into its warm aqueous solution, forms CHCl₂SO₂C₄H, [59°].—4. PCl₂ gives the chloride [58°], and at 110° forms C₆H₃SO₂CCl₂COCl, which on treatment with water gives C₄H₃SO₂CHCl₂ (Otto, J. pr. [2] 40, 540).

Salts.—BaA', 2aq.—CuA', 2aq.—CaA', 21aq. -PbA', 2aq.—AgA'. Sparingly soluble needles.

Methyl ether MeA'. Oil (Otto, J. pr. [2] 86, 436).

saponified by NaOHAq, while KOHAq gives phenyl methyl sulphone. Bromine at 90°, followed by NaOHAq, forms C_hH_sSO_xCHBr_s [76°]. Alcoholic potash forms Ph.SO_xMe (Michael a. Milner, Am. 7, 65). NaOEt forms the compound C_nH.,SO, CHNa.CO,Et, which yields Ph₂S₂, Ph₂S, PhSEt, and Ph.SO,Me on distillation (Otto a.

Rossing, B. 22, 1455; 23, 1647).

Chloride Ph.SO, CH, COOI! [58°]. Needles (trom water). Yields Hg(C,H,NSO,), [215°] on boiling with HgO.

PHENYL-SULPHONO-ACETONE v. PHRNYL METHYLENE METHYL SULPRONE-METONE.

Di-phenyl-di-sulphono-acetone v. DI-PHENYL DI-METHYLENE DISULPHONE-KETONE

PHENYL-SULPHONO-ANGELIC ETHER

C,H,SO, i.e. C,H,SO,CH(C,H,SO)Et. [64:5°]. Got from PhSO,CINA.CO,Et and allyl iodid: (Michael, Am. 7, 67). Prisms (from alcohol). PHENYL-SULPHONO-n-BUTYRIC

C.H.SO.CHELCO.H. [124°]. Formed from benzene sulphinic acid, a-bromo-butyric acid, and Na₂CO₃Aq (Otto, B. 21, 996). Needles, m. sol. water. Yields phenyl propyl sulphone on heating.

Di-phenyl-di-sulphono-butyric ether

(C.H., SO.), CMe.CH., CO.Et. [97°]. Got by oxidation of (PhS), CMe.CH., CO.Et (Autenrieth, A. 259, 367). Small crystals, insol. water. Converted by KOHAq into benzene sulphinic acid and B-plienyl-isocrotonic acid.

PHENYL-SULPHONO-CROTONIC ACID

C.H., SO. CMc:CH.CO.11. [158]. S. ½ 38; 122 25. Formed by heating the Na salt of β-chloro-crotonic acid [94·5°] with sodium henzene sulphinate in aqueous solution at 170° (Autenrieth, A. 259, 343). Plates (from water), m. sol. ether. At 210° it slowly changes to the following isomeride [127°]. -KA' 1 aq. - BaA' aq. - MgA'₂ 7aq. - ZnA'₂ 6aq. - CuA'₂ aq. - AgA'. [200°]. Matted needles (from water).

Phenyl-sulphono-isocrotonic acid C.H., SO, CMe: CH.CO.H. [127°]. S. 26 at 15°; 5 at 150°. Formed by heating β -chloro-isocrotonic acid with sodium benzene sulphinate in aqueous solution at 145°. Got also by saponifying di-phenyl-di-sulphono-isobutyric ether (Autenrieth, A. 259, 335). Feathery needles. Yields benzene sulphinic acid [81°] on boiling with Dotash.— KA' 3aq.—BaA', 2½aq.— MgA', 6aq.— ZnA', 6aq. [120°] (hydrated).—AgA'. [c. 243°]. Ethyl ether EtA'. Oil.

DI-PHENYL-DI-SULPHONO-DI-ETHYL OXIDE C₁₆H₁₈S₁O₃ i.e. O(C.H₁SO₂Ph)₂. [70°]. Formed from C₃H₃SO₂C₂H₃Cl and dry Ag₂O (Otto, J. 27. [2] 30, 202). Needles, sol. benzeno. A polymeride [88°] is got by heating the compand (O.H. SO) C.H. with KOHAG. pound (CoH.SO2)2C2H, with KOHAq.

DI-PHENYL-DI-SULPHONO-DI-ETHYL SULPHIDE S(C,H,SO,Ph), [124°]. Got from C,H,SO,C,H,Cl and alcoholic KSH (Otto, J. pr. [2] 80, 348). Needles (from dilute alcohol).

DI - PHENYL - DI - SULPHONO - HEXOIC ETHER (C.H., SO.), CMe. CHEŁ. CO.Et. [111°]. Got by oxidising (PhS), CMe. CHEŁ. CO.Et (Autenrieth, A. 259, 372) Crystals, v. sol. alcohol.

DI. PHENYL . DI . SULPHONO . DI . PHENYL OXIDE (C.H., SO., C.H.), O. [70°]. (above 200°). Got by heating C.H.(SO.Ph), with alcoholic potash at 165° (Otto a. Rössing, B. 20, 187). Needles, v. e. sol. alcohol, insol. water.

PHENYL-a-SULPHONO-PROPIONIC ACID C₆H₃,SO₂,CHMe,CO₂H. [116°]. Formed by heating a-bromo-propionic ether with sodium benzene sulphinate and ether. Minute needles. -NaA'.-BaA', 2aq.-EtA'. [c. 17°

Phenyl. B. sulphono. propionic acid ChH., SO., CH., CO., H. [124°]. Got from B-bromo-propionic acid, benzene sulphinic acid. and Na₂CO₃Aq (Otto, B. 21, 89). Plates, sl. sol.

cold water. DI-PHENYL SULPHOXIDE (C₄H₃)₂SO. [71°]. Formed by the action of SO₂ or SOCl₂ on benzene in presence of AlCl₃ (Colby a. McLoughlin, Am. 9, 67; B. 20, 195). Triclinic McLoughlin, Am. 9, 67; B. 20, 195). Triclinia crystals, v. sol. alcohol. Oxidised by KMnO, to Ph.SO.. Reduced by sodium to Ph.S. NaNO, and II.SO, give SO(C₆H₄.NO₂)₂ [116°] and SO₂(C₆H₄.NO₂)₂ [163°].

Di-phenyl-di-sulphoxide v. Phenyl ether of

BENZENE THIOSULPHONIC ACID.

PHENYL-SULPHURIC ACID v. PHENYL SULPHATE and PHENOL. Reaction 19.

PHENYL SULPHUROUS ACID v. BENZENE SULPHONIC ACID.

PHENYL SULPHYDRATE v. PHENYL MER-CAPTAN.

PHENYL-SULPHYDRO-ACETIC ACID v. PHENYL-THIOGLYCOLLIC ACID.

PHENYL - SULPHYDRO - ACETOPHENONE C_sH_s.CO.CH_x.SPh. [53°]. Formed from ω-bromo-acetophenone and NaSPh (Delisle, B. 22, 306).

Crystals, v. sol. ether and acetone.
DI - PHENYL - DI - SULPHYDRO - BUTYRIC ETHER C, M, S, O, i.e. (PhS), CMe.CH, CO, Et. [58°]. Got by passing HCl into a mixture of acctoacetic ether and plienyl mercaptan (Escales a. Baumann, B. 19, 1790). Pearly plates (from alcohol), v. sol, ether.

PHENYL-SULPHYDRO-CROTONIC CH3.CH:C(SPh).CO2H. [86°]. Formed by the action of Na and phenyl mercaptan on the Na salt of a-chloro-crotonic acid [97°] (Antenrieth, A. 254, 246). Needles or plates. Its K salt is

hygroscopic, S. (alcohol) 20 8.

Isomeride CHMe:C(SPh).CO.H. [80°]. Got in like manner from the stereo-isomeric liquid chloro-crotonic acid. White plates. Its K salt is hygroscopic, S. (alcohol) 10.4.

Phenyl-B-sulphydro-crotonic acid

CH₄.C(SPh):CH.CO₂H or CH₂:C(SPh).CH₂.CO₂H. [177°]. S. (alcohol) 2 in the cold. Formed, together with small quantities of an isomeride [145°], by warming di-phonyl-di-sulphydrobutyric ether with alcoholic soda (Escales a. Baumann, B. 19, 1791). Plates (from alcohol), insol. water.—BaA', 2aq.—AgA', amorphous pp.

Isomeride CH, C(SPh):CH.CO₂H. [158°].

Formed from phenyl mercaptan and the Na salt of chloro-crotonic acid [95°] (Autenrieth, A. 254, 230). Both acids form a chorry-red solution in H.SO

DI-PHENYL SULPHYDRO-ETHYLIDENE DISTLIPHONE. Phenyl derivative (C.H.,SO.),CMe.SPh. [194°]. Got by heating (C.H.,SO.),CH.SPh with alcoholic soda and MeI at 1006 (Laves, B. 23, 1416). Crystals (from | chloroform)

DI - PHENYL - DI - SULPHYDRO - HEXOIC ETHER CH₂.C(SPh)₂.CHEt.CO.Et. [71°]. Got from ethyl-acetoacetic ether, phenyl mercaptan, and HCl (Autenrieth, A. 259, 371). Shining crystals, v. sol. ether and alcohol.

DI-PHENYL SULPHYDRO-METHENYL DI-

SULPHONE. Phenyl derivative (C.H.SO.), CH.SPh. [175°]. Got by the action of KMO, and dilute H.SO, on CH(SPh), dissolved in benzene (Laves, B. 23, 1414). Silky needles, m. sol. chloroform, nearly insol. water and alcohol, sol. alcoholic NaOH. May be oxidised to CH(SO,Ph), [215°].
DI-PHENYL-DI-SULPHYDRO-PHENYL-

ACETIC ACID C.H. C(SPh)...CO.H. Formed from phenyl-glyoxylic acid, phenyl-mercaptan, and HCl (Escales a. Baumann, B. 19, 1789). Insol. water, v. sol. ether. Crystallises from benzene with \(\frac{1}{2}C_{\text{H}_0}^{\text{H}_0} - \text{KA'} 1\)\)aq. \(\text{PHENYL - SULPHYDRO - PHENYL - THIO-} \)

 $\stackrel{N\mathrm{Ph.N}}{CS-S}\!\!\searrow\!\!C.\mathrm{NH.NHPh.}$ BIAZYL-HYDRAZINE

[142°]. Got by reducing the corresponding azocompound with alcoholic ammonium sulphide (Freund a. Kuh, B. 23, 2830). Plates, sl. sol.

DI-PHENYL - DI - SULPHYDRO - PROPIONIC ACID CH3.C(SPh) CO.H. [117°]. Got from pyruvic acid, phenyl mercaptan, and RCl (Escales a. Baumann, B. 19, 1787). Needles (from ligroin). - NaA'. BaA', 2aq : v. sol. hot Aq. Amide. [93°]. Needles (from alcohol). DI-PHENYL SULPHYDRO-PROPYLENE

Phenyl derivative DISULPHONE. C.H., SO, CH., CMe(SPh), SO, C.H., [149°]. Formed by oxidising C.H., SO, CH., CMe(SPh), with KMnO, in the cold (Otto a. Rossing, B. 21, 234). Crystalline granules, sl. sol. cold alcelol.

DI-PHENYL-DI-SULPHYDRO-VALERIC ACID CH, C(SPh), CH, CO,H. [69°]. Got from phenyl mercaptan, 8-acetyl-propionic acid and HCl (Escales as Baumann, B. 19, 1795). Prisms (from chloroform-ether).—BaA'...

PHENYL-TETRIC ACID C₁₁H₁₀O₂

CH2Ph.CH.CO CO.CH. >0. Formed by heating bromo-

benzylacetoacetic ether (Moscheles, B. 21, 2608). Not affected by HClAq at 170°. Yields a benzoyl derivative CuH, BzO, [110°] crystallising in needles.

PHENYL-THIAZOLE C,H,NS i.e.

N CH .S [52°]. (273° cor.). Got by the diazo- reaction from the amido-phenyl-thiazole that is produced by the action of thio-urea on bromo-acetophenone (Popp, A. 250, 279; cf. Arapides, A. 249, 25). Sl. sol. cold water.— "B'HCl. [80°]. Needles.—B',H,PtCl, 2aq. [196°]. -*B'HHgCl₂. [155°].-Picrate. [165°]. *B'HAuCl₄. [175°]. Needles (from alcohol).

N≪CH :CH. μ -Phenyl-thiazole Formed by heating thio-benzamide with edichloro-di-ethyl oxide at 100°. Oil.-B'HCl 2aq.

chloro-di-ethyl oxide at 100°. Oil.—B'HG zaq. [62°].—B'H.PtCl.2aq. [175°] (when anhydrous).
—Picrate. [125°]. Yellow needles.

Dibydride N CPh.S.
CH., CH. Phenyl-thiasoline. (276). Got by heating thio-bensamide

with ethylene bromide (Gabriel a. Heymann, B. 23, 158; 24, 784). Formed also by the action of PCl₂ on S₂(C₂H₂NHBz)₂ (Gabriel a. Coblent#, B. 24, 1124). Oil. Yields a crystalline dibromide. — B'₂3HCl₂ — B'C₂H₂N₃O₃. [172°]. Yellow needles .-- B' H. PtCl.

v-Phenyl-thiazole. Tetra-hydride

NPh CH.S. Got by reducing ethylene phenyl-di-thio-carbamate [128°] with tin and HCl (Fönster, B. 21, 1871). Oil. B', H. PtCl.

Di-phenyl-thiazole N CPh.S CPh.CH [93°]. (above 360°). Got from thiobenzamide and bromo-acetophenone in alcohol (Hubacher, A. 259, 237). Plates, v. sol. alcohol and ether.

Tri-phenyl-thiazole NCPh.S Got from thiobenzamide and bromo-deoxybenzoïn (Hubacher, A. 259, 245). Prisms (from ether), in. sol. alcohol, nearly insol. HClAq.

Reference.—Oxy-PHENYL-WHAZOLE.

PHENYL-DITHIENYL C.H.S.C.H.PhS. [209]. A product of the action of \hat{S} on toluene at a real heat (Renard, C, R, 111, 48). Plates, v. sl. sol, alcohol and ether. Gives a blue colour with isatin and H2SO4, and a green colour with phenanthraquinone and H_2SO_4 . Gives rise to $C_{14}H_1Br_8S_2$ [320] and $C_{14}H_8(NO_2)_2S_2$ [273°].

PHENYL THIENYL KETONE v. THIENYL' PHENYL KETONE.

(α)-PHENYL-(β)-THIO-ALLOPHANIC ACID

Ethyl ether. C₁₀H_{1,}N₁SO₂ i.e. NH₂CS.NPh.CO₂Et. [127°], Formed from NHAc.CS.NHPh and ClCO₂Et (Seidel, J. pr. [2] 32, 275). Monoclinic tablets, converted by alcoholic NH, at 100° into phenyl-thio-urea.

(B)-Phenyl-thio-al'ophanic acid. ether NHPh.CS.NH.CO.Et. Got from phenylthio-urea and ClCO₂Et (Seidel, J. pr. [2] 32, 270). Oil. AcCl at 60° forms NHAc.CS.NHPh [170°].

Phenyl di-thio-allophanic acid. Isoamyl ${\rm NHPh.CS.NH.CO.SC.H_{H}}.$ ether [102°]. Formed from phenyl-thio-urea and Cl.CO.SC, H₁₁ (Schöne, J. pr. [2] 32, 256). Needles. Very unstable. Forms an acetyl derivative [246

Di-phenyl-thio-allophanic acid. Ethyl ether NHPh.CS.NPh.CO.Et. [95°]. Formed from di-phenyl-thio-ures and ClCO,Et (Seidel,

J. pr. [2] 32, 262). Prisms (from alcohol). Alcoholic AgNO₃ ppts. C₁₆H₁₆N₂SO₂AgNO₃. Reactions.—1. Caustic potash regenerates CS(NHPh).—2. Aqueous ammonia at 100° forms NHPh.CS.NH₂ and NHPh.CO₂Et. — 3. Alcoholic aniline at 100° forms CS(NHPh)₂ and NHPh.CO₃Et. — 3. NHPh.CO,Et .- 4. HgO in presence of alcoholic ammonia forms (NHPh.CO.NPh.CO.Et), HgO [129°], a crystalline body that is reconverted by H2S into di-phenyl-thio-allophanic ether .- 5. By heating in a current of HCl it is converted into CS(NHPh)2, aniline, and phenyl-thiocarbimide.

Di-phenyl-di-thio-allophanic acid. amyl ether NPhH.CS.NPh.CO.SC.H ... [87°] Got from di-phenyl-thiures and Cl.CO.SC, H, (Schöne, J. pr. [2] 32, 258). Needles (from alcohol). It is insoluble in cold water, but decomposed by hot water. Its alcoholic solution is ppd. by AgNO, HgCl, or PtCl. HgO and NH, convert it (in alcoholic solution) into di-phenyl- | Formed also by the action of alcoholic potash guanidine, [147°].
TRI-PHENYL-THIO-AMMELINE

 C_nH_1,N_sS i.e. $C(SH) \leqslant N - C(NPh) > NH$. [238°]. Formed from phenyl-cyanamide and phenylthiocarbimide, and got also by heating tri-phenylbiguanide with CS, at 100°, and by heating diphenyl-guanidine with phenyl-thiocarbimide, alcohol, and mercury sulphocyanide (Rathke, B. 20, 1065; 23, 1673). Plates (from chloroform). Converted by alcoholic potash into tri-phenylammeline. Alcohol and EtBr at 100° form C₁H₁,EtN₂SHBr, crystallising from alcohol in plates.—B'HCl.—AgC,HPh₂N₂S: yollow pp. DI-PHENYL-THIO-BENZAMIDE

Ph.CS.NPh₂. Formed by heating di-phen, l-benzamidine with H₂S or CS₂ at 130° (Bernthsen, A. 192, 38). Yellow triclinic crystals (from benzene); a:b:c = .927:1: .766, $\alpha = .93^{\circ} \cdot .29^{\circ}$, $\beta =$ 100° 55', $\gamma = 84^{\circ}$ 14'. Insol. ccld water, sl. sol. cold alcohol.

PHENYL-DI-THIO-BIURET C₈H₉N₉S₂ i.e. IPh.CS.NH.CS.NH₂. [174°]. Formed by NHPh.CS.NH.CS.NH,. heating aniline with perthiocyanic acid (Glutz, A. 154, 44). Got also by boiling carbinidophonyl-thio-urea with ammonium sulphide (Wunderlich, B. 19, 452). Prepared by adding phenyl-thiocarbimide (36 g.) to an alcoholic solution of cyanamide (11 g.) and Na (6 g.), and decomposing the pp. by dissolving in a solution of NH₄Cl (14.5 g.) containing NH₃Aq (50 c.e.), passing in H₂S, and heating to boiling (Hecht,

B. 25, 756). Pearly plates, sl. sol. hot water.—B'HCl.—B'HNO. Ethyl derivative C.H.Eth.S ..

Got by adding alcohol, NH, Aq, and Et to the base (Tursini, B. 17, 584). Trimetric tables. PHENYL-THIO-CARBAMIC ACID

NHPh.CO.SH. Methyl ether NHPh.CO.SMe. [84°]. Formed by heating di-phenyl-methyl-4thio-urea NHPh.C(NPh).SMc with dilute H.SO. (Will, B. 15, 339). Plates, sol. alcohol, ether, and benzene. Decomposed by KOH into aniline, MeSH, and CO. Boiling alcoholic NH, forms MeSH and phenyl-urea. Aniline gives methyl

with dilute H2SO, and by the action of aniline on Cl.CO.SEt (Will).

Isoamyl ether NHPh.CO.SC,H₁₁. [67°]. Got from aniline and Cl.CO.SC,H₁₁. (Schöne, J. pr. [2] 32, 249). Needles (from ether).

Got by heating di-phenyl-ethylene-v-thio-urea with dilute HClAq at 200° (W.). Formed also by the action of chloro-acetic acid on the ethylene ether of phenyl-di-thio-carbamic acid (Evers, B. 21, 976). Needles, sol. alcohol and ether, insol. acids and alkalis.

Phenyl other NHPh.CO.SPh. [125°]. Formed by heating phenyl mercaptan with phenyl cyanate (Snape, C. J. 47, 778; B. 18, 2432). Needles, v. sol. alcohol and ether.

Phenyl-v-thio-carbamic acid NHPh.CS.OH. Ethyl ether C.H., NSO i.e. NHPh.CS.OEt or NPh:C(SH).OEt. [72°]. Formed by heating phenyl-thiocarbimide with alcohol (Hofmann, B. 2. 120; 8, 772; Bamberger, B. 15, 2164).

on phenyl-thiocarbimide (R. Schiff, B. 9, 1316). Triclinic prisms, sol. alkalis and reppd. by CO, Resolved by distillation into alcohol and phenylthiocarbimide. Oxidised by alkaline K₂FeCy₅ to C₁₈H₂₀N₂O₂S₂ or S₂(C(NPh).OEt)₂ [102°], which is also got by the action of I on C.H. NOSAg (Liebermann a. Natanson, B. 13, 1575; Jacob-(Liebermann a. Natanson, B. 13, 1075; Jacobsen, B. 19, 1076).—(C₂H₁₀NO.S)₂Pb 2aq: small needles.— C₂H₁₀NOSAg.— C₂H₁₀NOSHgClHCl: needles.—(C₂H₁₀NOS).Hg. [78°] (Stephanovitch, B. 7, 692).—(C₂H₁₀NOS).HgAgNO₂. Needles.—(C₂H₁₀NOSMc. [260°-265°). Oil.—C₂H₁₀NOSEd. [30°]. (275°). Prisms; decomposed by dilute H.SO, at 200° into aniline and CO(OEt)(SEt) (Liebermann, B. 13, 682; A. 207, 148). -C_oH₁₀NOSC₁H₉. [75°] (Mylius, B. 5, 977). Phenyl ether NHPh.CS.OPh. Got by Got by

heating phenyl-thiocarbimide with phenol at 145° (Dixon, C. J. 57, 268). Sulphur-yellow octahedra; decomposed by heat.

Phenyl di-thio-carbamic acid NHPh.CS.SH. Splits up into CS, and aniline when set free from its salts.

Salts .- The salt NHPh.CS.SK is formed by boiling potassium xanthate EtO.CS.SK (1 mol.) with an alcoholic solution of aniline (1 mol.) (Rathke, B. 11, 958). Prepared from CS, aniline, ether, and alcoholic potash (Losanitsch, B. 24, 3024). Yellow monoclinic needles, v. c. sol. water and alcohol, insol. ether. Yields CS(NHPh), when heated. Boiling water forms phenyl-thio-carbimide and CS(NHPh),.—NHPh.CS.SNH,. Yellow prisms. Converted by I into (NIIPh.CS), S [138°]. BaA'₂: yellowish plates. - NiA'₂.

Methyl ether NHPh.CS.SMe. [93.5°].

Formed from the NH, salt and MeI (L.) and also by heating NHPh.C(NPh). SMe with CS, at 160° (Will, B. 15, 342). Decomposed by alkalis into MeSH and aniline.

Ethylether NY Ph.CS.SEt. [60°]. Formed from phenyl-thiocarbimide and mercaptan at 150° (Hofmann, B. 2, 120; Will, B. 15, 1305), and also by the action of EtI on the ammonium salt (L.). Tables, v. sol. alcohol, sol. alkalis.

Isoamyl ether C.H., A'. [171°].

Ethylene, derivative CS NPh.CH, [634°]. Formed, together with phenyl-thiocarbimide, by heating C(NPh) < NPh. CH2 with CS2 at 200° (W.). Needles. Converted by MeI into C,H,NS,McI [149°].

References .- Bromo-, Chloro-, and Nitro-PHENYL-THIO-CARBAMIC ACID

PHENYL-THIOCARBAMINE-CYAMIDE v. CARBIMIDO-PHENYL-THIO-UREA

PHENYL - THIOCARBAMINE - ETHYL . CYAMIDE v. ETHYL-CARBINIDO-PHENYL-THIO-

PHENYL-THIO-CARBAZIC ACID
NHPh.NH.CO.SH. The phenyl hydrazine salt
NHPh.NH.CO.SN.H.Ph [84°] is formed from phenyl-hydrazine and COS (Heller, A. 263, 269). . Phenyl di-thio-carbasic acid

NHPh.NH.CS.SH. Formed, as phenyl-hydrazine salt NHPh.NH.CS.SN.H.Ph [97°] by adding CS. to an ethereal solution of phenyl-hydrazine (Fischer, A. 190, 114). Plates, ev. sol. alcohol and ether. Readily decomposed by Leat into CS(N,H,Ph), CS, H,S, and NH,

PHENYL-THIO-SEMICARBAZIDE C.H.N.S i.e. NH, OS.NH.NHPh. [201°] (F.; P.); [190°] (S. a. R.).

Formation .- 1. By warming di-phenyl-thiocarbazide with alcoholic or aqueous alkalis (Fischer, A. 212, 324).—2. By heating phenylhydrazine sulphocyanide. - 3. By heating phenylhydrazine with thio-urea or with phenyl-thiourea (Pellizzari, G. 16, 203; Skinner a. Ruhemann, C. J. 53, 550; B. 20, 3373).

Properties.-Needles, insol. ether, sl. sol. hot water, v. sol. hot alcohol. Conc. HClAq at 120° forms phenyl-thiocarbiane C.H., N.S. COCl. forms CO:N., Ph.CS.NH₂ [c. 270°] crystallising from HOAc (Freund, A. 21, 2465).

Acetyl derivative NHPh.NH.CS.NHAc. [179°]. Formed by mixing solutions of acetylthiocarbimide and phenyl-hydrazine in dry benzene (Dixon, C. J. 55, 303). Small prisms.

Benzoyl derivative C₁H₁₃N₃SO. Silky needles. Does not melt at 220°.

CS(NH.NHPh)2 Di-phenyl-thiocarbazide [c. 150°]. Formed by heating the compound of phenyl-hydrazine and CS, at 110°-140° (Fischer). Formed also from phenyl-hydrazine and CSCl., (Heller, A. 263, 278). Triangular prisms (from alcohol). Dissolves in hot aniline, forming a solution which is green in thin layers, but red in thick layers. Hot alcoholic potash also forms this dichroic substance, di-phenyl-thiocarbazone C₁₃H₁₂N₄S).ZnO, and may be reduced by zinc-dust and NaOHAq to phenyl-thio-semicarbazide and aniline. Di-phenyl-thio-carbazone may be oxidised by ppd. MnO, in presence of alcoholic potash to red needles of di-phenylthiocarbodiazone CS(N.Ph)...

Di-phenyl-thio-semicarbazide NIIPh.NH.CS.NIIPh. [177]. Formed from phenyl-hydrazine and phenyl-thiocarbimide in alcoholic solution (Fisc. ct. A. 190, 122). Prisms (from alcohol), sl. sol. ether. COCl, forms CO:N,Ph.CS.NHPh [188°], crystallising in needles (Kreund, B. 21, 2466).

Butyryl derivative

C.H,O.NPh.NH.CS.NHPh. [156°]. Formed from sodium phenyl-hydrazine, phenyl thiocarbimide, and n-butyryl chloride (Michaelis a. Schmidt, A. 252, 309). V. sol. hot alcohol.

Benzoyl derivative

NPhBz.NH.CS.NHPh. [310°]. Obtained from NPhBz.NH, and phenyl-thiocarbimide (M. a. S.). Reference. - NITRO-DI-PHENYL-THIO-SEMICARB-

AZIDE. DI - PHENYL - THIO - SEMICARBAZIDE

CARBOXYLIC ACID C, H, N, O, S i.e. NHPh.CS.NH.NHC, H, CO, H. [204°]. Formed by warming m-hydrazido-benzoic acid with phenyl thiocarbimide and HOAc (Roder, A. 236,

Colourless needles.

PHENYL THIOCARBIMIDE C,H,NS i.e. C,H,N.OS. Mol. w. 135. (220°) at 750 mm. (Schiff, B. 19, 568). S.G. 1 1059 (Nasini a. Scala, G. 17, 66). S.V. 1434 (Schiff; Lossen. A. 254, 73).

Fornation.—1. By distilling phenyl-thioures with P.O. (Hofmann, Pr. 9, 274, 487; C. J. 18, 309; B. 15, 980).—2. By heating di-phenyl-thioures with conc. HClAq at 165° (Merz a. Waith, Z. 1869, 589).—3. By the action of I on a bensene solution of tri-phenyl-guanidine (Hof-

mann, B. 2.453; Rudneff, J. R. 10, 184).-4. By heating phenyl cyanate or phenyl-carbamic ether with P.S. at 160° (Michael a. Palmer, Am. 6, 258).—5. Formed, together with o- or p- tolyl-thiocarbimide, by heating phenyl-o- or p- tolylcyanamide (C,H,N:C:NC,H,) with CS, at 180°-200° (Huhn, B. 19, 2409).

Properties. - Pungent oil, volatile with

Reactions. - 1. Alcohol at 100° forms MHPh.CS.OEt, while mercaptan gives rise to NHPh.CS.SEt. — 2. Alcoholic polash forms CS(NHPh)₂ and CO(NHPh)₂ — 8. Ammonia forms CS(NHPh)₁ (NH₂), and inciding gives CS(NHPh)₂ and other amines act in like manner. - 4. PEt, acts violently, and forms $C_{12}H_{20}NPS$, while PMe₃ forms oily $C_{10}H_{20}NPS$, which yields crystalline B'HCl. - 5. Chlorine passed into its solution in chloroform forms (PhNCS)₂Cl₂ [150°-160°]• and PhNCCl₂ (212°). The chloride (PhNCS)₂Cl₂is converted by H.S into CS(NHPh)₃. and by warm spirit into (PleNCS)2O, crystallising in yellow needles [118°] (Helmers, B. 20, 786). 6. Bromine in chloroform or HOAc forms red crystals of (PhNCSBr.), decomposed at 100° into pale-yellow plates (PhNCSBr), [190°] (Helmers; cf. Proskauer a. Sell, B. 9, 1262). -7. SO. forms C,II,NS,O, [180°-183°], crystallising from benzene, and converted by water at 100° into amido benzene p sulphonic acid, CO2, and H2S (Magatti, B. 11, 2267).—8. PCl, at 100° forms $C_v H_s NCCl_2$ and $C_v H_s < N > CCl (248°)$ (Hofmann, B. 12, 1126).-9. CISO3H forms C11H10N2S3 [151°], insol. water, and SO₃H.C₃H₄NOS aq, sol. water (Pawlewski, B. 22, 2200).—10. Reduced copper at 200° forms benzonitrile.—11. H.S forms phenyl-thio-urea.—12. Boiling water forms CS(NHPh),, CO., and H2S (Bamberger, B. 14, 2642). — 13. HOAc forms, on heating, CO(NHPh)₂, Ac₂O, H₂S, and CO₂; the di-phenylurea being further split up into aniline and CO, with formation of Ac₂O (Cain a. Cohen, C. J. 59, 327; cf. Gumpert, J. pr. [2] 32, 294).—14. Chloro-acctic acid and alcohol at 170° form PhN:C S.CH. [148°], which yields aniline, CO. and thioglycollic acid on boiling with water (Liebermann a. Voeltzkoff, B. 13, 276).— 15. Sodium malonic ether in presence of alcohol forms C14H16SNO4Na, whence acids liberate Gi,H.,SNO, or (CO_Et),CH.CS.NHPh [60°] (Michael, J. pr. [2] 35, 451).—16. Sodium cyanamide and alkyl iodides form cyano-phonylalkyl-thio-ureas (Hecht, B. 23, 1664). In this way the following compounds may be prepared: NHPh.CS.NMeCy [186°], NHPh.CS.NECy [144°], NHPh.CS.NCyC,H, [100°], crystallising in needles, NHPh.CS.NCyC,H, [108°], crystallising in needles, and NHPh.CS.NCy.CH,Ph [189°]. 17. Aldehyde ammonia forms C 2H, N, 8, 0, [148°], crystallising from alcohol in silvery needles (R. Schiff, B. 9, 567; G. 6, 244).—18, Benzamidna hydrochloride and dilute NaOHAq form CPh(NH).NH.CS.NHPh [125°] (Pinner, B. 22, 1609). Prisms.

References .- BROMO-, CHLORO-, IODO-, NITRO-, and Oxy- PHENYL-THIOCARDIMIDE.

PHENYL-THIOCARBIZINE C.H.N.S i.a. CS NH. [129°]. Formed by heating phenyl-

thio-semicarbazide (10 g.) with dilute (20 p.c.) HClAq (80 c.c.) for 12 hours at 130° (E. Fischer, A. 212, 326). Plates (from water), v. e. sol. alcohol. May be distilled. McI forms C, H, MeN, S Does not reduce Fehling's solution. HIAq at 200° forms aniline, H.S, CO2, and NH2. Aqueous NaOCl forms a violet pp. which dissolves in H2SO4 with deep-red colour. Br in chloroform gives C.H.BrN.S [210°] crystallising in needles.

Salts. — B'HCl. [240°]. Needles. — B'H_PtCl. Yellow prisms.—C,H_N_SAg: floc-culent m. cot by coldinary. culent pp. got by adding ammoniacal AgNO3.

Acetyl derivative C.H.AcN.S. [187°]. Got by heating phenyl-thiocarbizine with Ac.O. (F.). An isomeride [74°] (275°), got by heating acetyl-phenyl-hydrazine with CSCl, and benzene (Freund, B. 21, 2468), is converted by boiling with alcohol and HgO into acetyl-phenyl-carb-

Benzoyl derivative C.H.BzN.S. [180°]. Got from the base and BzCl (Fischer). An isomeride [110°] is got by heating NHBz.NPhH

with COCl, in benzene at 100° (F.).
PHENYL THIOCARBONATE THIOCARBONATE [97°]. Formed from NaOPh and CSCL, (Ber green, B. 21, 346). White crystals, sol. alcohol. PHENYL-TRI-THIO-ORTHOFORMATE

CH(SPh)₃. [40°]. Got by boiling aqueous NaSPh with chloroform (Gabriel, B. 10, 185). Thick prisms, sol. ether. Split up by fuming HClAq at 100° into formic acid and PhSII.

PHENYL-THIOGLYCOLLIC ACID C.H.SO., i.e. CH₂(SPh).CO₂H. [62°]. Formed by saponifying its ether, which is got by adding ClCO₂Et to a solution of NaSPh in absolute alcohol (Claesson, Bl. [2] 23, 441; Gabriel, B. 12, 1639). Thin tables, sl. sol. cold water. Oxidised by KMnO₄ to phenyl methyl sulphone (Otto, B. 19, Mano, to puerly merry merry approve (5.7.2), 3138). Salts.—KA'.—NaA'.—BaA'...—CaA'...—MgA'.28aq.—CdA'.2aq.—XnA'.22aq.—PbA'... [60°].
—MnA'.28aq.—CuA'...—AgA' aq: crystalline pp.
—Ethyl ether EtA'. (277°). S.G. ± 1·136;

15 1 127. Amide. [104°]. Tables (from alcohol). References. - AMIDO- and BROMO- PHENYL-THYOOLYCOLLIC ACIDS.

(a)-FHEDYL-THIOHYDANTOIC ACID

C.H., N.SO., i.e. NH., C(NPh). S.CH., CO.H. [148°-152°]. Got by heating aniline with ammonium sulphocyanide, chloro acetic acid, and alcohol (Claesson, B. 14, 732). Needles (from HOAc); m. sol. hot water and ether. Cold NaOHAq converts it into C18H11N2S2O4 [112°-115°] (Liebermann, A. 207, 129).

(B)-Phenyl-thio-hydantoic acid

NHPh.C(NH).S.CH...CO.H. Got by evaporating an alcoholic solution of ammonium chloroacetate and phenyl-thio-urea at 100° (Meyer, B. Decomposes on heating without 14, 1659). melting. Insol. water, alcohol, and ether. Boiling dilute HCl forms CO NPh.CO [148°].

Isomeride d. Phenyl-thio-hydantoin. Di-phenyl-hydantoïc acid

NHPh.C(NPh).S.CH.,CO.H. Got from potassium chloro-acetate and di-phenyl-thio-urea (Lange, B. 12, 597). Yellow octahedra. PHENYL-THIO-ψ-HYDANTOIN C_oH_aN_aOS,

i. C(NH) NPh.CO [178°]. Got from chloro-

acetic anilide and thio-ures, and obtained also by boiling (3)-phenyl-hydantoic acid with HOAo or conc. NH,Aq (Meyer, B. 14, 1661), and by the action of phenyl-cyanamide on thioglycollic acid (Andreasch, B. 15, 324). Needles, sol. NaOHAq.

Phenyl-thio-hydantoin CS</br/>
NPh.CO

NH.CH. by melting glycocoll with phenyl-thiocarbimide (Aschan, B. 17, 424). Monoclinic plates, decomposing near 200°. Boiling alcoholic potash converts it into a salt of an oils phenyl-thio-hydantoic acid NHPh.CS.NH.CH2.CO2H which, when set free, rapidly changes again to phenyl-thiohydantoin.

Di-phenyl-thio-hydantoin C13H12N2SO, i.e. CS NPh.CO ? [176°]. Got from chloro-acetic acid and di-phenyl-thio-urea (Lange, B. 12, 595). Iridescent plates, insol. water, v. sol. not alcohol. Boiling dilute HClAq forms the compound C₀H,NSO₂[148°].—B'₂H₂PtCl₆. Yellow needles.

Di-phenyl-thio-hydantoin CS NPh.CO [233°]. Formed by the action of alkalis on NHPh.CS.NH.CHPh.CO.Et (Kossel, B. 24, 4152). Reference. - OXY-DI-PHENYL-THIOHYDANTOIN.

PHENYL-DI-THIO - DI-METHYL-KETURET NH C(NH).8 CMc₂. [239°]. Formed from phenyl-di-thio-biuret and acetone (Fromm, B.

25, 1278). Sol. alkalis. Converted by benzyl chloride into C,H,N C(NC,H,).S CMe, [128°] which is insol. alkalis.

DI-PHENYL-THIO-OXAMIDE C.S. (NHPh) .. [133°]. Formed from di-phenyl-oxamide l successive treatment with PCl, and H2S (Wal-

lach, B. 13, 527). Golden plates.

(a) PHENYL-THIOPHENE C₁₀H_nS i.e.

Expend by heating either

C.SH₃Ph. [41°]. Formed by heating either Cll.Bz.CH(CO₂H)₂ or A-benzoyl-propionic acid with P.S. (Rues a. Paal, B. 19, 3141). Small tables, insol. water, v. e. sol. ether, v. sol. alcohol. Volatile with steam. With isatin and cold H.SO, it gives a splendid bluish-violet colour, changing to dark blue. Bromine gives rise to $C_{1e}H_aBr_aS$ [56°] and $C_iSBr_a.C_aH_aBr$ [1:4] [146°]. (8) Phenyl-thiophene C_iH_aPhS . [170°].

(330"). A product of the passage of the vapours of toluene and sulphur through a red-hot tube (Renard, C. R. 109, 699). White spangles, m. sol. cold alcohol. Gives a blue colour with isatin and H.SO4, and a green colour with phenanthraquinone and H.SO., Yields C,H₂BrS.C₆H₄Br[1:4] [195°], C,H₄(NO₂)S.C₆H₄,NO₂ [1:4] [178°], a disulphonic acid, and a tetrasulphonic acid.

Di-(a)-phenyl-thiophene SCPh:CH. [153°]

Formed by heating C.H.Bz. with P.S. at 180° (Paal, B. 21, 3058). White plates (from alcohol). Tri-phenyl-thiophene C,Ph,HS. [127°]. Got by heating desyl-acetophenone with P,S, at 150° (A. Smith, C. J. 57, 647). Plates, v. sol. benzene. Gives a greenish-yellow colour with H₂SO₄ and

Tetra-phonyl-thiophene C22H20S i.e. S CPh:CPh. Thionessal. [182°].

isatin or phenanthraquinone.

Formation.—1. By the dry distillation of thiobenzoic aldehyde (Laurent, A. 52, 354).—2. By distilling bensyl sulphide or bensyl di-

sulphide (Märcker, A. 136, 94).-8. By distilling benzylidene sulphide (Fleischer, A. 140, 239; 144, 194) .-- 4. By distilling barium phenyl-acetate with S (Forst, A. 178, 376).—5. By heating phenyl-acetic acid with S for 6 hours at 260° Cliegler, B. 23, 2473) -6. By heating phenyl benzyl ketone with S. -7. By heating s-diphenyl-ethylene with S at 250° (Baumann a. Klett, B. 24, 3311). Minute needles, sl. sol. alcohol, v. sol. benzene and CS. Yields a sulphonic acid, and also the following derivatives: C.,H.,Cl.,S [219°] (Dörn, A. 153, 350), C.,H.,Er,S [265°-270°], C.,H.,(NO.),S [above 250°]. DI - PHENYL - DI - THIO - DI - PHENYL - KE.

TATE CPh.(SPh)₂. Phenyl-mercaptol of benzo-phenone. [139°]. Formed by passing HCl gas into a hot mixture of benzophenone, phenylmercaptan, and ZnCl₂ (Baumann, B. 18, 888). Short prisms, sl. sol. alcohol and ether.

THIOPHOSPHATE PHENYL PS(OPh)_s [49°]. (above 360°). Gobby boiling PSCl₃ with phenol (Schwarze, J. pr. [2] 10, 222) and by heating phenyl phosphate with K.S (Kreysler, B. 18, 1718), or with S at 190° (Anschütz, A. 253. 118). Needles (from alcohol), turning red in air and light. Not decomposed by water.

Phenyl tri-thiophosphate PO(SPh), [72°]. Got by boiling PhSH with POCla. Prisms (from alcohol). Decomposed by warm water.

Phenyl tetra-thio-phosphate 1

tetra-thio-phosphate PS(SPh).. [80°]. Got from PhSH and PSCl,. Silky white needles, not affected by boiling water.
PHENYL THIOSULPHURIC ACID

C.H.S.SO2.OH. Phenyl hydrogen thiosulphate. Got by dissolving Ph₂S in H₂SO₄ (Stenhouse, Pr. 17, 62; A. 149, 254).—BaA', 2aq: crystalline.

PHENYL-THIO-URAMIDO-ACETIC ORTH-

ALDEHYDE. Di-ethyl derivative

NHPh.CS.NH.CH2.CH(OEt)2. [96°]. mixing phenyl-thiocarbimide with amido-acetal NH₂.CH₂.CH(OEt)₂ (Wohl a. Marckwald, B. 22, 569). Needles (from dilute alcohol), insol. water and ligroin, ve sol. other. Cold conc. H.SO. forms NHPh.CS.NH.CH, CH(OH)(OEt) [94°] which yields, by loss of H.O, the salts (C11H11N2SO)2H2PtCle and C11H11N2SOCH3N3O, (190°

PHENYL-THIO-URAMIDQ-BENZOIC ACID v. m-Amido-Benzoic acid.

o-PHENYL - THIO - URAMIDO - CINNAMIC ACID NHPh.CS.NH.C,H,.CH:CH.CO,H. [237]. Formed by heating o-amido-cinnamic acid with phenyl-thiocarbimide on the water-bath (Rothschild, B. 23, 3343).

DI-PHENYL DI. THIOURAMIDO . TETRA. OXY-DI-PHENYL. Tetra-methyl derivative C₁H₄(OMe)₄(NH.CS.NHPh). [184]. Formed from C₂H₂(OMe)₂(NH₂).C₃H₂(OMe)₄(NH.) and phenyl thiocarbimide (Baessler, B. 17, 2128). White flakes, sol. hot alcohol and benzene.

PHENYL-THIOURAMIDO-PHENYL-ACETIC ETHER NHPP.CS.NH.CHPh.CO.Et. [1624]. Formed from phenyl-amido-acetic ether and phenyl-thiocarbimide (Kossel, White crystals, sol. hot alcohol. B. 24, 4151).

PHENYL-THIO-URAMIDO-THIO-FORMIC ACID v. PHENYL-DI-THIO-ALLOPHANIC ACID.

PHENYL . THIOURAMIDO . TOLYL . CARB . AMIC ETHER NHPh.CS.NH.C.H., Me.NH.CO.Et. [155°] Formed, together with CS(NHPh), by the action of phenyl-theocarbimide on amido-

tolyl-carbamic ether (Schiff, B. 23, 1818).

risms (from alcohol), v. sl. sol. alcohol.
DI-PHENYL-DI-p-THIOURAMIDO-DI.
TOLYL-O-SULPHIDE C₂-H₂₈N₄S₄. i.e.
S(C₄H₃Me.NH.CS.NHC₄H₃), Thio-p-tolyt-di-plenyl-thiourca. [134°]. Formed by the action of phenyl-thiocarbimide upon di-p-amido-di-tolyl-sulphide (Truhlar, B. 20, 670). White prismatic needles. V. sol. alcohol, ether, and benzene.

PHENYL-THIO-UREA C.II, N.S i.e. NHPfl.CS.NH... Mol. w. 152. [154°]. S. 26 at 18°; 5 93 at •00°. S. (alcohol) 5.59 at 16°; 68 at 78°.

Formation .- 1. By heating phenyl sulphocyanide with alcoholic NH, (Hofmann, Pr. 9, 27).—2. By boiling aniline with ammonium sulphocyanide Schiff, A. 148, 338; Rathke, B. 18, 3104).—3. By heating aniline sulphocyanide at 190' (Salkowski, B. 24, 2728; cf. De Clermont, C. R. 82, 512).-4. By passing H.S. into a solution of phenyl-cyanamide in benzene Weith, B. 9, 819).

Properties. - Needles, sol. alkalis and reppd. by acids. Tastes bitter.

Reactions .- 1. Heated in a scaled tube at 180° it yields CS(NHPh)2, ammonium sulphocyanide, NH₂, H₂S, and aniline.—2. Ammonia at 140° forms aniline and ammonium sulphocyanide.—3. Boiling aniline forms CS(NHPh),-4. HGlAq at 120° forms aniline, H₂S, NH₃, and CO₂.—5. By boiling with alkaline lead actate solution it gives phenyl cyanamide N:C.NHC,H, which polymerises on heating to tri-phenyl-isomelamine (PhN:C)3(NH)3.-6. When boiled for several hours with freshly-precipitated HgO it yields asymmetrical tri-phenyl-melamine PhN C(NH).NPh C.NHPh (Hofmann, B. 18, 3220). - 7. Cl.CO.CO.Et forms oxalyl-di-phenylbiuret, NH CS.NPh C2O2 (v. Chloro-GLY-OXYLIC ETHER) .- 8. ClCO .Et forms phenyl-thioallophanic ether .- 9. Silicon tetrabromide gives solid SiBr₄(C,H₈N₂S)₄, sol. hot benzene, but decomposed by boiling alcohol (Reynolds, C. J. 53, 856).—10. An alcoholic solution of allyl by comp.—10. An alcoholic solution of alliptomide forms a base C₁₀H₁₂N₂S (Werner, C. J. 57, 362).—11. Benzyl chloride in algebol.—forth CS(N₂H₃Ph)C,H,Cl [112°] (W.).—12. Ethylene bromide forms C₁₀H₁₈N₂S [139°], which gives the salts B"2HBF [214°], B"2HCl [218°], B"H_PtCl₁₈D, B"30 [14] (N.). Out 1160° (B.). and B"2C_aH₂(NO₂)₂OH [196°] (Bertram, B. 25, 59).—13. H₂O₂ oxidises it, in alcoholic solution, to di-phenyl-di-amido oiazthiole (Hector, B. 22. 1176).

Salts. -B'₂H.PtCl₆.-B'₆Cu₂Cl₂ 6aq. [145°] (Rathke, B. 17, 305). Trimetric crystals (from alcohol).

Acetylderivative NHPh.CS.NHAc. [173°]. Formed from acetyl sulphocyanide and aniline (Miguel, A. Ch. [5] 11, 318), and by the action of Ac2O on the product of the action of phenyl thiocarbimide on aldehyde-ammonia (Schiff, B. 9, 570). Tables (from delute alcohol).

—B'HBr. [270°]. Prisms, v. e. sol. water.

Benzoyl derivative NHPh.CS.NHBz. [149°]. S. (alcohol) 4 at 78°. Needles, insol. water (Miguel).

o-Oxy-bensoyl derivative NHPh.CS.NH.CO.O.H.OH. [192°]. Formed from salicyl-thiocarbimide and aniline (M.).

Di-phenyl-thio-ures C, H,2N,S i.e. CS(NHPh), Mol. w. 228. [151°] (Lellmann, A. 221, 21; Losanitsch, B. 19, 1821).

Formation .- 1. By boiling aniline with CS. and alcohol (Hofmann, A. 57, 266; 70, 144). 2. By heating aniline with potassium sulphocyanide and H,SO, (Laurent a. Gerhardt, A. Ch. [8] 22, 103; 24, 196). — 3. From aniline and phenyl-thiocarbimide.—4. From di-phenyl-cyan-amide and H₂S (Weith, B. 7, 1303).—5. By boil-ing s-di-phenyl-guanidine with CS₂ (Hotmann,

Properties .- Trimetric crystals (from alcohol), nearly insol. water, v. sol. alcohol and ether. Sol. alkalis and reppd. by acids. Has a

very bitter taste.

Reactions.—1. Partially decomposed on dis-tillation into tri-phenyl-guanidine, CS₂, and H,S.-2. P,O,, ZnCl,, or HCl split it up into aniline and phenyl-thiocarbimide. -3. Roiling alcoholic potash forms di-pheny urea. 4. Diphenyl-ures is formed when the alcoholic solus tion is boiled with HgO. -5. A cold solution of nitrous ether in alcohol forms tri-phenyl-guanidine, phenyl thiocarbimide, and S (Claus, B. 4, 143).—6. Iodine, added to its boiling alcoholic solution, forms tri-phenyl-guanidine and phenyl thiocarbimide. - 7. Aniline forms, on heating, tri-phenyl-guanidine and H,S.-8. Sodium. amalgam reduces it to aniline, H2S, and CH, (Merz a. Weith, Z. [2] 4, 612).—9. When heated with HgCl, it yields tri-phenyl-guanidine (Buff, 2, 498).—10. Fuming H₂SO, decomposes it on heating, forming aniline, COS, and SO2 (Fleischer, B. 9, 998).—11. COCl, forms C, Hi, N, SO [87°], crystallising in prisms and split up by heat into COS and di-phenyl-cyanamide (Will, B. 14, 1486).—12. CSCl₂ in benzene forms C₁H₁₀N₂S₃, orystallising in yellow needles [156°], sl. sol. alcohol. In presence of ether CSCl2 forms alcohol. In presence of emer CSO₁₂ forms NPh:C \langle NPh>CS [79°] (Freund a. Wolf, B. 25, 1459).—13. H₂S at 170° forms aniline and CS. (Weith, B. 7, 1304).—14. Alkyl iodides form alkyl derivatives, which may perhaps be formulated as derivatives of ψ -thio-urea. Thus, MeI forms HEP. C(SMe):NPh [110], which is decomposed by hear int. MeSH and C(NPh), and by alcoholic potash into MeSH and CO(NHPh). like manner EtI forms C1.3H1.6N2S [79°] (v. DI-PHENYL-ETHYL- ψ -THIO-UREA), and ethylene bromide gives $C_{1b}H_{11}N_{2}S$ [136°] (Will, B. 14, 1490).— 1b. Allyl bromide in alcohol yields C, H, N, SBr, erystallising in trimetric prisms [171°] (Werner, orystanising in trimetric prisms [1:1] (Werner, C. J. 57, 303).—16. Benzyl chloride in alcohol forms C₂₀H₁₈N₂SO, crystallising in prisms [153°] (W.).—17. Phenyl cyanate in presence of benzene at 180° forms di-phenyl-ures and phenyl-ures. ene at 180° forms di-phenyl-urea and phenyl sulphocyanide (Goldschmidt a. Meissler, B. 23, 271).—18. Ac,O yields acetanilide and some phenyl-thiocarbimide (Werner, C. J. 59, 398).—19. Chloro-glyoxylic ether forms di-phenyl-di-thio-parabanic acid C₀-H₁,N₂S,O₂ [215°] and O₁-H₁,N₂S,O₂ [215°] and O₂-H₁,N₂S,O₃ [215°] and O₃-H₂,N₃S,O₄ [215°] and O₃-H₃,N₃S,O₄ [215°] and O₃-H₃ [215°] and O₄-H₃,N₃S,O₄ [215°] and O₅-H₃ [2 [235°] (Stojentin, J. pr. [2] 32, 8).

Tri-phenyl-thio-urea NHPh.CS.NPh,. [1529]. Formed by heating phenyl-thiocarbimide with diphenylamine at 280° (Gebhardt, B. 17, 2092, 3036). Long white needles, v. sol. hot alcohol.

3036). Long white needles, v. sol. not account.

Tetra-phenyl-thio-urga CS(NPh.)₂. [1967].

Formed by heating tetra-phenyl-guanidine with CS, at 270°; the yield being 60 p.c. of the theoretical amount (Bernthsen a. Friese, B. 15, 1530). Formed also from NHPh, and CSCl. (Bergreen, B. 21, 340). Long needles, sol. hot alcohol, insol. alkalis. Yields diphenylamine on heating with diluted (70 p.c.) H.SO.

Di-phenyl-thio-drea v. DI-PHENYL-DI-PHENYL-THIO-UREA.

References .- AMIDO-, BROMO-, CHLORO-, IODO-, NITRO, and OXY- PHENYL-THIO-UREA.

PHENYL-THIO-UREA CAMBON 7.
v. m-Amido-benzoto acid, Reaction 7.
DI-PHENYL-TOLENYL-AMIDIFE C. H₁₈N₂
Of by i.e. C.H.Me.C(NPh).NHPh. [168°]. Got by warming C.H.Me.C(NEt):NH2CI with aniline and alcohol (Glock, B. 21, 2656). Plates (from benzene), v. sol. alcohol.

PHENYL-TOLUENE v. METHYL-DIPHENYL. DI-PHENYL-TOLUIC ALDEHYDE C. HISO i.e. CPh2H.C6H1.CHO. [-15°]. (190°-195° at 46 mm). Formed by heating terephthalic aldehyde with benzene and conc. H₂SO₄ at 100° (Oppenheimer, B. 19, 2028). Oil. Reduces ammoniacal AgNO₃, being itself oxidised to tribunal mathena and should be a support of the support phenyl-methane carboxylic acid. KMnO4 gives tri-phenyl-carbinol p-carboxylic acid. Reacts with phenyl-hydrazine. Yields C, H16ONaHSO,

PHENYL-0-TOLUIDINE C₁H₁N t.e. [1:2]C,H,Me.NHPh. [41^o]. (805^o i.V.) at 728 mm. (Graebe, A. 238, 368). Formed, together with NHPh and distallaring the particular telescope. with NHPh, and ditolylamine by heating o-toluidine with aniline hydrochloride at 280° (Girard a. Willm, Bl. [2] 25, 248). Coloured violet-blue by HNO,

Phenyl-m-toluidine. (300°-305°). Got by rnenyi-m-toluidine: (300°-305°). Got by heating [1:3:5] C₀H₂Me(NHPh). OH with zincdust (Zega a. Buch, J. pr. [2] 33, 542). Oil. Coloured green by H₂SO, containing HNO₂.

Phenyl-p-toluidine C.H., NHPh. [879].

(318° i.V.) at 728 mm. (Graebe, A. 238, 363). Formed by distilling tri-tolyl-rosaniline acetate (Hosmann, A. 132, 291). Obtained also, together with diphenylamine and ditolylamine by heating p-toluidine (1 mol.) with aniline (1 mol.) and HCl (1 mol.) at 230° (De Laire, Girard, a. Chapoteaut, Bl. 1867, i. 360; A. 140, 347). Prepared by heating phenol with p-toluidine and ZnCl, or p-ore-sol with aniline and ZnCl, at 200° or with SbCl, (Buch, B. 17, 2634). Crystals. Coloured blue by HNO. With benzoic acid and ZnCl2 at 260° it yields phenyl-methyl-acridine C20 H13N (Bonna, A. 239, 60). Bromine vapour forms a tetra-A. 239, 60). Bromine vapour acting a lesson bromide [135°], a hepta-bromo derivative [185°], and a compound NC₁₃H₁₂Br, or NC₁₃H₂Br, and a compound NC₁₃H₁₂Br, and a compound NC₁₃H₂Br, Br. 254°]. Excess of Br at 310° forms NC₁₃H₂Br₁₃ [296°] (Bonna). Bromine in HOAc added to an alcoholic solution forms a tetra-bromo-derivative f15697.

Salt .- B'HCl: plates.

Acetyl derivative O.H., Acn. [519].
Yields C., H., BrAcn. [729], crystallising in plates.
Bensoyl derivative O.H., NO. Crystals
Yields crystalline C.H. (NO.). NBz. C.H., NO.
Nitrosamine C.H., NPh. NO. [829]. Yellow

medles (from ligroin). Br forms C₁₂H₁₁BrN₂O [166°] (Bonna, A. 239, 56).

PHENYL-TOLYL-ACETAMIDINE C₁₃H₁₄N₂ i.e. CH₂C(NC,H₁).NHPh. (76°). Formed from acetyl p-toluidine by successive treatment with PCl₃ and aniline (Wallach a. Fassbender, A. 214, 206).—B'₂H₂PtCl₄.

PHENYL-p-TOLYL-ACETIC ACID

C,H,CHPh.CO,H. [115°]. Formed from abromo-phenyl-acetic acid, toluene, and zincdust (Zincke, B. 10, 4916; Neure, A. 250, 149). Plates (from water), v. sol. alcohol.—KA' 4aq.—NaA' 6aq.—CaA' 2aq: needles (from dilute alcohol).

Ethyl ether EtA'. [34°]. Plates. Amide C₁₈H₁₈NO. [151°]. Nitrile C₇H₇CHPh.CN. [59°].

Phenyl-di-tolyl-acetic acid C. H., O. 178°-83°]. Got by oxidising (C.H.), CPh.CQ.C.H., (Thorner, A. 189, 123). Amorphous powder, insol. water, v. sol. alcohol.

PHENYL-TOLYL-AMINE v. PHENYL-TOLU-

PHENYL-p-TOLYL-BENZYL-BIURET NHPh.CO.N(GH,Ph).CO.NHC,H Me. [c. 100°]. Formed from p-tolyl-benzyl-urea and phenyl cyanate (Kühn a. Henschel, B. 21, 505). Needles

PHENYL-p-TOLYL-BENZYL-UREA

 $C_{21}H_{20}N_2O$. [113]. Got from p-tolyl-benzyl-carbanic chloride and aniline (Hammerich, B. 25, 1823). Dimorphous: prisms or plates, solether and alcohol.

PHENYL-DI-p-TOLYL-BIURET C_xH_{x1}N_xO_x i.e. NHPh.CO.N(C_aH₁Me).CO.NHC_aH₄Me. [140°]. Formed by heating di-p tolyl-urea with phenyl cyanate at 170° (Kühn a. Henschel, B. 21, 505). Crystals (from alcohol).

Di-phenyl-tolyl-biuret

(from dilute alcohol).

NHPh.CO.NPh.CO.NHC.W.Me. [216°]. Got by heating di-phenyl-urea with p-tolyl cyanate at 170° (K. a. H.).

PHENYL-p-TOLYL-CARBINOL C₁₁H₁₁O i.e. C₂H₁Me.CPhHOH. [53°]. Got by reducing phenyl tolyl ketone in alcoholic solution by sodium-amalgam (E. a. O. Fischer, A. 194, 265). Stellate groups of needles (from ligroin).

Di-phenyl-tolyl-carbinol C_∞H_{1N}O i.e. • C_∗H₄Me.CPh..OH. [150°]. Formed by oxidising di-phenyl-tolyl-methane with CrO, and HOAc (F.). Crystals (from ligroïn). May be distilled.

PHENYL-p-TOLYL-CARBINOL O-CARB-OXYLIC ACID. Lactone v. Tolyl-Phthalide. Di-phenyl-tolyl-carbinol carboxylic acid.

Lactone $\begin{bmatrix} 5_1^2 \end{bmatrix}$ C₆H₃Me<CO^{Ph₂}>O. [147°].

(above 360°). Formed by oxidising di-phenylm-xylyl-methane with chromic acid mixture (Hemilian, B. 16, 2361; 19, 3063). Prisms.

The isometic [42] C₆H₁Me C^{CPh}_{CO} O₁ [179°], (above 360°), is got by oxidation of diphenyl-p-xylyl-methane, and is accompanied by [1:2:5]OPh₂(OH).O₂H₁Me.OO₂H₁, which yields BaA'₂ and CaA'₂, and does not form a lactone.

PHENYL-o-TOLYL-CARBINYLAMINE
[1:2]C₀H₄Me₄CHPh.NH₂ (299°) at 721 mm.
Formed by reducing the oxim of phenyl o-tolyl ketone dissolved in alcohol by adding sodium-

amalgam and HOAc (Goldschmidt a. Stöcker, B. 24, 2806). Yields an acetyl derivative [124°].

R'HCl. [249°]. Needles, m. sol. water.

-B'HCl. [249°]. Needles, m. sol. water. • m. Isomeride. (299°) at 724 mm. Yields 'HCl [243°] and an acetyl derivative [97°].

m-neumerage. (2997) as 724 mm. Helds B'HCl [248°] and an acetyl derivative [97°]. p-Isomeride. (296°) at 723 mm. Yields an acetyl derivative [181°] and the salts B'HCl [252°], B'_LH_PtCl, 2aq [119°], B'C,H_O, [157°], B'C,II,O, [73°]. The hydrochloride is converted by potassium sulphocyanide into the compound 'C,H_Me.CHPh.NH.CS.NH, [101°] and by potassium synante into the urea derivative C,H_Me.CHPh.NH.CO.NH, [158°].

PHENYL TOLYL - CARBINYL KETONE CARBOXYLLC ACID Challing i.e. Call Me.CH., CO.L. [112°]. Formed by heating Call. (CH.Calline) O with KOHAq at 100° (Heilmann, B. 23, 3160). Vitreous prisms.—AgA'. Converted by heating with an alcoholic solution of hydroxylamine hydrochloride into Call. (CGII...Calline) N

PHENYL-o-TOLYL-CYANAMIDE

NPh:C:NC_aH,Me. Carbophenyltolytimide. (320°-325° uncor.). Formed by adding HgO to a boiling solution of phenyl-o-tolyl-thiouses in dry benzene, the yield being 65 p.c. of the theoretical. Oil. On keeping, it polymerises to a brittle glassy solid [68°-71°]. V. sol. benzene, sl. sol. ether. By boiling with dilute alcohol it is converted into phenyl-o-tolyl-urea. H₂S passed into its boiling solution in dry toluene converts it into phenyl-o-tolyl-thiourea. Heated with CS₂ at 180°-200° it yields a mixture of phenyl- and o-tolyl-thiocarbinides. It combines with o-toluidne, forming u-phenyl-dio-tolyl-guanidine (Huhn, B. 19, 2410).

Phenyl-p-tolyl-cyanamide NPh:O:NO,H,, (325°-330° uncor.). Resembles the preceding isomeride in mode of preparation and properties.

DI-PHENYL-TOLYLENE-TETRA-AMIDO-METHANE C₂₀H₂₂N₄ i.e.

C₁H₀\NH\ NH\ C(NHPh)₂(?). [161°]. Formed by heating C(NPh)₂ with tolylene-o-diamine at 1282 (Dahm a. Gasiorowski, B. 19, 3057. Needles (from henzene).—B'₃BHCl. [174°].—B'H₂SO₀.

DI-PHENYL-m-TOLYLENE DIAMINE $C_{1p}H_{1s}N_2$, i.e. $[1:3:5]C_sH_1Me(NPhH)_2$. $[105^\circ]$. Formed by heating orein (1 pt.) with aniline (4 pts.) and a mixture of $2nCl_2$ and $CaCl_2$ at 220° (Zega a. Buch, $J.\ pr.\ [2]\ 33,\ 542$). White needles (from glacial HOAc).

Di-acetyl derivative [160°].
Di-benzoyl derivative [190°].
Dinitrosamine C₁₁H₁₆N₁O₂ [170°].
Reference. — DI-NITRO-PHENYL-TOLYLENE-DI-

PHENYL-o-TOLYLENE-GUANIDINE

C,He\NH\C:NPh. [167°]. Mol. w. 229 (calc. 22:i). Formed from o-tolylene-diamine and diphenyl-cyanamide (Keller, B. 24, 2514). Needles (from warm alcohol). Di-p-tolyl-cyanamide

forms C,H, C:NPh C(NHC,H.), [193°], while phenyl cyanide gives the compound

>0:NPh [234°].-B'HCl.~

B', H, PtCl. -B', H, SO,: white needles.

Mono-acetyl derivative. [147]

Di-benzoyl derivative. [2220]. Prisms. Nitrosamine C₁₄H₁₂N₄O. [125°]. DI-PHENYL-m-TOLYLENE-DI-METHYL-

DI-AMINE C₂₁H₂₂N₂i.e. C_cH₃Mc(NPhMe)₂ [124°]. Formed from C₂H₆(NHPh)₂, NaOH, and McI (Zega a. Buch, J. pr. [2] 33, 546). White lamine (from HOAc).

DI - PHENYL-o-TOLYLENE - DI - THIO - DI-UREA [1:3:4]C.H.Me(NH.CS.NHPh)2. [c. 150°]. Formed from tolylene-o-diamine and phenylthiocarbimide in alcohol (Lellmann, A. 221, 19). Thin plates (from dilute alcohol), v. sol. waren NaOHAq, sl. sol. water.

Di-phenyl-m-tolylene-di-thio-di-urea

[1:2:4]CaHaMe(NH.CS.NIIPh), [168°]. Formed from tolylene-m-diamine and phendl thio-carbimide (Lussy, B. 8, 670; Gebhardt, B. 17, 8046; Billeter a. Steiner, B. 18, 3293; 20, 228).

Di-phenyl-p-tolylene-di-thio-di-urea [1:2:5]C₆H₃Me(NH.CS.NHPh)₂. [181°] a Formed from tolylene-p-diamine and phenyl-thiocarbimide in alcohol (Lellmann a. Würthner, A. 228, 206). Plates, nearly insol. alcohol. DF-PHENYL-TOLYLENE-DI-UREA

C,H_s(NH.CO.NHPh)_z. [above 300°]. Formed by adding phenyl cyanate to an othercal solution of tolylene-diamine [99°] (Kuhn, B. 18, 1477). white pp. Insol. water, alcohol, ether, and benzene, v. sl. sol. acetic acid. By boiling with aniline it yields s-di-phenyl-urca.

PHENYL-p-TOLYL-ETHANE C₁₃H₁₆, i.e.

C₁₅H₁₆, (286° un CH₂Ph.CH₂.C. H₄Me. [27°]. (286° uncor.). Formed by reduction of tolyl benzyl ketone by HI and P (Mann, B. 14, 1646). White plates.

Phenyl-p-tolyl-ethane CH3.CHPh.C,H,Me. (279°). Formed from CaH3.C2H4Br, toluenc, and zinc-dust (Bandrowski, B. 7, 1016). Oil. Yields p-benzoyl-benzoic acid on oxidation.

PHENYL-p-TOLYL-ETHYLENE C,5H, i.e. CIIPh:CH.C.H. Methyl - stilbene. Formed by boiling p-tolyl-benzyl-carbinol with dilute H.SO, (Mann, B. 14, 1646), and also by Section 25.4 (January B. 17, 1976), and also by Garding p-tolyl cinnamate (Anschütz, C. J. 47, 898; B. 18, 1945). Pearly plates with blue fluorescence, v. sl. sol. alcohol, v. c. sol. ether. Yields

C_{1.}H_{1.}Br₂ [187°]. DI - PHENYL - DI - p - TOLYL - ETHYLENE OXIDE? C₂₈H₂₁O. Phenyl tolyl (a)-pinacolin. [215]. Formed by the action of zinc and HClAq on phenyl p-tolyl ketone in alcohol, and got also by heating a mixture of the ketone with phenyl-tolyl-carbinol, alcohol, and ZnCl, (Thorner a. Zincke, B. 11, 71; A. 189, 104). Minute needles, m. sol. hot alcohol. Conc. HClAq at 150°

changes it into the isomeric (β)-pinacolin C,H,CO,CPh(C,H,Me), [187°].

PHENYL P-TOLYL ETHYLENE DISUL-PHONE C,H,SO,C,H,SO,C,H, [162°]. Got by boiling C,H,NO,C,H,Cl with an alcoholic solution of sodium toluene p-sulphinate (Otto, J. pr. 1320, 103).

[2] 80, 199).
PHENYL - TOLYL - ETHYLENE - \psi - THIO-UREA NPh:C<N(C,H₁)>CH₂. [128°]. Formed by boiling the methylo-iodide of the ethylene derivative of tolyl-di-thio-carbamic acid with

aniline (Will a. Bidschowski, B. 15, 1315). Silky plates.

PHENYL - p - TOLYL - ETHYL - THIO-UREA C₁₆H₁₈N₂S, i.e. NPhEt.CS.NHC,H. [90°]. Formed from p-tolyl-thiocarbimide and ethyl-aniline (Gebhardt, B. 17, 2091). Colourless crystals.

s-PHENYL-DI-o-TOLYL-GUANIDINE

C₈H₃N:C(NHC₇H₇)₂. [102°]. Formed by the action of an alcoholic solution of aniline upon di-o-tolyl-thiourea in presence of PbO. Got also by the combination of C.H., N:C:N.C,H, with amiline (Huhn, B. 19, 2412). Folted needles. V. sol. warm abohol, ether, and benzene.

B'HCl.—B',H₂Cl,PtCl₄: orange-yellow tables.

u-Phenyl-di-o-tolyl-guanidine
C,H,N:C(NHC,H,)(NHC,H), [112°]. Formed from o-toluidine and C,H,N:C:NC₆H₃ (Huhn). Long needles, v. sol. alcohol. Salts .- B'HCl. -

B'₂H₂FtCl₄: orange-yellow tables. s.Di-phenyl-p-tolyl-guanidine C.H,N:C:(NHC₆H₅)₂. [121°]. Formed by the action of an alcoholic solution of p-toluidine upon di-phenyl-thiourea in presence of PbO (Hofmann, B. 2, 459; Huhn, B. 19, 2412). Felted needles. V. sol. alcohol and ether.— B'HCl.—B'₂H₂Cl₂PtCl₄: reddish-yellow pp. *u*-Di-phenyl-p-tolyl-guanidine C₂₀H₁₉N₂, *i.e.*

C,H,N:C(NHC,H,)(NHC,H,). [127°].

Formation. -1. By heating phenyl-p-tolylthiourea with an alcoholic solution of aniline in presence of PbO.-2. By the combination of C.H.N:C:NC,H, with aniline (Huhn, B. 19, 2109). -B'HCl. -B'2H2Cl2PtCl1: sparingly soluble pp.

PHENYL TOLYL-IMIDO-BENZYL KETONE C₆H₅.CO.C(NC₇H₇).C₆H₅. Formed by heating o-toluiding with benzil at 100° (Bandrowski, M. 9, 689). Yellow plates (from alcohol).

PHENYL O-TOLYL KETONE C14H12O i.e. C_aH₅.CO.C_bH₁Me [1:2]. (314°) at 735 mm· (Smith, B. 21, 4046); (295°) at 722 mm. (G. a-S.). Formed by the action of AlCl, on a mixture of o-toluic chloride and benzene (Ador a. Rilliet, B. 12, 2301; Goldschmidt a. Stöcker, B. 24, 2805). Formed also, together with a much larger quantity of the p- isomeride, from BzCl, toluene, and AlCl3 (Elbs, J. pr. [2] 35, 466). Oil. Yields anthracene on long boiling or on heating with zinc-dust.

'syn-Oxim C,H,,C.C,H,. [69°]. HO.N

Phenyl-m-tolyl ketone C, H, CO.C, H, Me [1:3]. (315° i.V.) at 745 mm. S.G. 17.6 1.088. Formed by the action of AlCl₃ on a mixture of *m*-toluic chloride, benzene, and AlCl₃ (A. a. R.; G. a. S.). Got also by cautious oxidation of phenyl-m-tolyl-methane (Senff, A. 220, 252). Oil, miscible with alcohol. Reduced by HIAq at 200° to C,H, (269° at 725 mm.). Oxim. [101°].

Reduced by sodium-amalgam in presence of HOAc to m-toluic anilide and

gam in presence of HOAC to me some anime and O.H., Mc.CPh.H.NH.,
Phenyl.p-tolyl ketone C.H., CO.C.H., Me [1:4],
[60°]. (327° i.V.).

Formation.—1. Togethet with the o-isomeride

Formation.—1. Togethet with the o-isomeride

by heating benzoic acid with toluene and P2O, at 200° (Kollarits a. Merz, B. 6, 446; Thörner, A. 189, 83).—2. By oxidising C.H.Me. 6PhH. (Zincke a. Plascuda, B-7, 982).—8. By distilling a mixture of calcium p-tolunte and benzoate (Radziszewski, B. 6, 810).—4. By heating BzCl with toluene and zinc at 190° (Grucarevic a. Merz, B. 6, 1243) .- 5. By the action of AlCl. on a mixture of p-toluic ahloride and benzene (A. a. R.).—6. From BzCl, toluene, and AlCl.

Properties.—Prisms, m. sol. alcohol, v. sol. ether. Dimorphous. Yields p-benzoyl-benzoic acid on oxidation. Reduced to C,H,Me.CH,Ph acid on oxidation. Reduced to C_{11} Met. C_{12} In by distillation over zinc dust. Sodium amalgam forms phenyl-tolyl-carbinol. Zinc and HClAq acting on the alcoholic solution form two pinacolins C_{12} H_{24} O. The (α) -pinacolin (215°) may be converted into the (8)-isomeride [137°] by heating with HOAc.

C_eH₄.C.C_eH₄Me. HO.N anti-Oxim [154°]

(Hantzsch, B. 23, 2325, 2776; 24,658; cf. Wegerhoff, A. 252, 11). Converted by HOAc and HCl into p-toluic anilide. Yields an acetyl derivative[124°] and a benzoyl derientive [85°] (Auwers, B. 23, 399).

syn-Oxim C.H.,C.C.H.Me. [116°]. Con-N.OH

verted by HOAc and HCl into benzoyl-toluidine and some toluic anilide. Yields an acetyl derivative [118°-122°] and a benzyl derivative [51°].

Phenyl p-tolyl diketone C_aH₃CO.COC,H₃.
Formed by heating di-bromo-deoxybenzoïn with water at 183° (Bucher, B. 22, 2819). Yellow oil, solidified by cold.

References .-- DI-AMIDO-, NITRO-, OXY-AMIDO-, and Oxy. PHENYL TOLYL-KETONE.

PHENYL TOLYL KETONE CARBOXYLIC ACID v. Toleyl-BENZOIC ACID.

Phenyl p-tolyl ketone dicarboxylic acid C₁₆H₁₂O₆ i.e. C₆H₅.CO.C₆H₂Me(CO₂H)₂ [1:4:2:6]. Benzoyl-uvitic acid [245°]. Formed by oxidising phenyl mesityl ketone with dilute HNO, (Elbs, J. pr. [2] \$5, 489). Needles.—Ag₂A".

An isomeric acid, got by oxidation of phenyl ψ-cumyl ketone C_cH₃.CO.C_cH₂Me₁ [5:1:2:4], yields

PHENYL-o-TOLYL-METHANE C₁₄H₁₄ i.e. C₄H₄,CH₄,C₈H₄Me [1:2]. o-Benzy'-toluene. Mol. w. 182. (284°). Formed, together with the p-isomeride, by heating benzyl chloride with toluene and zinc-dust (Zincke, B. 6, 906; Senff, A. 220, 249). Got also from C.H.Mc.CH.C.P. benzene, and zinc-dust (Barbier, B. 7, 1544). Yields anthracene when passed through a redhot tube.

Phenyl-m-tolyl-methane

C₆H₈.CH₂.C₆H₄Me [1:3]. (275° i.V.). S.G. 17.6 .997. Got by reducing the ketone with HI and P (Ador a. Rilliet, B. 12, 2300). Prepared by heating ω -chloro-m-xylene (1 pt.) with benzene (7 pts.) and AlCl, (Senff, A. 220, 230; cf. Barbier, C. R. 79, 660). Oil, sol. alcohol and ether. Gives a di-nitro- derivative [141°].

Phenyl-p-tolyl-methane
C₄H₃.CH₄.C₄H₄Me [1:4]. (280° i.V.). Formed,
with the o-isomeride, by heating benzyl chloride,
with toluene and zinc-dust (Zincke, B. 7, 1163; A. 161, 98). Formed also by the action of zincdust on benzyl chloride (Prost, Bl. [2] 46, 248), and by heating phenyl p-tolyl ketone with ammo-nium sulphide and S at 320° (Willgerodt, B. 20, 2470). Gil. Yields p-benzoyl-benzoic acid on oxidation. Does not form anthracene when Vol. IV.

passed through a red-hot tube. Yields a disulphonic scid [38°], which gives K,A" 3 aq,
BaA" 8 aq, and CuA" 4 aq.

Pheny di-tolyl-methane CHPh(C,H,), [56°]. Got by heating (C,H,), CPh.CO.C,H, with sodalime at 300° (Thorner a. Zincke, B. 11, 70).

Di-phenyl-o-tolyl-methane C₂₀H₁₁ i.e. (C₄H₃, CH.C₄H₄Me. [59·5°]. (B54°). Formed from leucaniline by diazotising and boiling with alcohol (Fischer, A. 194, 282; Rosenstiehl a. . Gerber, A. Ch. [6] 2, 342). Spherical groups of prisms (from McOH), v. sol. ether. Oxidised by CrO₂ and HOAc to $(C_cH_a)_2C(OH).C_cH_4Me$ [150°].

ni-pheny m-tolyl-methane. [62°]. (above 3609). Formed by distilling its carboxylic acid with baryta (Hentilian, B. 16,-2368). Long thin needles (from alcohol), v. sol. ether. The crystals emit light when powdered. Its dilute solutions fluoresce blue.

Di-phenyl-p-tolyl-methane. [71°]. (above 36(*). Formed by distilling its o-carboxylic acid, and also by the action of P2O, on a mixture of toluene and di-phenyl-carbinol or of benzene and phenyl-p-tolyl-carbinol (Hemilian, B. 7, 1209; 19, 3066; Fischer, A. 194, 263). Needles or prisms, v. sol. hot alcohol.

References - DI-AMIDO-, CHLORO-, NITRO AMIDO, and OXY- PHENYL-TOLYL-METHANE. PHENYL p TOLYL METHANE -0 CARB OXYLIC ACID C₀H₁Me.CH₂, C₀H₄, CO₂H₄ [134°], Formed by warming C₀H₄Me.CO.CH₄CO.H with NII, Aq and zinc-dust (Gresly, A. 234, 236). Needles (from alcohol), nearly insol. water .-BaA',: plates, v. sol. water.

Phenyl-tolyl-methane dicarboxylie CO_H.C₆H₄.CH(C,H₇).CO₂H. [154°]. ((above 300"). Got by saponifying the nitrile, which is prepared by treating an alcoholic solution of CN.C. H, CH, CN with benzyl chloride and KOH (Eichelbaum, B. 21, 2679). Prisms, sol. alcohol.

Amide. [224]. Small plates.

Imide C₆H. CH(C₇H₇) > CO.

(above 300°). Got by heating the amide with conc. HClAq. Needles, v. sol. alcohol.

Nitrile. [110°]. (above 300°). Plates.

Di-phenyl-p-tolyl-methane carbox be cond C.H.Me.CHPh.C.H., CO.H. [155°]. Formed by warming p tolyl-phthalide with benzene and AlCl, (Gresly, A. 234, 242). Needles (from alcohol).—BaA', 21aq: sl. sol. water.

Di-phenyl-p-tolyl-methane carboxylic acid CIIPh₂.C₆H₄Mc.CO₂H[4:2:1]. [217°]. Formed from di-phenyl-p-tolyl-carbinol carboxylic acid, NaOHAq, and zinc-dust (Hemilian, B. 16, 2363). Transparent tables, v. sol. alcohol. -BaA', 4aq. AgA': minute needles, insol. water.

Di-phenyl-p-tolyl-methane carboxylic acid CHPh...C, H, Me.CO, H [4:1:2]. [203°]. Formed from di-phenyl-methyl-phthalide, NaOHAq, and zinc-dust (Hemilian, 3. 19, 3064). Needles or

zinc-dust (Hemilian, %. 19, 3064). Needles or tables, sol· hot alcohol.—BaA', 3aq.—AgA'.

PHENYL-p-TOLYL DI.METHYMENE DI.

SULPHONE KETONE C., H., S.O., i.e.
C.H., SO., CH., CO.CH., SO., C.H., Me. [112°].

Formed from CH, Br. CO.CH., SO., C.H., Me by treatment with C.H., SO., Na and obtained also from C.H., SO., CH., CO.CH., Br and C.H., Me. SO., Na (Otto, J. pr. [2] 36, 427). Plates, m. sol. alcohol v. sol. CHC! hol, v. sof. CHCl...

PHENYL - o - TOLYL - METHYL - PYRROLE (a. Ebenhardt, B. 23, 3271). They are oils, NC,H, CPh:CH . [44°]. (827°). Formed by heating its carboxylic acid [199°] Lederer a.

Paal, B. 18, 2596). Plates, v. e. sol. alcohol.

Phenyl-p-tolyl-methyl-pyrrole. [91°].
(above 350°). Got by heating its carboxylic acid

Tables (from ligroin).

PHENYL - 0 - TOLYL - METHYL - PYRROLE

CARBOXYLIC ACID C.H.MeN CPh:CH [199°]. Got by saponifying its ether, which is formed by boiling acetophenone-acetoacetic sther with o-toluidine and HOAc (Lederer a. P.c.al, B. 18, 2596). Small prisms (from alcohol).
p-Isomeride. [227°]. Made in like in oner from p-toluidine. Plates, v. sol. alcohol.

Ethyl ether Eth. [115°]. Crystals. PHENYL-0-TOLYL-METHYL-THIO-UREA C₁₃H₁₆N₂S i.e. NMePh.CS.NHC,H,., [121°]. Formed from methyl-aniline and o-tolyl-thiocarbimide (Gebhardt, B. 17, 2091, 3035). Plates.

Phenyl-p-tolyl-methyl-thio-urea. Formed in like manner from p-tolyl-thiocarb-imide (G.). Small trimetric tables. By disti-lation with steam it is resolved into the parent substances, which slowly recombine in the dis-

THENYL-TOLYL-NAPHTHYL-GUANIDINE C₂,H₂,N₂ i.e. CN₂H₂Ph(C,H₂).C₁₀H₂. [belowe 60°]. Formed by boiling an alcoholic solution of phenyl-tolyl-thio-urea and naphthylamine with Pbo (Tiemann, B. 3, 6). Brittle resin,

forming a crystalline hydrochloride. PHENYL-DI-TOLYL-PHOSPHINE

PHENYL-DI-TOLYL-PHOSPHINE

(C₄H₄Me)₂PC₆H₁, [57°]. Formed from p-bromotoluene (2 mols.), C₄H₄PCl₂ (1 mol.), and Na

(Dörken, B. 21, 1512). Crystals, v. sol. ether.

Di-phenyl-tolyl-phosphine C₄H₆P(C₆H₅)₂PCl,

[68°]. Formed from (C₆H₃)₂PCl,

p-bromotoluene, and sodium (Dörken, B. 21, 1511).

Small prisms. Yields (C₆H₃)₂PC(C₆H₄Me)

[180°] and (C₆H₃)₂PS(C₆H₄Me) [139°].

PHENYL-TOLYL-(a)-PINACOLIN C₆₀H₂₄O 2.

DI-PHENYL-DI-TOLYL-(ETIVLEND GUIDE.

Di-PHENYL-DI-p-TOLYL-ETHYLENE OXIDE.
Phenyl-tolyl-(3)-pinacolin

C.H. CO.OPh(C.H.), [137°]. Formed by the action of AcCl on phenyl tolyl-(a)-pinacolin or on phenyl tolyl-pinacone (Zincke a. Thörner, B. 10, 1477; 11, 65, 1396; A. 189, 110). Prepared by boiling phenyl p-tolyl ketone with alcohol, HClAq, and zinc. Small dimetric tables, sl. sol.

cold alcohol. On heating with soda-lime at 300°

tyields phenyl-di-tolyl-methane.

PHENYL-TOLYL-PINACONE C₂H₂₀O₂ i.e.
C,H,,CPh(OH).CPh(OH),O,H,. [165²]. Formed
by treating an alcoholic solution of phenyl ptolyl ketone with zinc and B₂SO₄ (Zincke a.
Thörner, B. 10, 1476). Minute needles (from alcohol). Decomposed by fusion and by boiling alcoholic potash into phenyl tolyl ketone and phenyl-tolyl-carbinol. Converted into phenyltolyl-(8)-pinacolin by heating with dilute H2SO, at 160°, with HOAc at 190°, with Accl, or with HClAq. Alcoholic HCl in the cold forms HCIAq. Alcoholic Horan phenyl-tolyl-(a)-pinacolin. PHENYL-TOLYL-PROPANE PHENYL-TOLYL-PROPANE

CH, CHPh.CH, C, H, Me. The o- (817°), m. (312°), and p- (803°) compounds are formed by the action of conc. H₂SO₄ on a mixture of styrene and o-, m-, and p-xylene respectively (Kraemer, Spilker, miscible with alcohol and ether.
PHENYL-TOLYL-PROPIONIC ACID

CH.Ph.CH(C,H,Me).CO.H. o. [95.5°], m. [80°], p. [105°]. Formed from the corresponding p- [105°]. Formed from the corresponding nitriles, which are got from the tolyl-acetonitriles by treatment with NaOEt and benzyl chloride (Päpcke, B. 21, 1331). The o-nitrile is an oil (\$40°.858°); the m-nitrile [58°] (350°.
\$60°), and the p-nitrile [79°] are crystalline.

Di-phenyl-p-tolyl-prophonic acid. Nitrile

CH,Ph.CPh(C,H,Me).CN. [121°]. Formed from phenyl-pticyl-acetonitrile, NaOEt, and benzyl chloride (Neure, A. 250, 150). Needles. DI-PHENYL-TOLYL-PYRROLE C, H, N i.e.

NC,H, CPh:CH. The o- [115°] (above 300°) and p- [203°] sompounds are formed by distilling the corresponding carboxylic acids with lime (Baumann, B. 20, 1492; Paal a. Braikoff, 22,

3089). Both crystallise in white needles.
DI-PHENYL-TOLYL-PYRROLE CARBOXY-LIC ACID N(C,H₇) CPh:C.CO₂H. The o-acid [227°] and its p-isomeride [206°] are got by saponification of the ethers, which melt at 135° and 145° respectively, and are formed by boiling the corresponding toluidine with phenacylbenzoyl-acetic ether CH2Bz.CHBz.CO2Et and HOAc (Paal a. Braikoff, B. 22, 3088). Both acids are crystalline and al. sol. ether.

Di-phenyl.p-tolyl.pytrole dicarboxylic acid N(C,H,) C(C,H,CO,H):CH [253°]. Formed by heating C,H,(CO,C,H,CO,H); with p-toluidine on a water-bath (Baumann, B. 20, 1489). Yellowish needles, v. sol. alcohol and CS, PHENYL P.TOLYL SULPHIDE Ph.S.C,H, An oil yet by the setting of NeSPh on prilars.

An oil got by the action of NaSPh on p-diazo-

toluene chloride (Ziegler, B. 23, 2471) Phenyl p tolyl disulphide P Thenyl p tolyl disulphide Ph.S.C.H.,
Formed by adding Lr to an ethereal solution of
PhSH and C.H.SH. Got also, together with Ph.S., by heating toluene p-sulphinic acid with PhSH (Otto a. Rössing, B. 19, 3133). Thick oil, insol. water, scarcely volatile with steam.

PHENYL p.TOLYL SULPHONE C, H, SO, i.e. C, H, SO, C, H, Me. [125°]. S. (alcohol) 1.62 at 20°. Formed by the action of P,O, on a mixture of toluenc and benzene sulphonic acid, or of benzene and toluene p-sulphonic acid (Michael a. Adair, B. 11, 116). Formed also from benzene sulphonic chloride, toluene, and AlCl, (Beckurts a. Otto, B. 11, 2068). Prisms or tablets, PHENYL-o-TOLYL-SEMI-THIOCARBAZIDE

C, H, N, S i.e. NHPh.CS.NH.NH.C, H, Me. [146°]. Formed from phenyl-thiocarbimide and o-tolyl-hydrazine (A. E. Dixon, C. J. 57, 260). Pearly prisms, v. 8l. sol. water, v. sol. hot-slochol. Isomeride C.H.MeNH.CS.NH.NHPh. [163°].

Formed from o-tolyl-thiocarbimide and phenyl

hydrazine. Vitreous prisms v. sl. sol. water. PHENYL o-TOLYL-THIO-UREA C14H14N28 i.e. NHPh.CS.NHC, H, Me. [140°]. Formed from o-tolyl-thiocarbimide and aniline (Staats, B. 13, 157) and by passing H.S into a boiling solution of phenyl-tolyl-cyanamide NPh:C:NC,H, in dry benzene (Huhn, B. 19, 2411). Long needles, sl. sol. water. Boiling HClAq (34 p.c.) splits it up into aniline, o-toluidine, phenyl-thiocarbimide, and o-tolyl-thiocarbimide (Mainzer, B. 15, 1419). HgO, added to its solution in boiling benzene, forms phenyl-tolyl-cyanamide.

Phenyl-p-tolyl-thio-urea NHPh.CS.NHC,H,Me. [1 NHPh.CS.NHC, H, Me. [\$37°] (S.); [141°] (F. a. W.). Formed from p-tolyl-thiocarbimide and applies (S.) and from the p-tolyl-thiocarbimide and applies (S.) and aniline (S.), and from phenyl-p-tolyl-cyan-amide and H₂S (H.). Plates, sl. sol. water. Split up by HClAq in the same way as the o- isomeride (M.), and decomposed by HgO in like manner. COCl, passed into its solution in toluene forms NPh:O (N(C,H,)) CO [89°], crystallising in white needles (Freund a. Wolf, B. 25, 1466).

white needies [recuise a. 105.]

Tetra-w-phenyl-dio-tolyl-thio-tres

C₂₀H₂N₂N₂S i.e. (CHPh₂C₂H₄NH)₂CS. [123°].

Formed from CHPh₂C₂H₄NH₂ and CS₂ (Fischer and CS₂) a. Franckel, A. 241, 368). White needles, insol. cold alcohol.

References. NITRO- and OXY- PHENYL-TOLYL-THIO-UREA.

PHENYL - p - TOLYL - THTO - UREA-w-CARB-

OXYLIC ACID. Nitrile NHPh.CS.NH.C.H., CH., CN. [141°]. by warming phenyl-thiocarbimide with amidophenyl-acetonitrile (Freund a. Immerwahr, B. With furfuraldehyde it forms 23, 2856). NHPh.CS.NH.C.H., CCy:CH.C.H., O [160°] crystallising from alcohol.

PHENYL-O-TOLYL-UREA C1.H1.N2O i.e. NHPh.CO.NHC, H, Me. [212°]. Formed by boiling NPh:C:NC, H, with dilute alcohol (Huhn,

B. 19, 2410). Slender needles.

Phenyl-m-tolyl-urea. [165°]. Formed from phenyl cyanate and m-toluidine in ether

(Buchka a. Schachtebeck, B. 22, 840). Needles.
Phenyl-p-tolyl-urea. [2112] (H.); [2182]
(Freund a. Wolf, B. 25, 1467). Formed by boiling phenyl-p-tolyl-cyanamide with dilute alcohol (Huhn, B. 19, 2408).

Phenyl-di-p-tolyl-urea C, H, N,Oe Formed from (C₆H,Me),NCOCl and aniline (Hammerich, B. 25, 1821). Needles, sol. alcohol.

Di-phenyl-p-tolyl-urea NPh2.CO.NHC.H,. [130°]. Formed from NPh. COCl and p-toluidine (Michler, B. 9, 713). Needles.

References. - OXY-PHENYL-TOLYL-TIREA

(B)-PHENYL-UMBELLIFERONE C15H10O, i.e. $\begin{bmatrix} 4_2^1 \end{bmatrix}$ C_4 H_2 OH CPh:CH O-CO[244°]. Prepared by the action of H,SO, on a mixture of benzoylacetic ether and resorcin (Pechmann a. Duisberg, B, 16, 2126). Plates (from dilute alcohol).
PHENYL - URAMIDO - ACETO - NITRILE

C.H..CH(CN).NH.CO.NH, Phonyl-aceto-Formed by heating equimolecular quantities (Pinner a. Lifschütz, B. 20, 2355). Prisms. V. sol. alcohol, m. sol. hot water. By boiling with dilute HCl it is converted into di-oxyphenyl-glyoxaline CHPh.N C.OH.

PHENYL-URAMIDO-BENZOIC ACID v. vol. i. p. 157.

PHENYL - a - URAMIDO - CROTO - NITRILE C.H., CH:CH.C(CN)H.NH.CO.NH, Phenyl-crofomitrile-urea. [160° with decomposition]. Prepared by heating equivalent quantities of cinnamical dehyde-cyanhydrin and urea to 96° for several hours; the yield is 40 p.c. of the cyanhydrin (Pinner a. Lifschütz, B. 20, 2353). Needles.

M. sol. hot alcohol. By boiling with dilute HCl it is converted into di-oxy-styryl-glyoxaline CO NH.CH.CH:CHPh

PHENYL - URAMIDO - PHENYL - ACETIC NHPh.CO.NH.CHPh.CO.H. ACID Formed by the action of potash on di-phenyl-thiohydantoin (Kossel, B. 24, 4153). Sol. water.

Ethyl ether EtA', [165°]. Formed from phenyl-amido-acetic ether and phenyl cyanate

(K.). Crystalline powder, sol. hot alcohol. PHENYL-UKAMIDO-PROPIONIS C₁₀H₁₂N₂O₃ i.e. C₅H₁NH.CO.NH.CH₂.CH₂CO₂H₄. [172°]. Formed by heating β-amido-propionic 172. Formed by neating stando-propione acid with phenyl-urea at 140° (Hoogewerff a. var borp, R. T. C. 9, 49). Tablets and needles, m. sol. cold alcohol. AcCl forms C₁₈H₁₀N₁O₂

NPh < NH.CO NPh. [264°]. Formed heating plienyl semicarbazide at 160° (Pinner, B. 21, 2329) or phenyl-carbazic other at 240° (Heller, A. 263, 282). White needles, v. sol. warm HOAc. Yields the acetyl derivatives the other C, II, EtN, O, [137].

PHENYL-URAZOLE v. DI-OXY-PHENYL-TRI-

PHENYL-UREA C.H. N.O i.e. NHPh.CO.NH,. [147°]. Formation.—1. By passing cyanic acid vapour into cooled aniline or from aniline sulphate and potassium cyanate (Hofmann, A. 53, 57; 57, 265; 70, 130; 74, 14; Weith, B. 9, 810). 2. From aniline and moist cyanogen chloride.—3. From phenyl cyanate and NH₃.—4. From mercuric fulminate and aniline (Steiner, B. 8, 518). • 5. From benzamidoxim, NaOH, and benzene sulphonic chloride (Pinnow, B. 24, 4171).

Properties. - Monoclinic needles, v. sol. alcohol and boiling water, sol. ether. Decomposed at 150° into s-di-phenyl-urea, CO2, and NH2

Reactions .- 1. Conc. KOHAq yields aniline, NH₂, and CO₂ - 2. Baryta-water yields phenylbiguanide (Emich, M. 12, 16).—8. Assiste at 190° forms s-di-phenyl-urea .-- 4. Fuming sul-and phenyl-parabanic acid.

Acetyl derivative NHPh.CO.NHAc. [183°]. Needles (McCreath, B. 8, 1181; Kühn, NHPh.CO.NHAc. B. 17, 2880; Pinnow, B. 24, 4171).

Propionyl derivative. [137°]. Prisms. Benzoyl derivative NHPh.CO.NHBz.

[199] Silky needles, v. sol. alcohol.
s-Di-phenyl-urea C₁, H₁₂N,O, i.e. CO(NHPh),
Mol. w. 212. Carbanilide. [235°]. (260°).

Formation .- 1. From aniline and phenylcyanate (Hofmann, A. 57, 266; 74, 15).—2. From aniline and COCl. (Hofmann, A. 70, 488; Hentschel, J. pr. [2] 27, 499).—3. By heating diphenyl-thio-ures with alcoholic potash.—4. By. distilling phenyl-urea (H.; Pinnow, B. 24, 4172). 5. By dry distillation of aniline oxalate (Hofmann, Pr. 15, 335).—6. By heating urea (1 pt.) with aniline (3 pts.) at 160° (Baeyer, A. 131, 251) or phenyl-ures (1 mol.) with aniline (1 mol.) at

185° (Weith, B. 9, 821).—7. Together with NH,, benzamide, and benzanilide, by heating dibenzoyl-ures with aniline at 180° (Holleman, 80. T. C. 10, 72).—8. By the action of an ethereal solution of ClCO₂COl₂ on aniline (Hentschel, J. pr. [2] 36, 310).—9. From NHPh.CO₂Et and aniline at 160° or NaOPh at 220°.—10. From CO(OPh). and aniline at 150° 180° (Eckenroth, B. 18, 516). 11. From C(OEt), and aniline at 280° (Bender, B. 13, 699).-12. By heating carbamic ether with aniline (3 mols.) at 180°-185° (Smolka, M. 11, 200).—13. From benzamidine hydrochloride, phenyl cyanate, and NaOHAq (Pinner, B. 22, 1607).

Properties.—Prisms (from alcohol), v. al. sol. water, v. sol. alcohol and other. May be distribed.

Reactions.—1. Conc. H.SO, forms CO, and

C.H.(NH2)SO2H.-2. Alcoholic NH3 forms urea and aniline (Claus, B. 9, 693) .- 3. PCl, forms phenyl cyanate (Weith, B. 9, 810). QCO_CCl₃ also forms phenyl cyanate on heating.—4. P.O. forms phenyl cyanate and aniline.—5. Pry NaOEt at 220° forms aniline and tri-phenyl-guanidine.—6. CICO.CO.Et forms di-phenylparabanic acid.

Acetyl derivative NHPh.NPhAc. [115°].

Jaminæ (from water) (McCreath, B. 8, 1181).

4-Di-phenyl-urea NPh, CO.NII. [189°].

Formed from NPh, COCI [85°] and alcoholic NH, at 100° (Michler, B. 8, 1665; 9, 396, 715). Needles. Gives a blue colour with H₂SO₄. Split up by distillation into evanicacid and diphenyl-

Tri-phenyl-ures NPh2.CO.NHPh. Formed by heating a solution of NPh. COCL dissolved in chloroform, with aniline at 130° (Michler, B. 9, 396, 715). White needles. Resolved by heat into diphenylamine and phenyl cyanate.

Tetra-phenyl-urea CO(NPh₂)₂ [183°]. Formed by heating NPh₂-COCl with NPh₂H and zinc dust (Michler, B. 12, 1166). Got also from diphenylamine and COCl, (Girard a. Willm, Bl. [2] 25, 248). Resolved by HClAq at 250° into diphenylamine and CO...

References. — Amido-, Bromo-, Chloro-, Chloro-, Nitro- and Oxy- Phenyllurea.

NHPh.Co.NH.C.H.CO.H. [270°]. Formed by heating m-amido benzoic acid with phenyl cyanate at 100° (Kühn, B. 17, 2882). Prisms, sol. alcohol, sl. sol. ether.

Di-phenyl-urea di-m-carboxylic acid C₁₅H₁₂N₂O₅, i.e. CO(C₆H₁.NH.CO₂H)₂.

Formation .- 1. By heating m-uramido-benzoic acid (Griess, Z. 1868, 650; B. 9, 796). - 2. By heating a mixture of m-uramido-benzoic acid with m-amido-benzoic acid at 175° (Traube, B. 15, 2122).-3. From m-amido-benzoic acid and. COCl₂ (Sarauw, B. 15, 44).— 4. By boiling CS(C₄H_a,NH.CO₄H)₂ with HgO and KOHAq (Griess, A. 172, 169).—5. By heating urea with m-amido-benzoic acid at 130° (T.).

Properties. - Minute needles, almost insol. water, alcohol, and ether.

Estata.—Bah" 3aq.—Pbh".—Ag.h".

Ethyl ether Et.h". [162°]. Needles.

Amide CO(C.H., NH.CO.NH.)... Got by heating urea with m-amido-benzamide at 140° (Schiff, A. 232, 140). White powder, insol. water, de-composing above 270°.

Di-phenyl-ures di-p-carboxylic acid. Formed when urea is heated with ρ -amido-benzoic acid (Griess, J. pr. [2] 5, 370). Small needles.—BaA". TETRA - PHENYL - UVINONE $C_{11}H_{20}O_{1}$.

Formed in small quantity in the preparation of di-phenyl-furfurane by heating di-phenyl-fur-furane dicarboxylic acid (Perkin a. Schlosser, C. J. 57, 956). Thin yellow needles, not melting at 280°. H,SO, forms a dark-green solution with brick-red fluorescence.

DI-PHENYL-VALERAMIDINE C17H20N2, i.e. C,H,,C(NPh).NHPh. [111°]. Formed by heating isovaleric acid with aniline and PCl, at 150° (Hofmann, J. 1865, 416). Crystalline, nearly insol. water.

B-PHENYL-n-VALERIC ACID

CHPhPr.CO.H. [52°]. Formed by heating its nitrile with FECIAq at 185° (Rossolymo, B. 22, 1235). Needles.

Nitrile CHPhPr.CN. (261°). Formed from

phenyl-acetonitrile, PrI, and NaOH. Oil.
β-Phenyl-iso-valeric acid C₁₁H₁₁O₂ CH,Ph.CHEt.CO,H. (272°). Formed by reduction of phenyl-angelic acid with sodium-amalgam (Baeyer a. Jackson, B. 13, 118). Formed also by heating benzyl-ethyl-acetoacetic ether with conc. KOHAq (Anschütz, A. 261, 306). Oil.-AgA'.

Chloride (c. 147° at 24 mm.). Oil. A mide ChiHis NO. [89°]. Monoclinic A mide $O_{17}H_{19}NO$. [89°]. Mon-crystals; $a;b:c=817:1:1\cdot189$; $\beta=70^{\circ}28'$.

γ-Phenyl-valeric acid

CH_Ph.CHMe.CH_CO_H. (176.5° at 15 mm.). Got by potash-fusion from 'diethyl carbo-benzonic' acid, which is a product of the action of alcoholic potash on deoxybenzoin (Anschütz, A. 261, 302). Oil, yielding benzoic acid on oxidation.

Ethyl ether C₁₃H₁₈O₃. (146° at 15 mm.). Chloride C₁₁H₁₈OCl. (131° at 11 mm.). Anilide C₁₇H₁₈NO. [102°]. Trimetrio Anilie C, H, NO.

peedles; a:b:c = 6851: 608. δ -Phenyl-valeric acid

CII, Ph.CH., CH., CH., CO., H. [659°]. Formed by reducing CHPh:CH.CH.CH.CH.CO.H (Baeyer a. Jackson, B. 13, 122). Leatlets, sl. sol. water.

Bensyl ether. (330°-340°). S.G. 172 1.027. Got by heating benzyl butyrate with Na at 130° (Conrrd a. Hodgkinson, A. 193, 318).

Isomeride v. BENZYL-ISOBUTYRIC ACID.

Reference.—Anido-, Di-Bromo-, Di-Bromo-Amido-, Nitro- and Oxy- Phenyl-Valeric acids.

PHENYL-VINYL- v. STYRYL-.

DI-PHENYL-VINYL-DIAMINE C, H, N, i.e. NHPh.CH, CH:NPh. [105°]. Formed by heating CH,Cl,CH:NPh with aniline (Berlinerblau, M. 8, 187). Sol. alcohol and ether.

PHENYL VINYL KETONE CARBOXYLIC ACID v. BENZOYL-ACRYLIC ACID.

DI-PHENYL-VINYL NITRITE $C_{i,i}H_{i,i}^{*}NO_{2}$ i.e. CPh.:CH.NO. [87°]. Formed by gradually adding HNO. (1 pt.) to a hot solution of di-phenyl-ethane (1 pt.) in HOAc (10 pts.) (Anschütz a. Romig, A. 233, 327). Needles, v. sol. alcoffol and ether.

* TRI - PHENYL VINYL TRISULPHONE C,H,SO,CH,CH(SO,C,H,)2. [86°]. Formed by oxidising the product of the action of NaSPh on CHCl2.CH2Cl (Otto, B. 24, 1835). Crystalline.

PHENYL-XYLENE v. DI-METHYL-PIPHENYL and RHENYL-TOLYL-METHANE.

PHENYL-XYLIDINE C₁₄H₁₅N i.s. C₄H₃M_{3r}, NHPh. [52°]. (173° at 15 mm.). Formed by heating xylidine with aniline hydrochloride (Girard a. Vogt, Bi. [2] 18, 67). Sol. alcohol.

PHENYL-0-XYLYL-CARBINOL C₁₃H₁₀O i.s. C₂H₁,CH(OH),C₂H₃Me₂[1:3:4]? [68°]. (336°1.V.) at 744 mm. V.D. 107·7 (for 106). Formed from the ketone, KOH, and zinc-dust (Elbs, J. pr. [2] 35, 469). White radiating needles (from alcohol). Somewhat decomposed by distillation.

Phenyl.m. xylyl.carbinol C_aH_..CH(OH).C.H_aMo_s [1:2:4]? [57°]. (331° i.V.) at 744 mm. V.D. 102·7 (for 100). Formed from the corresponding ketone by reduction (Elbs,

J. pr. [2] 35, 472). Phenyl-p-xylyl-carbinol

C_sH_s.CH(OH).C_sH_sMe_s[1:2:5]. [88°]. Formed from the ketone, KOH, and zinge-dust (Elbs). Prisms (from alcohol); v. sl. sol. water, m. sol. HOAc, v. e. sol. alcohol and ether.

PHENYL-p-XYLYL-p-CYMYL-METHANE [2:5:1] Me₂C₆H₃.CHPh.C₆H₃MePr[1:2:5]. Formed from phenyl-p-cymyl-carbinol, p-xylene, and P.O. (Elbs, J. pr. [2] 35, 498). Oil.

DI - PHENYL - o - XYLYLENE - DIAMINE C20 H20 N2 i.e. C8 H4 (CH2.NHPh)2. [172°]. Formed by boiling di-ω-bromo-o-xylene with an alcoholic solution of aniline (Lesser, B. 17, 1825). Small plates (from alcohol).

PHENYL o-XYLYL KETONE C15H14O i.e. C.H.,CO.C.,H.,Me., [1:3:4]? [48°]. (310°. i.V.) at 741 mm. V.D. 102-2 (for 105). Formed from BzCl, o-xylene, and AlCl.; the yield is 80 p.c. (Elbs, J. pr. [2] 35, 467). Groups of snowy needles (from alcohol). Insol. water, sl. sol. cold HOÀc, v. sol. alcohol.

Phenyl m-xylyl ketone C₆H₃.CO.C₆H₃Mc₂ [1:2:4]. (321° i.V.) at 744 mm. V.D. 102·3 (for 105). From m-xylen, BzCl, and AlCl, (Söllscher, B. 15, 1682; Elbs, J. pr. [2] 35, 469). Oil. Partly converted by long boiling into (B. 2)-methylanthraquinone. In presence of a little of the corresponding phenyl - xylyl - carbinol, (B. 2)methyl-anthracene is formed.

anti-Oxim CsHy.C.CsHs. [126°]. verted by PCl, into C, H, CO.NHPh (Smith, B. 24, 4048). Yields an acetyl derivative [91°], crystallising in flat prisms.

syn-Oxim C_nH_y.C.C_sH_s. [152°]. Formed, as well as the preceding body, by the action of an alcoholic solution of hydroxylamine on the ketone. PCl, at -20° forms C.H., CO.NHC, II,

Yields an acetyl derivative [103°

(Elbs, B. 17, 2847; J. pr. [2] 35, 472); the yield is 65 p.c. Transparent prisms (from alcohol), ir sol. water, m. sol. HOAc, v. e. sol. ether and al-cohol. Very slightly volatile with steam. Yields

methyl-anthracene when boiled for a long time.

Reaction.—10 H.SO, has no action in the cold, but on warming HOBz is aplit off...

2. H.S.O., forms a disulphonic acid
C.H.Me..CO.C.H.(SO.H)... whose salt BaA"2aq
is v. e. sol. water...—3. HNO. (S.G. 1.15) at 180°
forms benzophenone dicarboxylis acid C.H., CO.C.H., (CO.H), [1:2:5].

PHENYL-O-XYLYL-KETONE or CARB OXYLIC ACID

[4:3:1] C_aH,Me,CO.C,H,CO₂H [2:1]. $Xulene \bullet$ phthaloglic acid. [162°]. Formed by the action of AlCl, on a mixture of phthalic anhydride and o xylene (F. Meyer, B. 15, 636). Minute prisms (containing aq). Yields benzoic and (4,3,1)-di-

methyl-benzoic acids when fused with potash.

Phenyl-m-xylyl-ketone o-carboxylic acid [4:2:1] C.H.Me., CO.C.H., CO.H. Formed in like manner from m-xylene (M.). Needles, sl. sol.

water, sol. alcolol.

Phenyl-p-xylyl-ketone o-carboxylic acid [5:2:1] C₀H₃Me₂.CO.C₀H₄.CO₂H [1:2]. Formed in like manner from p-xylene. Amorphous solid,

insol water, sol. alcohol and benzene.

henyl-m-xylyl-ketone (a)-carboxylic acid
C_bH₃CO.C_oU.Me_a.CO_.H [4:5:3:1]. [160°]. Formed, together with the following isomeride, by oxidising benzoyl-mesitylene with chromic acid mixture (Louise, Bl. [2] 44, 418; A. Ch. [6] (1, 218). Needles, v. sol. other, insol. cold water.—BaA', 2aq.—MgA', 6aq.—AgA': needles.

Phenyl-m-xylyl-ketone (\$\beta\$)-carboxylic acid

C₈H₄.CO.C₄H₂Me₂.CO₂H[2:5:3:1]. [185°]. Formed as above. The Mg salt is more soluble than that of the isomeric acid. Efflorescent needles, v. sl. sol. hot water. Converted by P.O. into di-methyl-anthraquinone [158°]. - AgA': needles.

Phenyl-xylvl-ketone dicarboxylic C.H. CO.C. HMe₂(CO₂H)₂. Bensoyl-cumidic acid. [85°]. Formed by oxidation of phenyl duryl ketone (F. Meyer a. Ador, J. 1879, 562). Melts

Retono (F. Meyer a. Ador, J. 1879, 562). Metts at 86°, becomes solid, and melts again at 173°. — BaA'₂ 2° aq: long silky needles. PHENYL - DI · p · XYLYL - METHANE C. H. Cll(C. H. Mc.)₂ [1:2:5]₂. [93°]. (above 360°). From phenyl p-xylyl carbinol and p-xylene (Elbs, J. pr. [2] 35, 476). Or from di-p-xylyl carbinol, benzene, and P.O. Prisms (from ligroin). Its solutions show blue fluorescence. ligroin). Its solutions show blue fluorescence.

Di-phenyl-o-xylyl-methane C₂₄H₂₀ i.e. (C₆H₃)CH.C₆H₃Me₂(1:3:4]. [68:5°]. (above 360°). Formed from di-phenyl-carbinol, o-xylene, and P.O. Hlemilian, B. 19, 3070). Needles, v. sol. alcohol and ether.

Di-phenyl-m-xylyl-methane

C_aH_aCH_aC_bH_aMe_a[1:2:4] [61:5°] (above 860°). Formed by boiling di-phenyl-carbinol with m-xylene and P₂O₃ (Hemilian, B. 19, 3061). Prisms, v. sol. alcohol and ether. Oxidised by chromic acid mixture to methyl-di-phenyl-phthalide and di-phenyl-phthalide carboxylic

Di-phenyl-p-xylyl-methane. [92°]. (above 360°). Formed by digesting di-phenyl-carbinol with p-xylene and P.O. (Hemilian, B. 16, 2360; Bt. [2] 34, 326; Petrieff, Bt. [2] 41, 316). Monoclinic crystals, v. sol. alcohol and ether. Oxidised by chromic acid mixture to di-phenylmethyl-phthalide [170°], di-phenyl-tolyl-carbinol m-carboxylic acid [c. 253"] and di-phenyl-phthalide carboxylic a..d [245°].

Reference.-NITHO-DI-AMIDO-PHENYL-DI-XYLYL-

PHENYL-DI-XYLYL-METHANE o-CARB-OXYLIC ACID [4:2:1] C.H.Me.CH..C.H.,CO.H. [158°]. Formed by reducing phenyl-m-xylyl-ketone carboxylic acid with zinc-dust and NH,Aq (Gresly, A. 234, 237). Small needles (from alcohol).—BaA', aq: plates (from dilute alcohol). - PHENYL-P.XYLYL-(8).PINACOLIN C₂₀H₂₀O
6.8. C.H. C(C.H.Me₂)₂CO.C.H., [146°]. Formed
by the action of ziac and HClAq on phenyl
p.xylyl ketone (Elbs, J. pr. [2] 35, 477). Clumps
of prisms (from ligroin), nf. sol. alcohol and ether.
Soda-lime at 320° splits it up into benzoic
acid and phenyl-di-xylyl-methane.
PHENYL-XYLYL-PROPANE C., H₂₀ 6.6.

PHENYL-XYLYI-PROPANE O, H., e.s. C, H., CHMc. CHL, C, H., Me., (324°). Formed from ψ -cumene, styrene, and conc. H., SO₄ (Kraemer, Spilker a. Ebenhardt, A. 23, 3273).

PHENYL-XYLYL-PROPIONIC ACID
C,H,Me,-CHPh.CH,-CO,H. Formed from cinnamic acid, m-xylene, and H,SO, (Liebermann
a, Hartmann, B. 25, 959). Amorphous, v. sol.
warm benzene. When allocinnamic acid is used
it is accompanied by another, acid [220°].
DI-PHENYL-XYLYL-PYRROLE CARB-

DI-PHENYL-XYLYL-PYRROLE CARB-OXYLIC ACID O.H.N CPh:C.CO.H. [254°].

Formed by saponifying its oly ether which is got from phenacyl-benzoyl-acctic ether and (4.2,1)-m-xylidine (Pasl a. Braikoff, B. 22, 3000).

Small needles, m. sol. hot alcohol and benzene.

PHENYL-XYLYL SULPHONE C.,II.,SO., i.e.

C.H., SO., C.H.Me., [80°]. Formed from benzene sulphonic chloride, m-xylene, and AlCl. (Beckurts a. Otto, B. 11, 2063). Vellowish needles.

THENYL m.XYLYL-UREA C₁₅H₁₈N₁O i.e.

THENYL m-XYLYL-UREA C₁₅H₁₆N₁O i.s. C₅H₅NH.CO.NHPh. [131°]. Formed by mixing m-xylidine with phenyl cyanate (Brömme, B. 21, 2703). White matted needles, sol. alcohol. PHENYTHRONIC ACID 2. PHENYL-METHYL-

PHENYTHRONIC ACID 2. PHENYL-METHYL-FURFURANE DIGARBOXYLIG ACID.

PHILLYRIN C₂,H₂,O₁, 1½aq. [160°]. S. ·08 at 9°; S. (alcohol) 2·5 at 9°. A glucoside in the bark of Phillyrea latifolia (Bertagnini, A. 92, 109; 118, 124). Crystalline, insol. ether. Split up by dilute acids into glucose and crystalline phillyenin C₂,H₂,O₄, v. sol. ether. A glucoside C₂,H₂,O₁ ([184°]; S. ·05 in the cold, 12·5 at 100°) in Olea fragrams is perhaps identical with phillyrin. It is split up by acids into glucose and C. H₂,O₁ (70°) (Eykman, R. T. G. 5. 127).

C₂₈H₂₂O₂ [70°] (Eykman, R. T. C. 5, 127).

PHLEIN C₂₈H₃₂O₃, [215°]. S.G. 1.48. S.
26 at 10°. [a]₂ = -48·5. Occurs in the bulbs of cat's-tail grass (Phieum pratense) and in the roots of Baldigera arundinacea (Ekstrand a. Johnnike., B. 20, 3310; 21, 597). Carbohydrate resembling starch, but not coloured blue by iodine. Reduces AgNO₃, but not Fehling's solution.

PHLOBAPHENE C₁₈H₁₈O₁₁. Named from φλοιδε, bark, and βαφή, colour. Occurs in oak bark, and formed by boiling quercitannic acid with dilute acids (Hofstetter, A. 51, 63; Grabowski, A. 145, 8; Oser, J. 1876, 903; Böttinger, A. 202, 270; 240, 338). Reddish-brown powder, insol. water, ether, and cold alcohol. Alkalis form a reddish-brown solution, which absorbs oxygen from the air. Turned black by FeCl., Potash-fusion yields protocate-buis oxid (Procter, C. J. 36, 979). Yields C₃;H₁₉Ac,O₁, C₃₈H₁₉B₂,O₁₁, and C₃₈H₃₈K₁O₁₁, which is insol. alcohol, v. sol. water. Bromine yields C₃;H₁₉Br₁₆O₁, and C₃₈H₃₂Br₄O₁, which forms C₃₈H₁₈Br₄O₁, and C₃₈H₃₂Br₄O₁, which forms C₃₈H₁₈Br₄O₁, and C₃₈H₃₂Br₄O₁, thick forms C₃₈H₁₈Br₄O₁, and C₃₈H₃₂Br₄O₁, thick forms C₃₈H₁₈Br₄O₁, and C₃₈H₃₀Br₄O₁. Seembling phlobaphene occurs in hops (Etti, A. 180, 223; D. P. J. 228, 354).

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PHLORANIES C.H., NO., 4.c.

C.H., (OH), (NH.). Amido-resorcin? Formed by passing NH, over phloroglucin (Hlasiwetz a. Pfaundler, A. 119, 202). Thin plates (from water), al. sol. cold water, v. sol. alcohol, insol.

water), sl. sol. cold water, v. sol. atconol, misol.
ether. Turns browne in air. Decomposed by
alkalis. Its solutions are not coloured by FeCl.,
—B'HCl.—B'₂H₂SO, 2aq:long yellowish needles.
PHLOREIN C₁₈H₁₁NO₂, Formed by passing

PHLOREIN C₁₂H₁₁NO₂. Formed by passing nitrous acid gas into an ethereal solution of phloroglucin (4 g.) containing HNO₂ (4 c.c. of S.G. 1°25) (Benedikt, B† 7, 445; A. 178, 93). Lustrous dark-green powder, insol. water, v. sol. alcohol and ether, forming a dark-brown solution. Alkalis form a purple solution. Yields phloroglucin when fused with potash. Zinc and dilute H₂SO₄ form a colourless body, re-oxidised to phlorein by air.

PHLORETIC ACID v. p-OXY-a-PHENYL-PRO-

PHLORETIC ACID v. p-OXY-a-PHENYL-PRO-PIONIC ACID. It yields a crystalline di-bromoderivative (Fllasiwetz, A. 102, 145).

derivative (Hasiwetz, A. 102, 145).

PHLORETIN C₁₅H₁₄O₅. [255°]. Formed by boiling phlorizin or glyoyphyllin with dilute acids (Stas, A. 30, 200; G. Roser, A. 74, 178; Hlasiwetz, A. 96, 118; Schiff, A. 156, 2; 172, 357; 229, 374; Rennie, C. J. 49, 860). Small lamine, with sweet taste, v. sl. sol. hot water and ether, v. e. sol. alcohol. Inactive to light. Bromine forms C₁₅H₁₆Br₁O₅ (295°-210°) (Schmidt a. Hesse, A. 119, 103). Alkaline solutions absorb oxygen and turn orange in air; boiling cone. KOHAq splits it up into phloretic acid and phloroglucin. Aniline at 170° forms C₁₈H₁₈NO₄, a scarlet powder. AcCl gives amorphous C.,H₁₈NO₄, a scarlet powder.

Salts. $-C_{15}H_{11}(NH_{_3})_2$: amorphous. Gives off $NH_{_3}$ in air. $-C_{29}H_{18}Nb_2$ 0; and $-C_{15}H_{12}Aa_2$ 0.

winstable pp.

PHLOBIZIN C₂₁H₁₁O₁₀ 2nq. Named from φλοιόs, bark, and φίζα, root. [109°] (when anhydrous). S.G. ½ 1·43. S.·1 in the cold. [a]₁ = -49 at 15°. Occurs in the root-bark of the apple, pear, plum, and cherry tree, from which it may be extracted by dilute alcohol (Stas a. De Koninck, A. 15, 75; 30, 193; A. Ch. [2] 69, 367; Mulder, Rev. Scient. 3, 50; Roser, A. 74, 178; Strecker, A. 74, 184; Rennie, C. J. 51, 635). Silky needles with slightly bitter taste, sl. sol, cold water, v. e. sol. hot water and alcohol, insol. ether. Melts at 109°, becomes solid, and melts again at 171°. Lævogyrate. Decomposed by dilute acids into glucose and phloretin. Gives pps. with baryta and McOH, with time-water, and with lead subacetate. Air and ammonia form reddish-brown amorphous phlorize n C₂₁H₂₀N₂O₁₂. Gives a violet colour on boiling with ZnSO₄ and KNO₂ (Nickel, Fr. 28, 248). FeCl, gives a brownish-red colour. Aniline at 180° forms $C_{s_0}H_{s_1}N_2O_s$, a yellow powder, yielding a mono- and a tri- acetyl derivative.

 $\begin{array}{cccc} A \ cotyl & derivatives & O_{21}H_{22}AcO_{10} \ 2aq: \\ needles & (from water). & & C_{21}H_{21}Ac_2O_{12}. & & \\ C_{21}H_{12}Ac_2O_{12}aq: & amorphous solid. & & \\ \end{array}$

Tri. bensoyl derivative. Powder.

Isophlorisin C₂₁H₂₂O₁₉. [105°]. Occurs in the leaves of the apple-tree (Rochleder, Z. [2] 4, 741). Silvery needles. Its ammoniacal solution turns brown in air. Its solution is ppd. by lead subacetate. Dilute H₂SO₄ splits it up into glucose and isophloretin C₁₂H₁O₃, which is v. sol. ether, and yields phloroglucin when heated with cone. KOHAq.

philorobrowine C.Br.HO. [182°]. Formed by the action of excess of bromine on a very dilute aqueous solution of phloroglucin (Benedikt, 4. 189, 165; C. J. 34, 499). Dimetric prisms; a: b=1:1-2. Insol. water. Not attacked by potash or HNO,. Warm alcohol decomposes it, forming penta-bromo-acetone [76°]. NH,Aq ferms CBr,H and C,Br,H,N₂ crystallising from water in colour-less lamins [124°].

PHLOROGLUCIN C.H.O. i.e. C.H.(OH). [1:3:5]. Mol. w. 126. [219°] (Baeyer, B. 19, 218°). H.F. 153,348 (Stohmann, J. pr. [2] 33, 471).

Formation.—1. By boiling phloretin with cone. KOHAq (Hlasiwetz, A. 96, 118).—2. By potash-fusion from quercetin, maclurin, catechin, scoparin, gamboge, dragon's blood, limetin, and bergaptene (Hlasiwetz, A. 112, 96; 119, 199; 127, 357; 134, 118, 283; 138, 190; Zwenger, A. 123, 154; Gautier, Bl. [2] 33, 583; Tilden a. Beck, C. J. 57, 323; Pomoranz, M. 12, 387).—3. By fusing resoroin with a large excess of NaOH, the yield being 65 p.6. (Barth a. Schreder, B. 12, 503).—4. By soda-fusion from phenol, benzene, trisulphonic acid, orein, and naringenin (Barth a. Schreder, B. 12, 422; M. 3, 649; Will, B. 20, 297).—5. By fusing its tricarboxylic ether with potash (Bacyer, B. 19, 3458).—6. By fusing z-di-bromo-phenol with potash (Blau, M. 7, 632).

Preparation.—By soda fusion from resorcin (Tiemann a. Will, B. 14, 954; 18, 1323).

Properties.—Trimetric crystals (containing 2aq); a:bic = *825:1:3*417. Melts at 200°. 200° when slowly heated. V. sol. water, alcohol, and ether; sl. sol. NaClAq. Tastes sweeter than sugar. May be sublimed. Its solution is ppd. by lead subacetate. FeCl., gives a bluish-violet colour. Reduces Felhing's solution and ammoniacal AgNO. Its alkalme solution absorbs oxygen and turns brown in air. Colours acidified pine-wood red. An alcoholic solution gives a red colour with HClAq and vanillin (Lindt, Fr. 26, 260), oil of cloves, or oil of pimento (Ihl, Chem. Zeit. 13, 264).

Reactions.—1. Browsine forms crystalline tribromo-phloroglucin and finally phlorobromin.

2. Chlorine passed into its aqueous solution forms tri-ohloro-phloroglucin C₀Cl₁(OH), 3aq [136°], which soon decomposes into tetra-chloro-acetone hydrate, and di-chloro-acetoacid (Webster, C. J. 47, 423; Zincke a. Kegel, B. 22, 1476). Chlorine passed into its solution in HOAc forms CHCl₂CO.CHCl, 4aq [49°]. Chlorine passed into a cooled solution of dry phloroglucin in chloroform forms CO CCl₂CO CCl₂ [48°], (269°), decomposed by water into CO, di-chloro-acetio acid, and CO (CHCl₂)₂—3. Dilute HNO, formanitro-phloroglucin.—4. Ammonia produces phloramine.—5. Nitrous acid in its ethereal solution forms phlorein. In acetic acid solution it gives tri-nitroso-phloroglucin (vol. iii. p. 619).—6. Aqueous HI at 140° forms nearly tasteless scales of phloroglucide C₂H₂O, 2aq, al. sol. warmwater. Phloroglucide is also got by heating phloroglucin alone or with POCl₂.—7. Heated with salicylic acid it forms two compounds of the form ChH₂CO C₂H(OH) CO C₄H₄, one of these (described by Kostanecki and Nessler) which vields an acetyl derivative C₂H₄O (OAc)

[318°]; the other isomeride [826°] crystallises from HOAe in green-yellow tables.—8. With or amido bendot aldehads and NaOHAq it forms red C₁,H₂NO₂, possibly di-oxy-acridine C₂H₄(OH), C₂H₄, which forms B'₁H₂PtCl₄ and C₁,H₁Bz₂NO₄ (Eliasberg a. Friedländer, B. 25, 1752).—9. Phenyl cyanats unites, forming C₂H₃(O.CO.NHPh), a yellowish powder [128°] (Goldschmidta Meissler, B. 23, 269).—10. Bensens sulphonic chloride added to the slightly alkaline solution forms C₂H₃(O.SO₄C₂H₃), [117°] (Georgesen, B. 24, 418).—11. Antiline at 210° forms triphenyl-tri-amido-benzene [193°] (Minunni, B. 21, 1984).—12. Phloretic acid at 170° forms C₃H₂O₁₄, or stallising from water in lamine (HJSiwetz, A. 119, 199).

Tri-oxim C_sH_a(NOH),. Formed from phloroglucin and aqueous hydroxylamine (Baeyer, B. 19, 159). Colourless crystals, v. sl. sol. water and alcohol, sol. alkalis and acids. Explodes at

155°.

Phenyl-hydrazine defivatives. The salt C_{*}H_{*}O3N,H_{*}Ph [76°-83°] is got from phloroglucin (1 mol.) and phenyl-hydrazine (3 mols.) in alcoholic solution (Baeyer a. Kochendörfer, B. 22, 2190). Nodules, sol. alcohol and ether. Cod MaOHAq sets free phenyl-hydrazine. In alcoholic solution it changes on keeping to C_{*}H_{*}(OH)(N,H,Ph)₂ [144°], which crystallises from toluene in needles, and yields a pentabonzoyl derivative [176°].

Tri-acetyl derivative C.H.(OAc).. [106°]. Got by heating phlorogluoin with AcCl.

Di-benzoyl derivatives C_sH₃(OH)(OBz), Two isomerides [165°] and [191°-195°] are got from phloroglucin with BzCl. The compound [165°] is more sol. benzene than the other (Skraup, M. 10, 391, 722).

Tri-benzoyl derivative C.H. (OBz). [174]. Formed, together with C.H. (OBz). [199], by warming phloroglucin with BzCl and NaOH (S.). Plates, sol. benzene.

Tri-methyl other C.H.(OMe). [52°]. (256°). Formed by passing HCl into a solution of phloroglucin in McOH, the resulting C.H.(OH)(OMe). being treated with MeI and KOH (Will, B. 21, 603). Crystals, in: A water and alkalis, v. sol. alcohol and ether. Conc. HNO, forms a blue solution. Bromine gives C.Br.(OMe). [145°]. When phloroglucin is treated with KOH and MeI the products are C.H.Me,O. [184°]. C.H.Me,O. [114°], and C.Me,O. [80°] (Margulies, M. 9, 1052; 10, 459). When tetra-methyl-phloroglucin is heated in sealed tubes with HClAq it yields isopropyl ketone, isobutyric acid, HOAc, and CO... Hence it would appear to be CMe. CO.CMe. CO.CH (Spitzer, M. 11, 104, 237). Hexamethyl-phloroglucin heated with InIAq at 200° produces isobutyric acid and C.H... and, on oxidation, yields di-isopropyl ketone. Hence it would appear to

be CMe₂CO.CMe₂CO.

Diethyl ether C₂H₁(OEt)₂(OH). [Wo].

Made by passing HCl into an alcoholic solution of phloroglucin or its carboxylic acid (Will a. Albrecht, B, 17, 2106). Long white needles.

May be distilled.

Tri-ethyl ether C.H.(OEt). [43°]. Got by heating the di-ethyl ether with Etl and alcoholic potash (W. a. A.).

Penta-ethyl derivative v. vol. ii. p. 505. Tri-phenyl ether CoH3(OPh),? [175°]. A product of the action of Na on phenyl acetate A product of the action of the (Hodgkinson, C. J. Proc. 2, 188). V. sl. sol. Aq. (Hodgkinson, C. J. Proc. 2, 188). BEOMO-DI-IODO-,

References.—Tri-Bromo-, Bromo-di-1000-,
Tri-Chloro-, Nitroso-, and Nitro- Phloroducin. PHLOROGLUCIN CARBOXYLIC ACID v.

TRI-OXY-BENZOIC ACID.

Phloroglucin tricarboxylic ether C13H18O. Phloroglucin tricarboxylio_ether *C_{1,3}H_{1,0}O₂, e. C₄(OH)₄(CO,Et)₄. [106°]. Formed from malonic ether and ZnEt, (Lang, B. 19, 2937). Prepared by dissolving Na (144 g.) in malonic ether (200 g.) at 100° and heating the product for six hours at 145° (Baeyer, B. 18, 33√7; Bally, B. 21, 1766). In this preparation an inhydride C_s(OH)_s(CO₂Et)_s<O [170°] is also formed. Needles (from dilute alcohol), insol. water. Does not react with nitrous acid gas.

Reactions .- 1: Potash-fusion yields phloroglucin.—2. Bromine in CS₂ ppts. bromo-phloro-glucin dicarboxylic ether [128°].—3. Chlorine gives tri-chloro-acetamide.—4. Phenyl syanate and C.H. at 200° form C.(O.CO.NHPh),(CO2Et), [195°] (Goldsohmidt a. Meissler, B. 23, 270). Eri-acetyl derivative C_s(OAc)₃(CO₂Et)₃.

[76°]. Needles (from alcohol or ether).

Oxim C₄H₄(NOH)₅(CO₂Et)₅. [171°].

PHLOROGLUCIN PHTHALEIN C,H,O, Formed by heating phloroglucin with phthalic anhydride at 170° (Link, B. 13, 1652). Minute orange needles, sl. sol. water. Its alkaline solutions are orange-red, without fluorescence. Zincdust and NaOHAq reduce it to phloroglucinphthalin C20H11O2, an amorphous reddish-yellow

PHLOROGLUCIN SULPHONIC ACID

C.H.SO. i.e. C.H.(OH). SO.H. Formed by mixing phloroglucin with H.S.O. (Schiff, B. 6, 26; A. 178, 191). Yields a crystalline K salt. POCl. converts it into the anhydrides C12II10S2O11, v. e. sol. water, and C12H2S2O10, Bl. sol. water, and C24H18S2O15.

PHLOROL v. o-ETHYL-PHENOL.

PULORONE v. XYLOQUINONE.

PHOBONE C₀H₁O i.e. CO(CH:CMe.)₂, Mol. w. 188. [28°]. (197°) at 743 mm. S.G. $\frac{32}{2}$ *885. $\mu_{\rm D}$ = 1·500 at 20° (Brühl, A. 235, 15). R_☉ 70·93 in a 14·5 p.c. benzene solution. Formed, the state of t together with mesityl oxide, by leaving acctone in contact with quicklime (Fittig, A. 110, 32). Formed also by the action of conc. HClAq on acetone (Baeyer, A. 140, 301), and by heating nitroso-triacetonamine with potash (Heintz, A. 187, 250). Yellowish prisms. Yields acetone, oxalic acid, and CO on oxidation with KMnO, (Pinner, B. 15, 591). Slowly combines with NaHSO, forming di-isobutyl ketone di-sulphonic acid. Yields \u03c4-cumene on heating with P2Os and mesitylene on heating with conc. H.SO. Yields mestlyl oxide on distilling with dilute H₂SO₄ (Claisen, A. 180, 18). Bromine in CS₂ torms C₂H_{1,2}Br₄O [88°]. Zinc and H₂SO₄ reduce it, in alcoholic solution, to decxyphorone C₁₈H₂₈O [108°]. HI forms C₀H₁₀I₂O [13°] (Kasaneff, B. 8, 485). Phorone does not react with benzoic aldehyde (Claisen, B. 14, 352).

Oxim C,H,;:NOH. [48°]. (218°). Tables. v. sol. alcohol (Nägeli, B. 16, 496).

Isophorone. The substance to which this name has been given is a mixture (Laycock, A. 258, 230).

CPr (Königs a. Eppens, B. 25,

Camphor-phorone C.H., O i.e. CH, CH,

co 260). (208°) (Kachler, A. 164, 79). Got by distilling calcium camphorate (Laurent, A. Ch. (2) 65, 329; Gerhardt 4. Liès-Bodart, A. 72, 293) and by heating camphor (1 pt.) with H₂SO₄ (4 pts.) at 100° (Schwanert, A. 123, 298). Colourless oil with aromatic odour. Inactive to light. PCl, yields C.II, Cl (205°). Yields amethyl-glutaric and acetic acids on oxidation.

Na followed by MeI yields C₃H₁₃MeO (225²-230°). Na followed by AcCl yields C₁₈H₂₇AcO₂ (230°-240°). Bromine in CS₂ forms C₂H₁₃Br₃O [52°1

PHORONIC ACID C, H, O, [184°]. Formed by saponification of its nitrile, which is got by boiling the product of the action of gaseous HCl on acetone with alcoholic potash (Pinner, B. 14, 1071; 15, 585). Large prisms (from dilute al-

cohol), sl. sol. water. - KHA" 1 aq: needles, v. sol.

condy, s. sol. water. — Riff 1, and 1 needes, v. water. — CaA" 3aq: prisms. — Âg, A" aq: pp. Ethyl ether Et, A". [125]. A mide. [above 300°]. Prisms. A hydride C₁H₁₀O₂. [138°]. Got heating the end at 100° Got by

heating the acid at 190° Imide C₁₁H₁₆O₃(NH). [205°]. Formed from

the anhydride and alcoholic NHa.

Nitrile C₁₁H₁₈N₂O₂. [above 320°]. **PHOSENE** v. SYNANTHRENE.

PHOSGENE GAS. Another name for COCl2;

v. Carbon Oxychloride, vol. i. p. 692. PHOSPHAM. (?)PN,II. When dry NH, is passed into well-cooled PCl,, a solid colourless mass is obtained, said by H. Rose to contain PCI, and NH, in the ratio PCI,:5NH, (P. 24, 308; 28, 529). This substance is probably a mixture of various compounds" other substances are formed if the PCl, is not cooled. If PCl, is treated with NH, at the ordinary temperature, 5NH, are absorbed by PCl, (H. Rose, l.c.); from this product ether dissolves out NaPaCle (v. NI-TROGEN PHOSPHECHLORIDE, vol. iii. p. 570); if the product is heated, HCl and NH Cl are evolved. and a white, loose powder remains, to which Gerhardt (A. Ch. [3] 18, 188; 20, 225) gave the composition PN₂H and the name phospham. Liebig a. Wöhler (A. 11, 139) obtained this compound by passing PCl, or PCl, over heated NH,Cl, and washing and heating the product; MI, (c), and washing and nearing the product, they supposed it to be PN₂. The same substance was obtained by Pauli (A. 101, 41) by heating an intimate mixture of P₂S₂ and NH₂Cl, also by heating red P with S and NH₂Cl, and by heating powdered Ca phosphide with S and NH,Cl, and washing the residue with an acid. Pauli's analyses showed less N than's required by the formula PN.H. By treating PCl, with NH, washing for a long time with water, digesting with HClAq, then with KOHAq, washing with water and then with ether, Salzmann (B.7, 494) obtained a substance resembling phospham and approximately agreeing with the composition P.N.H.; Salzmann regarded this substance as probably a mixture of several very similar compounds of P, N, and H. Besson (C. R. 114, 1264) says that PCl, absorbs 8HN,, and that on

heating PN₂H is formed.

Phospham is a white, loose powder; insoluble in ordinary solvents; melts and vaporises when heated in absence of air; oxidised by heating in air; yields HPO, and HN, when moistened with water and heated (Gerhardt, l.c.); fused with KOH or BaO,H, forms N.H, and orthophosphate, with incandescence.

Phospham may be regarded as one of the nitriles of H₂PO₄: thus PO₂OII.(ONH₂)₂-4H₂O = PN₂H; the other nitriles would be PON, which is known (v. Phosphorus oxyntradde, p. 144) [PO(OH)₂ONH₄-3H₂O = PON], and PN₃H₁, which has not been isolated [PO(ONH)₃-4H₂O = PN₃H₄]. Mendelejeff (B. 23, 3472 note) thinks it likely that phospham is a polymeride of PN₂H, inasmuch as it is analogous to N₁H (hydrazoic acid, vol. iii. p. 559) and both P and Compounds show a greater regaliness to polymerise than N and compounds of N. M. M. P. M.

PHOSPHAMIC ACIDS AND ALLIED COMPOUNDS. Two amic acids may be derived theoretically from PO(OII),, viz. PONH₂(OH), and
PO(NH₂)₂OH; both acids have been isolated.
The compound PO(NH), is described as
Phosphamide, and PO.NH.NH₂ as Phosphamide acids,
PS.NH₂(OII), and PS(NH₂)₂OH are probably
formed by the action of NH₄ on PSCl₃ (v. Threphosphamic acids,
PS.NH₂(OII), and PS(NH₂)₂OH are probably
formed by the action of NH₄ on PSCl₃ (v. Threthree amic acids (or salts of these) derivable from Il,PO, are known: P2O,NH₂(OH),
P2O₃(NH₂)₂(OH)₂, and P₂O₃(NH₂)₃OH. By heating P2O₄(OH)N is obtained. There are also several
acids (or their salts) known, which may be derived
from hypothetical P2O₄(OH)₃(2P2O₃(OH)₄ + H₂O
= P4O₅(OH)₃| by replacing OH by NH₂ or NH.
Imidophosphoric acid, PO.NH.OH, perhaps
exists.

Phosphamic asid PO.NH.(OH), (Amidophosphoric acid.) Obtained by Stokes (Am. 15, 198 [1893]) by suspending the lead salt in a little ice-water, decomposing by excess of H.S. and filtering into alcohol. White microscopic crystals; easily sol. water; does not give NH, with caustic alkalis; heated to 100° is slowly changed to an NH, salt, perhaps NH, PO,; aqueous solution soon changes to NH, H.PO,. Acid and mormal salts have been prepared. The lead salt is formed by adding lead acetate to a solution of PO.NH, OH.OK, which salt is produced by adding alcoholic NH, to an alcoholic solution of PO.Cl(OPh), and saponifying the PO.NH, (OPh), thus formed by KOHAq.

PHOSPHODIAMIC ACID PO.(NH₂)₂OH. (Diamidophosphoric acid.) Stokes (B. 27, 565 [1894]) prepared this acid by saponifying the product of the action of NH₂Aq on POCl₂(OPh). The acid gives salts PO(NH₂)₂OM, and also salts of an acid P(NH₂)₂(OH), (Abstract in C. J. 66 [11], 188 [1894]).

PYROPHOSPHAMIC ACID P₂O₃(NH₂)(OH)₃. This is said by Gladstone (C. J. 17, 229) to be the chief product of the action of NH₃ on P₂O₃; Schiff (A. 103, 168) formulated this product as PO.NH.OH, imido-phosphoric acid; Stokes (Lc.) says the product is a mixture. For details v.

G. (l.c.; also C. J. 3, 135; 21 64); also G. a. Helmes (C. J. 17, 225).

Pyrophosphonamic actd P₂O₃(NH₂)₂(OH)₃(G., C. J. 19, 290; G. a. H., Lc.). Formed by action of water or alkalis on N₃P₃Cl_s, by treating POCl₃ with conc. NH₃Aq, and in many other ways. A white amorphous solid, easily soluble in water and alcohol. The acid is dibasic. The salts are difficult to obtain pure, as they easily change into pyrophosphamates; salts of Ba, Ag, and Zn are described.

Pyrophosphatriamic acid P₂O₄(NH₂)OH (G., C. J. 19, 1; 21, 64). Dry NII, is passed into POCl, until saturated, the product is heated to 220° and boiled for a short time with water, the residue is washed with cold water, and then with a little dilute alcohol. A white, amorphous, tasteless powder, nearly insoluble in water; slowly acted on by cold water, more quickly by hot water, yielding P₂O₄(NH₂)₂(OH)₂Aq and NH₄Aq; boiled with HClAqqives H₂PO₄ and NH₄. Pyrophosphotriamates of NH₄ Ba, Cd, Co, Cu, Cr, Fe, Pb, Mg, Mn, Hg, Ni, Pt, K, Ag, Tl, and Zu are described; the acid is said to be tetrabasic.

Pyrophosphonytrallic acid P.O. (OH)N. The NH, salt of this acid is said to be formed by heating P.O. (NH.), OH, and the K salt by heating P.O. (NH.), OK (G., C. J. 22, 19).

TETTAPHOSPHAMIC ACIDS AND ALLIED COMPOUNDS. By the reaction of NII, with POCI, under different conditions, Gladstone (C. J. 21, 261; 22, 15), obtained various compounds which may be regarded as (1) tetrophosphodiamic acid P₁O, (NH₂)₁(OH)₄, (2) P₂O, (NH₂)₁(OH)₂ tetraphosphotetramic acid, (3) *tetraphospho-inidotetronide P₄O, (NII₂)₁NII (called by G. tetraphosphopentazotic acid), (4) *tetraphosphotimido-diamide P₄O, (NH₂)₂(NH)₂ (called by G. tetraphosphottrimic acid). Some of the above acids are regarded by Mente (A. 248, 232) as mildo-acids. M. M. P. M.

PHOSPHAMIDES. I. Phosphoric TRIAMIDE O.P(NH₂), (Phosphory) triamide) [derived from O.P(OH)₃ = H₃PO₄]. This compound is said by Schiff (4. 101, 300) to be obtained by passing NH₃ gas into POCl₃, and treating the product with water. It is described as a snow-white, amorphous solid; heated out of air gives NH₃ and PON dused with KOH gives NH₄ and K phosphate; scarcely acted on by boiling water, KOHAq, or dilute acids; soluble in hot cone. H₂SO₄; slowly attacked by boiling cone. HNO₃ or HClAq. Gladstone (C. J. 22, 18) could not obtain this compound.

Thiophosphamide is described under Thiophosphonyl chloride, Reactions, No. 7, p. 148.

M.M. P. M.

PHOSPHAMIDO-IMIDE PO.NH.NH. (Phosphoryl imido-amide. Formerly called Phosphodiamide) (Gerhardt, A. Ch. [3] 18, 188; Schiff, A. 101, 330). Obtained by saturating PCl, with NH., boiling the product with water as long as HCl pusses into solution, then boiling

with potash, then with HNO,Aq or H,SO,Aq, washing, and drying over H,SO, A white powder,insoluble in alcohol, water, or turpentine; heated out of air gives NH, and PON; heated in moist air gives NH, and HPO,; luced with KOH gives K phosphate and NH,; slowly exidised by fusion with KNO, but resists action M. M. P. M. of most oxidisers.

PHOSPHATES. Salts of the phosphoric acids. Besides the salts directly derived from the three phosphoric acids HPO, H,PO, and H.P.O. (v. Phospuorio Acids, p. 124), phosphates exist which are probably derived from hypothetical di-, tri-, or meta- phosphoric acid nHPO;; and a few salts have been isolated which are perhaps derived from the hypothetical acids P₄O₇(OH)₄ and P₁₀O₁₀(OH)₁₂.

Composition .- Orthophosphates are derived from H₃PO₄; they may be divided into classes according to the replacing powers of the metals: (1) monovalent metals form MH,PO, M,HPO, and M,PO,; (2) divalent metals form MH,PO, and M,PO,; (3) trivalent metals form MH,PO, and M,PO, and M,PO,; (4) tetravalent metals form MH,PO, and M,PO, and

Pyrophosphates are derived from H.P.O.; (1) salts of monovalent metals M₂H₂P₂O, and M₄P₂O₇; (2) salts of divalent metals MH₂P₂O, and M₂P₂O₇, &c.

Metaphosphates are derived from HPO.: (1) salts of monovalent metals MPO; (2) salts of divalent metals MP Os, &c. Various modifications of Na (and other) metaphosphates are known, all having the empirical formula MPO, but differing both in physical and chemical properties from one another; these salts were classified by Fleitmann a. Hanneberg (A. 65, 304; F., P. 78, 233, 338) as: (1) dimetaphosphates, salts of H₂P₂O_e; (2) trimetaphosphates, salts of H₂P₂O_e; (3) tetrametaphosphates, salts of H₂P₂O₁; and (4) hexametaphosphates, salts of H.P.O. Tammann (Z. P. C. 6, 122) has examined the electrical conductivities, and the depressions of freezing-points, of aqueous solutions of several di-, tri-, and hexa-metaphosphates; he comes to the conclusion that Fleitmann's dimetaphosphates should be represented in solution as $M_2(PO_3)$, (i.e. as trimetaphosphates), and the table is tri-salts when in solution are really M_s(PO_s)_s (i.e. dimetaphosphates). Tammann's results point to the existence in aqueous solution of 8 isomeric hexametaphosphates which nay be represented as (i.) M₂M₂(PO₃)_e e.g. Na₂.Na₄(PO₃)_e, K₂Na₄(PO₃)_e, K₂Na₄(PO₃)_e, K₃Na₄(PO₃)_e, K₄Na₄(PO₃)_e, K₄Na₄(PO₃)_e + Giii.) M₂M₄(PO₃)_e e.g. Na₄Na₄(PO₃)_e, Mil₃Na₄(PO₃)_e, There are also, according to Tammann, three different Na metaphosphates insoluble in water (v. also T., J. pr. [2] 45, 417).

Tetra- and deka-phosphates. Salts of the compositions $Na_*P_*O_{1}$ and $Na_{12}P_{10}O_{31}$ are obtained by fusing together Na_*P_*O , and $Na_{42}(PO_{3})_a$; these salts may be regarded as derived from the hypothetical condensed acids $H_1P_1O_{12}$ (= $(H_1P_2O_1 - H_2O)$), and $H_{12}P_1O_{13}$ (= $(H_1P_1O_1 - H_2O)$), respectively.

The composition of all the phosphates may be represented empirically with the expression.

be represented empirically by the expression nMO.mP,0,xH,0, where MO stands for a basic

Occurrence. -Phosphates of Al and Ca occur

in large quantitie. ______, vocae, purepurates of Fe, Pb, Mg, NH, &c. are also widely distributed minerals. Coprolites (the fossilised excrements of former land-animals), and guano (the excrement of certain birds) consist very largely of Ca phosphate. Phosphates occur in some kinds of coal, in the ashes of plants, and in the bones of animals.

Formation.—Some of the orthophosphates are obtained by reacting on HaPO Aq with metallic oxides or carbonates; others are formed by double decomposition from the alkali phosphates; when a metaphosphate is fused with a metallic oxide or hydroxide a normal orthophosphate is generally formed. Many pyrophosphates are obtained by double decomposition from Na,P₂O, which is formed by strongly heating Na,HPO₁; other pyrophosphates are found by neutralising H,P₂O,Aq by basic oxides or hydroxides. Metaphosphates are generally formed by strongly heating orthophosphates MH_PO, or MRHPO, when M or R is a metal whose oxide is volatile; many are produced by double decomposition from NaPO,; some are formed by heating Cu₂(PO₃), with a metallic sulphide and filtering from CuS.

The processes by which any one of the three classes of phosphates is formed from another is perhaps best understood by representing the phosphates thus:

meta pyro P₂O₃.2M₂O P,O,.M,O P2O3.3M2O Metaphosphate becomes pyro- by gaining M.O. and becomes ortho- by gaining 2M.O. and so on. Metaphosphate fuscil with metallic oxide, on. hetaphospiate used with metalic oxice, hydroxide, or carbonate yields pyrophosphate or orthophosphate, according to the quantities used; thus (1) 2NaPO₂+Na₂O₃=Na₁P_{.O}+CO₂; (2) 2NaPO₂+2Na₂CO₂=2Na₂PO₂+2CO₂. The metaphosphate of a heavy metal yields an orthophosphate of a heavy metal yields an orthophosphate of a heavy metal yields. thophosphate and H.PO, by boiling with water: thus 8AgPO, + 3II, O = Ag, PO, + 2H, PO, change from a pyro- to an ortho- phosphate is often effected by boiling with water, the product being an acid salt, thus Na, P,O, +H,O = 2Na₂HPO₄; or the pyrophosphate is fused with hydroxide or carbonate, thus

 $\operatorname{Ba}_{2}\operatorname{P}_{2}\operatorname{O}_{7} + \operatorname{Ba}\operatorname{O}_{2}\operatorname{H}_{4} = \operatorname{Ba}_{4}(\operatorname{PO}_{4})_{2} + \operatorname{H}_{2}\operatorname{O}_{4}$ Acid orthophosphates with one atom of H yield pywo-phosphates when strongly heated, e.g. 2Na₂HPO₁ - H₂O = Na₄P₂O₂; and those with two atoms of H yield metaphosphates, e.g. NaTl₁PO₄ - H₂O = NaPO₄.

Similarly a double orthophosphate of the form M₂Rl'O₄ yields a pyrophosphate on heating if R forms a volatile oxide, e.g. 2Na₂(NII₄)PO₄ = $Na_1P_2O_1 + H_2O + 2NH_3$. The removal of M₂O from a normal orthophosphate with formation of a metaphosphate is often effected by fusing with SiO₂ or B₂O₃ or other anhydride which forms a salt with M₂O₄, e.g. Na₂PO₄+SiO₂

forms a sait with m_AU, e.g. Ma_BEU₄TEIU₂ = NaPO₄+Na_SiO₄.

The metaphosphates formed by the processes sketched above belong to several series of saits all of which have the empirical formula saits all of Which have the Empirical formula saits all of Which have the Empirical formula saits and the SiO According to Electronia Hampherg nMPO. According to Fleitmann a. Henneberg (A. 65, 304; F., P. 78, 233, 338), these salts belong to five series.

Monometaphosphates MPO. Not many of these have been obtained with certainty; they are produced by heating alkaline oxider with

equivalent quantities of H.PO, to redness until the residue ceases to give an acid reaction (the temperature not being high enough to melt the mass), and washing the residue with cold water; some of the salts—e.g. NaPO, and KPO,—are formed by heating MH,PO, or M,H,P,O, to redness (c. 315°) till the residue is almost wholly insoluble in cold water (Maddrell, C. S. Mem. 3,

Dimetaphosphates M.P.O. The salts of Cu, Zn, and Mn are prepared by heating equivalent quantities of MO and H3PO, to redness. The

Na and NH, salts are obtained by decomposing the Cu salt by Na SAq or NH, sulphide solution, filtering, and ppg. by alcohol. These salts yield others of the series by double decomposition. The salts of this series are soluble in water and crystallisable. Tammunn (Z. P. C. 6, 122) thinks these salts are really trimetaphos-

phates (v. Properties and Reactions).

Trimetaphosphates M.B.O.. The salts of this series are crystalline. The Na salt is prepared by slowly heating NaNH, HPO, with frequent stirring, till the residue has a faintly acid reaction, treating with cold water, filtering, and allowing the filtrate to crystallise. The salt is also formed by heating NaNH, HPO, till a glassy mass remains, and cooling very slowly. other salts are obtained from the Na salt by double decomposition. Tammann (l.c.) regards these salts as dimetaphosphates (v. Properties and Reactions).

Tetrametaphosphates M,P,O12 beated with H.PO, to redness, as in making the Cu, Zu, and Mn dimetaphosphates (v. supra); the crystalline salt which is formed is insoluble in water, and much more easily decomposed by acids than the Pb salt got from Na,P,O. The Na salt is obtained by decomposing the Pb salt by Na SAq; and other salts are obtained from the Pb salt by double decomposition. Salts of Bi and Cd are obtained similarly to the Pb salt. These phosphates are uncrystallisable. Tammaun (J. pr. [2] 45, 417) says that CuNa₂P₄O₁₂ is the only salt which certainly belongs to this scries.

Hexametaphosphates M.P.O. NaNH, HPO. is heated till a glassy mass remains, which is cooled rapidly (Graham, T. 1838, 253). The Na salt yields others by double decomposition. These salts are non-crystallisable, and dry to resinous-like masses. Tammann's experiments (Lc.) seem to show that Na_sP_sO₁₈ is a mixture of several isomeric salts (v. p. 118).

Tammann (l.c.) describes salts belonging to the series of penta-, okto-, deka-, and tetrakai-

deka- metaphosphates.

Tetraphosphates M₂P₄O₁₃. A few of these sales have been prepared, e.g. Na₂P₄O₁₃ by fusing 2NaPO₂ + Na₄P₂O₃, and Ba₁P₄O₁₃ by fusing the Na salt with BaCl₂ (F. a. H., A. 65, 304; Uelsmann A. 118, 90)

mann, A. 118, 99).

Dekaphosphates M₁₂P₁₀O₃₁. The Na salt was obtained by fusing Na,P₂O, +8NaPO, (F. a. H., l.c.); some other salts were obtained from the

Properties and Reactions .- The orthophosphates MH.PO, dissolve in water, forming acid solutions; the dimetallic salts M. HPO, dissolve in water when M is an alkali metal, the solutions are feebly alkaline. Of the normal salts M.PO.

only those of the alkali metals are soluble in water; the solutions have an alkaline reaction. and are decomposed very easily, even by CO, forming M,HPO,Aq. Most of the heavy metals form only M,PO. Solutions of alkali orthophosphates give a yellow pp. (Ag,PO,) with AgNO, Aq, and a yellow pp. on warming with NH, molybdate solution. The orthophosphates M,PO, are not decomposed by heating strongly, unless they are salts of volatile bases; M,HPO, give M.P.O. and H.O. and MH.PO. give MPO. and H.O. when strongly heated. M.PO., M—alkali or alkaline earth metal, are not changed by heating with charcosi, but M.HPO, and MH.PO, give M.PO, and P. When M is a heavy metal, the salts M.PO, generally give metallic pl. sphides by heating with C. Orthophosphates heated with K or Na yield alkali phosphide. Many insoluble orthophosphates are decomposed by fusion with alkali carbonate, but those of the. alkaline earths are only partially decomposed. H.SO, decomposes all orthophosphates. When the salts M.PO, are heated with SO.Aq under pressure, M.HPO, or MH.PO, are formed (Pitter, Chem. Indust. 1878. 398; Gerland, J. pr. [2] 4,

Of the pyrophosphates, the normal alkali salts are soluble in water, with feebly alkaline reactions; the others are generally insoluble but dissolve in Na, P2O, Aq, forming double salts (H. Rose, P. 76; 13; Schwarzenberg, A. 65, 133; Persoz, A. 65, 163). Solution of pyrophosphates give orthophosphates when boiled with the stronger acids, or heated with water to 280° (Reynoso). M₄P₂O, are not changed by heat unless they are salts of bases decomposed by heat; M.H.P.O, give MPO, and H.O when strongly heated. All the pyrophosphates are changed to orthophosphates by heating strongly with sufficient alkali or alkali carbonate. Pyrophosphates of metals whose oxides are not reduced by H give orthophosphates and P2Os when heated in H; those which contain metals whose oxides are reduced by H, but not by heat alone, give metallic phosphide when heated in H; and those containing metals the oxides of which are reduced by heat alone, yield metal, H₁O, H₂PO, &c., when heated in H (Struve, J. pr. 79, 345). Pyrophosphates in solution average a white pp. with AgNO, Aq; they do not give an immediate pp. with warm NH, molybdate, and they do not coagulate albumen when acidified by acetic acid.

Some metaphosphates are soluble, others are insoluble, in water; some are crystalline, others are amorphous (v. supra: Formation of different classes of metaphosphates). Solutions of these salts in water are changed to orthophosphates on long-continued boiling; they give a white pp. with AgNO, Aq, no immediate pp. with NH, molybdate, and they coagulate albumen after

acidification by acetic acid.

Tammann (Z. P. C. 6, 123) has examined the electrical conductivities of solutions of Fleitmann's di- and tri- metaphosphates of Na; his results indicate that the ions of the salts in solution are Na_x and (PO_z)_x. He has also measured the depression produced in the freezingpoint of water by dissolving these salts therein; and, taking the results along with the electrical conductivities, he concludes that Fleitmann's di-

salts are tri-salts, and F.'s tri-salts are really | H,PO,Aq, or by ppg. BaCl,Aq by Na,HPO,Aq di-salts. By the reaction of AgNO,Aq on the soluble in 10,000 to 20,000 parts water, easily di salts. By the reaction of AgNo, Aq on the Ne, P, O₁, of Graham and Fleitmann, Tammann obtained a crystalline salt Ag, P, O₁, and two salts Ag, Na, P, O₁, and from these he formed three Na salts which he formulates as Na₅P₅O_{1n}, Na₁Na₂P₅O_{1n}, and Na₅Na₁P₅O₁, Measurements of the electrical conductivities of these salts confirm the above formulæ, and they tend to show that the ions of the salts in solution are Na, and Na, P,O,,, and Na, and NaP, O in respectively. A fuller examina-tion of Graham's salt led T. to conclude that it contains another isomeric hexametaphosphate

Na, Na, P,O10.

For detection and estimation of phosphates a manual of analysis must be consulted.

ORTHOPHOSPHATES. Salts derived from H,PO. (For thioxyorthophosphates v. Phos-

PHONIC SULPHIDE, p. 147.)
Aluminium orthophosphates. Many occur in minerals, e.g. angelite, fischerite, wavellite, tyrquois. The pps. obtained by adding Na,HPO,Aq to alum solutions vary in composition. They may be represented as $x\Lambda l_0 O_{31}$ yP_1O_{32} x being chiefly 1, 2, 3, and y being 1 and 2 (Munroe, A. 159, 638; Wittstein, J. B. 27, 167; Fuchs, S. 24, 121; Millot, C. R. 82, 89).

The normal salt, AIPO, xH, O, is obtained by gradually pouring neutral alum solution into excess of Na, HPO, Aq; a white loose powder; soluble mineral acids, soluble organic acids, soluble NH, citrate solution (Erlenmeyer, B. 14, 1869), soluble Al salt solution (Fleischer, Fr. 6, 28), soluble in potash; infusible at red heat, fused with Fe and SiO₂ gives Fe phosphide (Schlösing, C. R. 67, 1247); partially decomposed by fusing with K₂CO₃ (Rammelsberg, P. 64, 405; cf. Vauquelin, A. Ch. [2] 21, 138). When air-dried x = 4 to 5; dried over H₂SO₄, x = 8 (Rammelsberg, Millot, Wittstein). For other phosphates of Al v. Rammelsberg (l.c.), Schweitzer (B. 3, 310; 6, 28), Ludwig (Ar. 1th. [2] 59, 19), Hautefeuille a. Margottet (C. R. 106, 135), Erlenmeyer (Z. 3, 572).

Double salts with phosphates of Ca, Li, and Mg have been described (v. Gm. K., i. 2. 670).

American orthophosphates. The normal salt, Am, PO, 3H,O, crystallises in short pyramids, obtained by treating Am2HPO, with conc. NH, Aq (Berzelius, Gm.-K. i. 2, 527). Loses twothirds NH, by boiling water (Kraut, C. C. 1855. 894). Sestini (B. 11, 1927) obtained a salt with The di-ammonium salt, Am, HPO, is formed in monoclinic prisms by allowing NH, or (NH₄)₂CO₃ in H₃PO₄Aq to evaporate; soluble four parts cold water, solution is alkaline; on boiling NH, is evolved; S.G. 1.62-1.67 (Rammelsberg, B. 3, 278; Schiff, A. 112, 88; Buignot, J. 1861. 15; Proust a. Brooke, Gm. K. i. 2, 528). The mon-ammonium salt, AmII, PO,, crystallises in quadratic forms, isomorphous with KH,PO,, by adding NH,Aq to H,PO,Aq till BaCl,Aq ceases to give a pp. S.G. 1758 (Schiff, Lc.; ceases to give a pp. S Mitscherlich, P. 19, 385).

Barium orthophosphates. The normal salt, Ba, P₄O₈, is a heavy white solid, obtained by ppg. BaCl.Aq by Na, PO, Aq (Graham; Rotondi, B. 15, 1441). Two acid salts have been obtained: -(1) Baliro, by boiling the normal salt with

soluble if NH, salts, BaCl, or NaCl is present soluble in H,PO,Aq or dilute HNO,Aq (Berzelius Ludwig, Rose, Brett, Wittstein, Bischoff, Malaguti, Gm.-K. i. 2, 272; Skey, C. N. 22, 61; Erlenmeyer, J.1857. 145; Sotschenoff, C. C. 1875. 97; Gerland, J. pr. [2] 4, 125); (2) BaH, P.O., from a solution of BaHPO, in H, PO,; white triclinic crystals; decomposed by much water to H.PO.Aq and BaHPO. (Berzelius).

Double salts.—(1) BBa,P.O.,BaCl. (Rose, P. 8, 211; Ludwig, Ar. Ph. [2] 56, 265; Deville

a. Caron, A. Ch. [3] 67, 451); (2) 4BaHPO, BaCl₂ (Erlenmeyer, J. 1857, 145); (3) BaNaPO, 10H₂O (Rose, Guyton, Berzelius, Gm.-K. i. 2, 313; de Schulten, Bl. [2] 39, 500; Joly, C. R. 104, 1702); (4) BaKPO, 10H₂O (de S., L.c.).

Beryllium orthophosphates. The normal salt, Be, P,O,, is a white pp., obtained by adding Na.HPO.Aq to solution of a salt of Be. An acid salt is obtained by dissolving the normal

salt in H₃PO₃Aq (Vauquelin, Gm.-K. i. 2, 269).

Double salts. Be.NH, and Be.K phosphates are known (Rössler, Fr. 1878, 148;

Ouvrard, C. R. 110, 1333).

Bismuth orthophosphate BiPO,. powder, obtained by adding Bi,O,xH,O to H.PO Aq; little known (Wenzel, Gm. K. i. 2, 832; Chancel, C. R. 50, 416).

Cadmium orthophosphates. salt, Cd, P,O,, is obtained as an amorphous pp. by adding Na, PO, Aq to a Cd salt solution (de Schulten, Bl. [3] 1, 473).

Acid salts (de S., l.c.): (1) Cd, H₂P₄O₁₆.4H₂O₄ by ppg. hot CdCl₂Aq by Na₂HPO₄Aq. (2) CdH, P.O. 2H.O. by dissolving the foregoing

salt in cold dilute H,PO,Aq and allowing to evaporate at ordinary temperature.

Double salt 3Cd₃P₂O₃, CdCl₂ (de S., l.c.). Calcium orthophosphates. Ca phosphates are widely distributed minerals.

Normal salf Ca, P,O,. Obtained, as a white amorphous powder, by adding NH,Aq to solution of bone-ash in HClAq or HNO₃Aq; by adding Na₃PO₄Aq, or a mixture of Na₂HPO₄Aq and NH3Aq, to CaCl Aq. For details of preparation from phosphorite, or bone-ash, &c. v. DICTIONARY of Applied Chemistry. The pp. from CaCl₂Aq in presence of NII₄ contains 5H₂O according to Wittstein (J. 1866, 168; v. also Ludwig, Ar. Ph. [2] 69, 286). Slightly soluble in water; one litre cold water dissolved 79 mgm. freshly ppd., and 31 mgm, strongly heated, Ca₃P₂O₈ (Völcker, J. 1862. 131). Decomposed slowly by boiling water into CaH₄P₂O₈ and 2Ca₃P₂O₈CaO₂H₂ (Warington, C. J. [2] 11, 983). Solubility in water is increased by small quantities of alkali salts (v. Wöhler, P. 4, 166; Liebig, A. 61, 128; Lassaigne, J. 1847. 341; Thomson, Ann. Philos. 17, 12; Völcker, J. 1862. 131; Fresenius, Fr. 10, 133; Hüncfeld, Delkeskampt, Morveau, Gm. K. i. 2, 367; Terreil, Bl. [2] 35, 548; Erlenmeyer, B. 14, 1253). Presence of starch and various organic substances increases solubility in water (v. Wöhler, A. 98, 143; Hayes, N. Ed. P. J. 5, 378). Soluble in CO_Aq; CaCO₂ and CaHPO₃ separate on standing (Liebig, A. 106, 196; Warington, C. J. [2] 4, 296; Dusart a. Pelouze, C. R. 66, 1327; von Georgievics, M. 12, 566).

Partially decomposed by boiling with NaOHAq, or by fusing with Na₂CO₂ (Wöhler, A. NaOHAQ, or by fusing with Na_cCO_c (Wöhler, A. 51, 437; Rose, P. 95, 437; Fresenius, Fr. 10, 133). Easily changed to CaC_cO_c by boiling with (NH_c)_cC_cO_cAq (Fresenius, Lc.).

Strongly heated with C and SiO_c gives Ca silicate, P, and CO; heated in CO, all P is set free (Schlösing, C. R. 59, 384; Anderson, B. 5, 1065).

1065). Heated with Na, K, or Mg, metallic phosphide is formed (v. Gm.-K. i. 2, 366).

Dissolved by SO₂Ag; on standing, CaHPO₄ and CaSO₂ separate (c. Gerland, C. N. 20, 20s; Aldred, C. N. 42, 177; Rotordi, B. 15, 1441). Dilute H,SO,Aq forms CaHPO, or CaH,P,O, or CaSO, and H,PO, according to the quantities of H2SO, and Ca2P2O, the temperature, and the time of action (v. Gm.-K. i. 2, 369; Kolb, C. R. 78, 825; Joulie, C. R. 76, 1288; Crum, A. 63, 394). For the (similar) reactions with HClAq and HNO, Aq v. Crum, l.c.; Piccard (J. 1886, 168); Bischof (S. 67, 39); Birnbaum, a. Packard (Z. [2] •7, 137); Tissier (C. R. 38, 192); Warington (C. J.

[2] 4, 302).

Double salts. (1) Ca,P,O,Ca,SiO, (Carnot a. Richard, C. R. 97, 316). (2) 3Ca₃P₂O₈.CaCl₂by fusing Ca₃P₂O₈ with NaCl, or heating to 250° with CaCl Aq, or passing PCl, vapour over glowing lime (Forehhammer, P. 91, 568; Debray, A. Ch. [3] 61, 424; Daubrée, Ann. M. (4) 19, 684; Deville a. Caron, A. Ch. [3] 67, 451). 584; Deville a. Caron, A. Ch. [3] 67, 451].
(3) 3Ca,P₂O, CaP₂; occurs native as apatite (with varying quantities of CaCl.); obtained by fusing Na,HPO, CaF₂, and CaCl. (D. a. C., l.c.; Briegler, A. 97, 95). (4) Ca(NH,)PO, xH, Cherical a. Fenerlein, Fr. 1881. 191).
(5) CaKPO, (Rose, P. 77, 291). (6) CaLiPO, (Rose, P. 77, 291. Rome, A. 172, 18).

291; Bungo, A. 172, 18).

Acid salts. I. Dicalcium phosphate
Ca.H.P.Q.. Obtained by adding Na HPO,Aq, or
NaNH,HPO,Aq, to excess of CaCl,Aq; pp. contains a little Ca,P,O_a; also by the action of CO,Aq on CaCO, and (MI), HPO, Aq (Becquerel, C. It. 34, 573); and by acting on powdered CaCO, with H, PO, Aq (Debray, A. Ch. [3] 61, 424); by passing CO₂ into H₂O, holding freshly ppd. Ca.P₂O₃ in suspension (Percy, P. M. [3] 26, 194; Reichardt, Ar. Ih. [3] 2, 236). Obtained in crystals by allowing solutions of (NH4),HPO, and CaCl, to mix slowly through a porous cell (Vohl, A. 88, 114), or through a layer of water (Drevermann, A. 87, 120); also by allowing a solution of amorphous CaHPO, in a weak acid to evaporate (Bödeker, A. 69, 206; Baer, P. 75, 152; Vorbringer, Fr. 9, 457; v. also Causse, J. I'h. [5] 21, 544). CaHPO, ppd. at low temperatures and dried quickly at 100° contains 2H₂O, which is lost by long drying at 100° in a stream of dry air. Forms Ca.P.O, when strongly heated; decomposed to Ca₂P₂O₃ and CaH₄P₂O₅ by long boiling with water. For description of various hydrates xCaHPQ.yH.O v. Vorbringer (Fr. 9, A57), Gerland (J. pr. [2] 4, 104), Millot (Bl. [2] 33, 194), Skey (C. N. 22, 61), Dusart a. Pelouze (C. R. 66, 1827), Davies (C. N. 64, 287). Soluble in boiling NH,ClAq (Kraut, Ar. Ph. [2] 111, 102); soluble SO₂Aq (Gerland, J. pr. [2] 4, 123), in HClAq and HNO₂Aq (Berzelius, Baer, Gm. K. 1.2, 372). Decomposed by boiling alkali carbonate solutions (Malaguti (Fm. K. i 2, 373)) solutions (Malaguti, Gm.-K. i. 2, 373)

II. Monocalcium phosphate CaH, P,O, H,O.

This salt is the chief constituent of artificial superphosphate of lime prepared by treating crushed bones, phosphorite, &c., with H₂SO₄ (r. Dictionary of Applied Chemistry). Prepared by dissolving Ca₂H₂P₂O₃ in 31 p.o. H₃PO₄Aq, crystallising, washing with absolute alcohol, then with ether, and drying (Stoklasa, Listy Chem., 13, 203, 240, 273; abstract in C. J. 58, 695). 13, 203, 240, 273; austract in C. J. ec, out, This salt is also formed by evaporating Ca,H,P,O, with HNO,Aq+H,SO,Aq. Also by leaving a solution of the commercial honey-like monocalcium phosphate in contact with Ca,P,O. for some time, and evaporating the solution formed at a gentle heat; the salt is thus obtained in crustals (Pointet, Bl. [3] 5, 254). Not hyg oscopic; the hygroscopic nature of the prepication made by Birnbaum and others is said by Stoklasa (l.c.) to be due to traces of H.PO. Thin rhombic plates (v. Haushofer, Z. K. 7, 263); S.G. 2-02 (Schröder, B. 11, 126). Loses H.O at 100°, decomposes at 200° to mixture of CaP,O. and Ca,P,O, (Birnbaum, B. 6, 898). Decomposed by H,O. Stoklasa (l.c.) represents the decomposing action of water as

 $xCaH_{\bullet}P_{\bullet}O_{\bullet}.H_{\bullet}O + H_{\bullet}O$ =(x-1)CaH $_{\bullet}P_{\bullet}O_{\bullet}.H_{\bullet}O + CaH_{\bullet}O_{\bullet} + 2H_{\bullet}O + H_{\bullet}PO_{\bullet}$; the greater the quantity of water the more salt is dissolved without decomposition; with 200 parts H₂O to 1 part salt a clear solution is formed without any free H,PO4; above this limit Call, P2O, is re-formed from the products of its decomposition (for older observations v. Birnbaum, Lc.; Erlenneyer, N. J. P. 7, 225; Warington, Pr. 1880, 243). According to Reynoso (C. R. 34, 795), water at 280° decomposes the salt, forming HaPO, and crystalline CasP.O.

salt, forming H₁PO₄ and crystalline Ca₂P₄O₄. Various salts produce Ca₂H₂P₂O₄ from solutions of Call₄P₂O₆ (v. Debray, A. Ch. [3] 61, 421; Dusart a. Pelouze, C. R. 66, 1327; Vorbringer, Fr_{e0}, 457; Erlenmeyer, L.:; Birnbaum, L.c.). Cerium orthophosphate CePO₄. By fusing Cc₂O₃ with KPO₃; also by digesting Cc₂K₄(PO₁)₂ with KClAq. Monoclinic prisms; S.G. 3.8 (Ouvrard, C. R. 107, 37). The double salt Ce_K₃(PO₄), is formed by fusing K₂PO₄ or K₄P₂O₇

Chromium orthophosphates. The normal chromic salt, Cr₂P₂O₈, is known in two forms, green and violet. Violet form, Cr.P. 72H.O. a violet crystalline pp. by adding Na, HPO, Aq to excess of Cr alum solution; loses 7H, O at 100°, becoming green; changed to green by conc. HNO, Aq. H. SO., or PCl. (Rammelsberg, P. 68, 383; Etard, C. R. 84, 1091). Green form, CraP2O.6H2O, by adding excess of Na.HPO.Aq to Cr alum; also by ppg. a slightly acid solution of a Cr salt by Na, IIPO, and Na acctate (llose, P. 77, 291, 298; Carnot, Bl. [2] 37, 482; Vauquelin, Cm.-K. i. 2, 304). Soluble mineral acids, also KOHAq (v. Dowling a. Plunkett, Chem. Gazette, 1858, 220; Känimerer, Fr. 12, 375). Gives alkali chromates by fusion with alkali sulphates (G. andeau, C. R. 95, 921). Forms a double salt with Ca (Dingler, D. P. J. 212, 532; Plessy, Rép. Chim. app. 1862. 453; Köthe, D. P. J. 214, 59). The acid salt CrH, P.O., 8H, O is probably formed by dissolving Cr.O., xH, O in H, PO, Aq (Vauquelin, Gm.-K. i. 2, 304; Haushofer, Z. K. 7, 263).

Chromous orthophosphate Cr.P.O. H.O. a blue pp. by adding Na,HPO,Aq to CrCl,Aq; quickly becomes green in air (Moissan, A. Ch.

[5] 25, 401). Cobalt orthophosphates. The normal salt Co.P.O..xH.O is formed by heating CoHPO..3H.O with water, or with Co(NO.).Aq, to 250° in a sealed tube (Debray, A. Ch. [3] 61, 438); also by treating Co(NH.)PO.6H.O with boiling water (Chancel, Precis d'analyse [Paris, 1862] 1, 263). In this salt x=2. A salt with x=8 is said to be formed by ppg. CoH₁P₂O₂Aq by alcohol (Reynoso, C. R. 34, 795; Reitler, Vierteigahr. Pharm. 7, 246). Two acid salts are known: (1) CdHPO₂, 3H₂O, by boiling CoCO₃ with H₃PO₂Aq, or boiling solution of a Co sait with Call, P.O., (Debray, J. Ph. [3] 40, 121); a salt with 5H,O was obtained by Bödeker (A. 94, 557). (2) CoH,P.O., by helying Co pyrophosphate with water to 280° (Reyndso, C. II. 34, 795). Double salts: NH, salts v. Dirvell, C. R. 89, 903; Popp, Z. [2] 6, 305. For luteo- and roseo- cobaltamine phosphates v. Gibbs a. Genth, Am. S. [2] 21,86; 23, 234, 319; Braun, Gm.-K. i. 8, 463; Porumbaru, C. R. 93, 463; Porumbar 842. For K and Na double salts v. Ouvrard, C. R. 106, 1729.

Copper orthophosphates. Normal salt Cu,P,O, 3H,O, obtained by adding a little Na,HPO,Aq to excess of a Cu salt solution (Mitscherlich, Gm.-K. i. 8, 614); also by heating CuCO, with H,PO,Aq to 70° (Debray, A. Ch. [3] 61, 437). A blue-green powder; decomposed by hot water under pressure (Debray; v. also Reynoso, C. R. 31, 1795; Jörgensen, Gm.: K. i. 3, 615). Basic salts and acid salts are known; composition doubtful (v. Rammelsberg, P. 68, 383; Metzner, A. 149, 67). For double salts with NH, v. Metzner, l.c., and Schiff, A. 123, 41; with Na, v. Weineck, A. 156, 57; with K, also with Na. v. Ouvrard, C. R. 111, 177. For an account of the salts produced by the reaction of Na,HPO,Aq with CuSO,Aq and Cu(NO₃),Aq v. Steinschneider, C. C. 1891, ii. 51 (abstract in C. J. 60, 1423).

Didymium orthophosphate DiPO,: also double salts with alkali metals (Ouvrard, C. R.

Iron orthophosphates. Ferrous salts. The normal salt Fo.P.O., SII, O occurs native as accounte; it is obtained by ppg. FeSO, Aq with oxcess of Na.HPO, Aq, and digesting at 60°-80° for eight days. Small monoclinic crystals (Ranmelsberg, P. 64, 251, 405), nearly colourless but becoming blue in air (Debray, C. R. 59, 40). A salt with one H.O is obtained by heating Fe₂H₂P₂O₈.4H₂O with water at 250° (Debray, A. Ch. [3] 61, 437). Various acid salts are obtained by dissolving Fe in H₂PO₄Aq; if the materials are air-free, and evaporation is effected in CO2, the salt Fe2H2P2O2.4H2O is formed (Erlenmeyer, Debray, Rammelsberg, l.c.). For double salts with NH, v. Otto, J. pr. 2, 409; and Debray, C. R. 59, 40. Ferric salts. The normal salt FePO, is

obtained by ppg. FeCl₃Aq by Na₂HPO₄Aq; dried at 50° contains 8H₂O, at 100° contains 4H₂O, dehydrated by heating strongly; also formed by oxidation in air of Fe₃P₂O₈ (Debray, Rammelsberg, Wittstein, *l.c.*). Whether the salt ppd. from FeCl, Aq in presence of acetic acid is the normal or a basic salt is undecided (v. Winkler, J.

Wackenroder a. Ludwig, Ar. Ph. [2] 53, 1; Mohr Fr. 2, 520). FePO, xH₂O is sol. c. 1500 parts boiling water; but is decomposed (Lachowicz, M 13, 357). Acid salts are obtained by dissolving 13, 357). Acid salts are obtained by dissolving Fe,O₄xH₂O in H₂PO₄Aq: Erlenmeyer got FeH₂P₂O₁ by evaporating quickly (v. also Waine, C. N. 36, 132; Wagner, Chem. Zeitung, 1881. 247). Hautefeuille a. Margottet (C. R. 106, 1357). obtained various ferric phosphates by dissolving Fe₂O₂xH₂O in glacial phosphoric acid.

Lanthanum orthoph sphate LaPO : tiouble salts with K and Na (v. Ouvrard, C. R.

107, 37).

Lead orthophosphates. The normal salt, Pb,P₂O₃o is ppd. as a white powder by adding Na,HPO₄O₄o to Pb acetate solution (Berzelius; Mitscherlich, Gm. 3; v. also Heintz, P. 73, 119; Gerhardt, A. Ch. [3] 22, 505; Haushofer, Z. K. 7, 264). A double salt with PtCl, is obtained 7, 204]. A abuste satt with Prof.; is obtained by action of Na,HPO, Aq on PbCl. (Debray, A.Ch. [3] 61, 419; Manröss, A. 82, 348; Deville a. Caron, A. Ch. [3] 67, 451). By ppg. boiling Pb2NO,Aq by H,PO,Aq, Heintz (P. 73, 119)

POZNOJAQ by H.PO.AQ, Heintz (P. 73, 119) obtained the acid sadt Pb.H.P.O.

Lithium orthophosphates. The normal salt, Li,PO.H.Q(?Li,PO.H.Q). By heating Na₂HPO.Aq with solution of a salt of Li (Mayer, A. 98, 183; v. also Berzelius, P. 4, 245; Rammelsberg, C. N. 38, 240, also B. 15, 283; Fresenius, Fr. 1, 42; Kraut, A. 182, 165). Loses H.O at 100°. Obtained in rhomboidal tables, S.G. 241 at 15°, by dissolving in fused LiCl (de Schulten, Bl. [3] 1, 479). Soluble in c. 2,540 parts water. Acid salts: LiH₂PO, and LiH₃P₂O₈.H₂O, by dissolving normal salt in

H.PO.Aq (Rammelsberg, l.c.).

Magnesium orthophosphates. The normal salt, Mg,P,O,xH,O, is obtained with 4H,O by ppg. Mg salts by alkali phosphate and drying at 100° (Graham; Rose, P. 76, f4; Gregory, A. 54, 98; Stein a. Tollens, A. 187, 79; gory, A. 54, 98; Stein a. Tollens, A. 187, 79; Fresenius). Forms monoclinic crystals (lifuushofor, Z. K. 6, 187). Very slightly soluble water (Völker, J. 1862. 131). For solubility in salt solutions v. Liebig (A. 106, 185), and in citric acid v. Erlenmeyer (B. 14, 1253). Soluble SO₂Aq (Gerland, J. pr. [2] 4, 126; Rotondi, B. 15, 141). Crystals with 6H₂O separate from MgSO₃Aq + Na₄HPO₄Aq at 36° and upwards; delta to the constant of t and at lower temperatures a salt with.14H,O is natural forms to the temperature a sair with 1411,0 is obtained (v. Percy, P. M. [3] 26, 194; Reischauer, N. R. P. 12, 43; 14, 57).

Acid salts. 1. MgHPO, xH, O (x = 6,7,8,9);

by dissolving magnesia alba in H₂PO₂Aq (Bergmann, Fourcroy, Gm.-K. i. 2, 446; Debray, J. pr. 97, 116; Haushofes, Z. K. 7, 257).

2. MgH₂P₂O₈; by boiling the foregoing acid salt with water (Schaffner; Rotondi, B. 15, 141).

Double salts. Magnesium-ammonium orthophosphate MgNH, PO, 6H,O. By adding Na, HPO, Aq to a Mg salt to which NH, ClAq and excess of NH, Aq have been added; or by adding a mixture of H.PO.Aq and excess of NH.Aq to a a mixture or H₁PO₁Aq and excess or NH₂Aq to a Mg salt. For experiments on different conditions of formation v. Graham (A. 27, 25); Riffault (At Ch. [2] 19, 90); Mohr (Fr. 12, 36); Gibbs (C. N. 28, 51); Lesieur (C. R. 59, 191); Steina. Tollens (Gm.-K. 1, 2, 476); Kubel (Fr. 8, 125); Kissel (Fr. 8, 164); Brunner (Fr. 11, 80); Berzelius (P. 4, 275); Heintz (Fr. 9, 16). Obtainer in large grystals by separating the reacting prokt. Pharm. 5, 837; Heydenrich, C. N. 4, zelius (P. 4, 275); Heintz (Fr. 9,16). Obtained 158; Struve, N. Peters. Acad. Bull. 1, 465; in large crystals by separating the reacting

liquids by a membrane (Vohl, A. 88, 114; Nonier, C. R. 78, 800; Millot, Bl. [3] 18, 20; Millot a. Maquenne, Bl. [2] 23, 238). Loses NH, in air; strongly heated gives Mg.P.Q., For in air; strongly heated gives Mg.P.O., For solubility in various solutions v. Fresenius (A. 55, 109); Ebermayer (Jopr. 60, 41); Liebig (A. 106, 196); Völcker (J. 1862, 131); Kissel (Fr. 8, 173); Gerland (J. pr. [2] 4, 127); Millot (Bl. [2] 18, 20); Ville (C. R. 75, 344). Another Mg.NH, phosphate is described by Gawalovski (G. C. 185, 791). (C. C. 1885. 721). For other double salts : with MgCl₂, v. Deville a. Okron (A. Ch. [3] 67, 456); with MgCl₂ and MgF₂, v. Bischof (D. P. J. 237, 51, 136); with MgCl₂ and CaF₂, v. D. a. C. (l.c.); with K, v. Haushofer (Z. K. 7, 257), Ouvrard (C. R. 106, 1729); with Na, v. Rose, Berzelius, &c. (Gm.-K. i. 2, 476), Ouvrard (l.c.).

Manganese orthophosphates. Normal manganic orthophosphate, MnPO, H,O, a greenish grey pp. by adding conc. Mn(NO3), Aq to H3PO, and a little boiling water (Christensen, J. pr. [2] 28, 1). For properties of products of reaction of 25, 1. For properties of produces treatment of the Pool of the Poo

Mn,P,O, wH,O. Obtained with 14H,O by ppg. MnSO,Aq by Na,HPO,Aq; loses 7H,O over H,SO, and one more H,O at 100° (Erlenmeyer, A. 190, 208). Salts with 9 to 11 H.O. 7H.O. and 3H2O are obtained by decomposing MnHPO ... xH2O by water, and drying under different conditions (E., l.c.). The salt without H₂O is formed by strongly heating the hydrates, also by heating Mn,P,O, in H (Struve, J. 1860. 73). A white amorphous pp., soluble mineral acids and acetic acid, and various salt solutions (v. Berzelius, Gm. K. i. 2, 472; Heintz, P. 74, 449; Joulin, A. Ch. [4] 30, 272; Gerland, J. pr. [2] 4, 97; Wittstein, Gm. K. 2, 472; Braun, 14. 7, 340; Erlenmeyer, B. 14, 1253).

Various acid salts have been described:— 1. MnHPO, 3H₂O (Bödeker, A. 69, 206; Heintz, P. 74, 449; Erlenngeyer, A. 190, 208].—2. MnH₁P₂O_{**}2H₂O (Heintz, Erlenneyer, l.c.).—3. Mn₁P₂O_{**}MnHl²O_{*}XH₂O (Erlenmeyer, l.c.; Haushofer, Z. K. 7, 257). Double salts: with MnCl. (Deville a. Caron, A. Che [3] 67, 459); with Fe.P.O. and MnCl. and with Fe.P.O. and MnF. (D. a. C., l.c.); with NH. (Otto, S. 66, 288; Heintz, l.c.); with K and with Na (Ouvrard,

C. R. 106, 1729).

Mercury orthophosphates. Normal mercurous orthophosphate, Hg,PO, by ppg. excess of Na₂HPO, Aq by HgNO, Aq (Gerhardt, J. 1819. 283). Brooks (P. 66, 63) describes a basic sait. A double salt with HgNO, is described by Gerhardt (l.c.; v. also Gm.-K. 3, 918). Normal mercuric orthophosphate, Hg.P.O., is obtained by heating Hg,PO, to low redness, also by adding strongly acidified Hg(NO₃),Aq to Na₂HPO,Aq (v. Gm. K. 3, 754, \$18; also Hanck, C. C. 1890. [2] 736). For a double salt Hg.NH,Hg,O.PO. v. Hirzel (Gm.-K. 3, 820).

Nickel orthophosphates. The normal salt Ni₂P₂O₂.7H₂O is obtained as a green floculent pp. by adding Na, HPO, Aq to a Ni salt; heated strongly loses 7H₀ (Rammelsberg, P. 68, 383; Struve, Gm.-K. 3, 543). Double salts: with NH₄ (Debray, C. R. 59, 40); with Mg (Rose,

Gm.-K. 8, 508); with Na and with K (Debray. Lc.; Ouvrard, C. R. 106, 1729).

Potassium orthophosphates. K.PO. A white solid, obtained by adding excess of K.CO, to H.PO.Aq, and evaporating; slightly soluble cold water, more soluble hot water. Acid salts: 1. K.HPO, [Graham, Funke, Gm.-K. 2, 30). 2. KH,PO,; by dissolving K,CO, in somuch H,PO,Aq that blue litmus paper is turned red but goes blue again on drying. Colourless tetragonal crystals; very soluble water; at red heat gives KPO,; S.G. 2.29 to 2.4 (v. Gm.-K. 2, 30; also Senarmont, A. Ch. [3] 33, 391; Schiff, A. 112, 88; Buignet, J. 1861. 15).

Silver orthophosphates. Normal salt Ag. O., a yellow solid, obtained by adding an al Mi phosphate to AgNO,Aq (Wetzlar, Gm. K. 3, 918; Skey, C. N. 22, 61; Lassaigne, ₱ Ph. [3] 16, 289; Joly, C. R. 103, 1071). The acid salt Ag, HPO, forms, in white hexagonal crystals, from a solution of the normal salt in H,PO,Aq (Berzelius, P. 2, 163; Hurtzig a. Geuther, A.111, 160; Schwarzenberg, A. 65, 162; Joly, C. R. 103, 1071).

Sodium orthophosphates. The normal salt, Na₃PO₆12H₂O, is obtained by adding excess of NaOHAq to Na₃HPO₆Aq and evaporating. Sixsided pyramids; melt at 77°; S.G. 1.618 (Schiff, A. 112, 18); soluble in 2 pts. water at 15°; solution absorbs CO₂ from air, giving Na,HPO,Åq. The anhydrous salt, Na,PO, is obtained by heating the salt with 12H,O, or by heating Na₂HPO₄.12H₂O with NaOH in equal molecular proportions (Graham, Mitscherlich, Gm.-K. 2, 163). S.G. 2.511 at 12°, 2.536 at 17.5° (Clarke's Table of Specific Gravities). For experiments on diffusion of the different Na orthophosphates v. an Bemmelen, B. 11, 1675; Hinteregger, B. 11, 1619; Tobias, B. 15, 2452. Disodium hydrogen orthophosphate

Na, HPO, .12H, O. (Ordinary sodium phosphate.) Occurs in urine of carnivorous animals. Prepared by adding a slight excess of Na₂CO₂ to H.PO.Aq, and crystallising. (For preparation from bone-ash &c. v. DICTIONARY OF APPLIED CHEMISTRY.)

Colourless, rhombic, prisms; for measurements v. Senarmont, A. Ch. [3] 38, 391. S.G. 1.5235 at 16° (v. Gm.-K. 2, 165); melts at 35° (Kopp, A, 93, 129; v. also Gm.-K. 2, 165); effloresces in air, losing 5H.O.

Solubility in water (Mulder, Gm.-K. 2, 165).

100 pts. water a	issoive Na ₂ HPO ₄ ,
at 0° 2.5 pts.	at 55° 87.7 pts.
5 2.8	60 91.6
10 3.9	65 93.8
15 5.8	70 95.0
20 9.3	75 95.8
25 15 4	80 96.6
30 24 1	85 97.2
85 39.3	90 97.8
40 63.9	95 984
45 74.8	99 98 8
50 82.5	100 99-4

Saturated Na.UPO, Aq boils at 105°, and freezes at -45° (Riddorff). S.G. of Na, HPO, Aq at 19° (Schiff, A. 110, 70); 2 p.c. = 1.0083, 4 p.c. = 1.0166, 6 p.c. = 1 · 025, 8 p.c. = 1 · 0332, 10 · p.c. = 1 · 0418, 12 p.c. = 1 · 0503 (p.c. of Na,HPO, 12H,O). 8.6. solution saturated at 15° = 1 · 0469, at 16° = 1 · 0511

(Michel a. Kraft, Stolba, Cim.-K. 2, 166). Loses 12H₁O in vacuo over H₂SO₄, or by heating to 100°; a salt with 7H₂O crystallises from Na₂HPO₄Aq at 33° (Blücher, Mulder, Clark, Gm.-K. 2, 166). For vapour-pressure of watergas when the salt is warmed v. Debray (C. R. 66, 195), Horstmann (A. Suppl. 8, 125), Pfaundler (B. 4, 773). For change of volume on melting v. Wiedemann (W. 17, 561).

Absorbs 11Cl, probably forming NaH2PO, and NaCl (Thomas, C. J. 33, 27). NaJHPO,Aq absorbs CO, (Pagenstecher, J. B. 21, 124; Liebig, A. 64, 349; 79, 112; Heidenhain a. L. Meyer, A. Suppl. 2, 157; Marchand, J. pr. 37, 321). The solution decomposes NH₄Cl (Rose, Gm.-K. 2, 166); boiled with S forms Na₂PO₄Aq with Na.S.O.Aq and Na polysulphides (Filhol a. Senderes, C. R. 94, 649; 95, 343; 96, 1057). remarks on character of reactions of Na HPO Aq with solutions of metallic salts v. Joly, C. R. 103, 1129,

Trisodium diphosphate Na₃H₄P₂O₃xH₂O; by exactly neutralising H₃PO₃Aq by NaOHAq, and

evaporating in vacuo (Filhol a. Senderens, l.c.). Sodium dihydrogen phosphate NaH,PO,H,O; by adding H,PO, to solution of Na,H,P,O, till BaCl2Aq is no longer ppd. (Mitscherlich, Berzelius, Gm. K. 2, 167). A salt with 4H2O was obtained by Joly a. Duffet (C. R. 102, 1391) by cooling a very conc. solution.

Double salts. 1. Sodium ammonium hydrogen orthophosphate Na(NH₁)HPO₁.4H₂O (Microcosmic salt). Occurs in guano. Obtained by dissolving 5 pts. Na₂HPO₄.12H₂O and 2 pts. (NH,),HPO, in water, adding a little NH,Aq, and allowing to crystallise in the cold (Berzelius). Large, clear, monoclinic crystals; S.G. 1.554 (Schiff); very soluble water, solution loses NH₃. The solid effloresces in air, losing all NH, and 4tl₂O, and leaving NaH₂PO₁; when strongly heated leaves Na₄(PO₁)₄. For double sults formed by fusing with metallic oxides v. Wallroth, B. 16, 3059.—2. NaKHPO₁, TH.O (Mitscherlich, Liebig, Schiff, Gm.-K. 2, 167). -3. Na(NH₂),PO₂4H₂O (v. Gm.-K. 2, 220).—4. Na₂(NH₄)PO₂,12H₂O (Herzfeld a. Fouerlein, Fr. 1881. 191).—5. Na₄K₂H₂(PO₁),22H₂O, and Na3(NH,)3H6(PO,)3H2O (Filhol a. Sendereman.C. R. 94, 649; 95, 343; 96, 1057).— 6. 2Na,PO,NaF.xH,O; x=19 and 22 (Baum-

garten, J. 1865, 219; Thorpe, C. J. (2) 10, 660).

Strontium orthophosphates. Normal salt
Sr,P.O., is ppd. by adding Na,PO,Aq or
Na,HPO,Aq + NH,Aq to excess of SrCl,Aq; also by adding cold ammoniacal solution of 90 pts. Na.HPO., 12H.O to 100 pts. SrCl. in Aq (Barthe, C. R. 114, 1267). By pouring SrCl, Aq into Na.PO.Aq at c. 10° gelatinous Sr.P.Q. is formed, but rapidly changes to crystalline SrNaPO., 9H.O (Joly, C. R. 104, 1702.) — Acid salt SrHPO,; by adding Na.HPO,Aq to SrCl.Aq (Skey, C. N. 22, 61; Berzelius, Brott, Wittstein, Gm.-K. 2, 324; Malaguti, A. Ch. [3] 51, 346; Barthe, l.c.). Barthe (l.c.) describes another acid sall, SrH, P.O., XI,O.

Double salts. 1. 3Sr,P₂O_{*}SrCl₂ (Deville s. Carou, A. Ch. [3] 67, 452).—2. SrKPO, (Rose, Weber, Gm.-K. 2, 324).—3. SrNaPO,9H₂O (R. W., Le.; Joly, C. R. 104, 905, 1702).

Thallium orthophosphates. Normal thallous thanks the Theorem 1.

orthophosphate Tl.PO.; by adding H.PO.Aq and

NH₂Aq to TiNO₂Aq, or mixing Tl₂SO₂Aq and Na₂HPO₂Aq with a little NH₂Aq (Crookes, C. N. 3, 193, 303; 7, 290; 8, 169; Lamy, Bl. (2] 4, 193). While silky mass, or needles; insoluble alcohol, easily soluble NH₄ salts (Carstanjen, J. pr. 102, 65, 129). Acid salts.—TiH_PO, and Tl_HPO, xH_O (Lamy, l.c.); according to Ranmelsberg (B. 15, 283) the second of these does not exist. Normal thallic orthophosphate 'TlPO₄.2H₂O, by adding H₃PO₄Aq to Tl(NO₅)₃Aq (Willm, Bl. [2] 2, 89; 5, 354; Strecker, J. pr. 102, 65, 129).

Thorium orthophosphates. Various double salts of Th and K, and Th and Na, are described by Troost and Ouvrard (C. R. 102, 1422; 105,

Tin orthophosphates. The compositions of the stannous salt, obtained by adding Na HPO, Aq to SnCl2 in dilute actic acid, and the stannic salt, by digesting SnO2 with H₃PO₄Aq, are somewhat doubtful (v. Lenssen, A. 114, 113; Reynoso, J. pr. 54, 261; Reissig, A. 98, 339; Girard, C. R. 54, 468). Ouvrard (C. R. 111, 177) describes various double Sn-K and Sn-Na phosphates.

Titanium orthophosphates. Various double salts of Ti and K, and Ti and Na, are described by Ouvrard (C. R. 111, 177).

Uranium orthophosphates. For double U-K and U-Na salts, v. Ouvrard (C. R. 110, 1333). Johnson (B. 22, 976) describes a salt UO, 2P,O5.

Zinc orthophosphates. Normal salt Zun orthopnosphases. Normals sales
Zun P.O., 4H.O.; by ppg. solution of a Zn salt by
Na, HPO, 4q; pp. is gelatinous, but becomes
crystalline. Insoluble water, easily soluble
in acids, NH, 4q, and NH, salts (v. Mischerlich, Gm.-K. 3, 16; Schindler, Mag. Pharm. 26, 62; Debray, Bl. [2] 2, 14; Heintz, A. 143, 356; Graham, A. 29, 23). The acid salt ZnH,P₂O_w2H₂O is obtained in large, triclinic crystals by dissolving ZnO in H, PO, Aq (Demel, B. 11, 1171).

Double salts. 1. With NH, v. Debray (C. R. 59, 40), Bette (A. 15, 129), Heintz (A. 143, 156), Schweikert (A. 145, 57), Rother (A. 143, 356).—2. With Na. v. Schoffer (A. 145, 53), Ouvrard (C. R. 106, 1729).—3. With K, v. Ouvrard (l.c.).

Zirconium orthophosphates. For double alts with K and Na, v. Ouvrard, C. R. 102, 1422; 105, 30.

PYROPHOSPHATES. Salts derived from H.P.O. (For Thiopyrophosphates v. Phosphotic sulphide, Reactions, No. 7, p. 147; and for Sclenopyrophosphates, v. Phosphotic selenide, p. 145.)

Aluminium pyrophosphate Al, (P2O7)3. White amorphous pp. by adding AlCl., Aq to Na, P.O., Aq; soluble NH, Aq, Na, P.O., Aq, and mineral acids (Schwarzenberg, A. 65, 147; Rose, A. 76, 16; Natherical Schwarzenberg, A. 65, 147; Rose, A. 76, 16; Wittstein, Repert. 63, 224). Forms a double salt with Na (Persoz, A. 65, 170; Pahl, Bl. [2] 22, 122).

Ammonium pyrophosphates. Normal salt (NH;),P2O,; by adding excess NH,Aq to H,P,O,Aq and recrystallising from alcohol. Solution boiled gives the acid salt (NH₄)₂H₂P₂O₇ (Schwarzenberg, A. 65, 141).

Barlum pyrophosphate Ba₂P₂O₂.xH₂O. White amorphous solid; by adding Na₁P₂O,Aq to BaCl₂Aq, or H₄P₂O,Aq to BaCAq. Heated in

steam gives off PH₃; gives orthophosphate by heating with alkali carbonates (Hesse, P. 80, 71; Schwarzenberg, l.c.; Birnbaum, Z. [2] 7, 139; Struve, J. pr. 79, 348; Rose, P. 76, 20). Forms

a double salt with Na (Baer, P. 75, 166).

Bismuth pyrophosphate Bi₄(P₂O₇), (Chancel,

C. R. 50, 416).

Cadmium pyrophosphate Cd.P.O., 2H.O (at

100°) (Schwarzenberg, A. 65, 153)

Calcium pyrophosphates Normal Ca2P2O, 4H2O, by adding Na P2O, Aq to CaCl Aq, or CaOAq to H.P.O.Aq; sol. in much Na P.O.Aq. Amorphous, but crystallises from solution in acetic acid or SO₂Aq (Schwarzenberg, A. 65, 145; Rose, P. 76, 16, 20, 230). For action of heat, v. Baer (P. 75, 155). Decomposed by heat, v. Baer (P. 75, 155). Decomposed by water at 280° to H₃PO₄Aq and Ca₄P₂O₈ (Reynoso, C. R. 34, 795). Partially decomposed by boiling with NaOIMq or fusing with alkali carbonate (Rose). The acid salt CaH₂P₂O₂2H₂O is said to be obtained by decomposing the normal salt by a little ILC.O.Aq (Pahl, Bl. [2] 22, 122). Von Knorre a. Oppelt (B. 21, 769) failed to obthis salt, but tain prepared the 2CaH₂P₂O₇.Ca₂P₂O₇.6H₂O by adding CaCl₂Aq to Na₂H₂P₂O₇Aq.

Double salt CaNa, P.O., 4H,O (Baer, P. 75,

Chromium pyrophosphate $\operatorname{Cr}_4(P_2O_7)_3$. reddish green pp. by adding Na,P2O,Aq to Cr alum solution; soluble Na,P2O,Aq, KOHAq, SO2Aq, and mineral acids (Schwarzenberg, A. 65, 149).

Cobalt pyrophosphates. Salts having the composition Co,P,O,, and Co,P,O,, are said to be formed by strongly heating luteo-cobalt phosphate (Braun, Fr. 3, 468; Gm.-K. 3, 463).

Copper pyrophosphates. The normal salt Cu_P2O, 2H2O, by adding Na,P2O Aq (not excess) to Cu salt solutions and drying at 100 q greenishwhite amorphous pp., becoming crystalline by boiling in SO₂Aq; soluble Na₄P₂O₅Aq, NH₅Aq, and mineral acids (Schwarzenberg, A. 65, 156; Stromeyer a. Gladstone, Cim.-K. 3, 615). Forms double salts with NII, K, and Na (v. Schwarzenberg, l.c.; Schiff, A. 123, 1; Persoz, A. Ch. [3] 20, 315; Fletimann a. Henneberg, A. 65, 387).

Iron pyrophosphates. The ferrous salt is obtained by ppg. FeSO, Aq by Na, P2O, Aq; come position not decided (v. Schwarzenberg, A. 65, 153; Struve, J. pr. 79, 318). The ferric salt Fe₄(P₂O₂)₂,9H₂O is a yellowish pp., formed by The ferric salt adding neutral FeCl, Aq to Na, P,O, Aq (acidified FeCl.4q gives FePO, Schwarzenberg). Gladstone (C. J. [2] 5, 435) obtained an allotropic form by heating the ordinary salt in dilute H2SO Aq.

Double salts, with Na (Gladstone, l.c.; Persoz, A. Ch. [3] 20, 315; Fleitmann a. Henneberg, A. 65, 390; Rieckher, N. J. P. 23, 1; Milck,

J. 1865. 263).

Lead pyrophosphate Pb₂P₂O₂. A white amorphous powder; by ppg. Pb(NO₃)₂Aq by Na₄P₂O₂Aq. Obtained in colourless, transparent, rhombic prisms by dissolving PbO in molten KPO, (Ouvrard, C. R. 110, 1333). Soluble ex-2088 of Na,P₂O,Aq, insoluble acetic acid or NH,Aq; decomposed by boiling water (Stromeyer, Schwarzenberg, Gm.-K. 8, 121; Gerhardt, A. Ch. 3] 22, 596). Forms a double salt with Na [Gerhardt, Lc.; Ouvrard, Lc.].

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Lithium pyrophosphate Li,P.O., 211.O: by adding Na₁P₂O₂Aq to LiClAq, dissolving in acctic acid, and ppg. by alcohol (Rammelsberg, B. B. 1883. 18; Merling, J. 1879. 1043). A double salt, Li₃NaP₂O₄, is formed in prismatic crystals by dissolving Li₂CO₃ in molten NaPO₄ (Ouvrard, C. R. 110, 1333).

Magnesium pyrophosphates. The normal salt Mg.P₂O.,3H₂O is formed by adding MgSO₄Aq to Na.P₂O.,Aq (Rose, P. 76, 16, 20), or by dissolving MgO in Na.H₂P₂O.Aq and heating (Schwarzenberg, Gm.-K. 2, 448). Pp. becomes crystalline by remaining under liquid from which it has been not Perpa. Z. (21, 6, 305) which it has been ppd. (Popp, Z. [2] 6, 305), also by boiling with SO Aq (Schwarzenberg, la.). The salt is obtained, without HO, by strongly heating MgNH,PO, Loses 3H O at 100°; fused with soda or heated with cone. ILSO, gives Mg,P.O. (lose; Weber, P. 73, 137). Easily soluble UClAq and HNO,Aq; ppd. incompletely by NH,Aq (Freschins; Weber). An acid salt, MggH2P2O,, combined with NO, is said to be formed by evaporating to dryness with HNO, Aq (Luck, Fr. 13, 255; Campbell, P. M. [4] 21, 380). Forms a double salt with Na (Persoz, A. 65, 169; Schwarzenberg, A. 65, 146; Beer, P. 75, 168).

Manganese pyrophosphates. The normal manganous salt Mn.P.O. 3H.O is a white amorphous powder; by ppg. a salt of Mn by Na, P.O, Aq (Schwarzenberg, A. 65, 133). Soluble Na₁P₂O,Λq (Pahl, Bl.,[2] 22, 122). Loses one H₂O at 120° (S., l.c.). The salt without H₂O is formed by strongly heating the hydrated salt, or MuHPO, 3H O, or MuNH, PO, HO (S., Le.; Heintz, &c., Gm.-K. 2, 475); white powder, S.G. 3.5847 at 20° (Lewis, Am. S. [3] 14, 281); heated to whiteness in H gives $Mn_3P_2O_8$; reduced by charcoal to Mn phosphide (Struve, J. 1860. 78). The acid salt MnH₂P₂O₇4H₂O is said to be formed by action of oxalic acid on the normal salt (Pahl, l.c.). Various double salts are described with K (Pahl, l.c.; Schjerning, J. pr. [2] 45, 515); with Na (Pahl, Rose; Christensen, J. pr. [2] 34, 41); with Na and NH, (v. Otto, J. pr. 2, 418). The acid manganio salt MnHP O, is said to be formed by heating MnPO, with H, PO, Aq to 170 - 190° (Chrir ansen, J. pr. [2] 28, 1).

Mercury pyrophosphates. The normal mercurous salt Hg,P,O,H,O is a heavy white powder obtained by adding Na, P.O, Aq to HgNO, Aq (Rose, Gm.-K. 3, 754; Schwarzenberg, A. 65, 183). The normal mercuric sall, Hg₂P₂O₃, is obtained by adding Na₁P₂O₃Aq to Hg(NO₃)₂Aq (S., I.c.; Reynoso, C. R. 34, 795).

Nickel pyrophosphate Ni P2O, A green pp. by adding Na, P2O, Aq to NiSO, Aq; soluble excess Na, P2O, Aq, NII, Aq, and acids; obtained crystalline by boiling with SOAq; decomposed by water at 280°-300° (S., l.c.; Reynoso, l.c.).

Potassium pyrophe sphates. The normal salt. K,P,O,xH,O, is obtained by strongly heating KHPO; also formed by reaction of POCl, with KOHAq (Gladstone, C. J. [2] 5, 435). Loses one H₂O at 100°, and is dehydrated at 300°. Solution in water does not change to K, HPO, on boiling (Schwarzenberg), nor on evaporation (Gladstone), but change is effected by heating to 280° (Reynoso, C. R. 34, 795); boiling with KOHAq produces the ortho-salt. The acid salt, K₂H₂P₂O₂,

acid and alcohol, and evaporating over H2SO4 (Schwarzenberg, λ . 65, 137). Forms a double salt with $2K_2(NH_4)HP_2O_2H_2O$ (S., l.c.); also with $Cr_2H_4(P_2O_2)_2$ (Schjerning, J.pr. [2] 45, 515).

Silver pyrophosphates. Normal salt, Ag, P,O,; a white pp. from AgNO, Aq and Na, P2O, Aq (Clark, Stromeyer, Gm.-K.3, 919). S.G. 5:306 at 7:5'; soluble NII, Aq, reppd. by HNO, Aq; boiled with Na, HPO, Aq gives Ag, PO, Heated with II, PO, Aq at 180° gives the acid salt Ag, H, P,O, (Hurtzig a. Glavthey, A, 111, 120). Geuther, A. 111, 160).

Sodium pyrophosphates. The normal salt, Na₁P₂O₂, is formed by strongly heating Na₂HPO₄; a glass-like solid, becoming opaque on cooling (Clark, N. Ed. P. J. 7, 298); gives Na, PO, and PH₃ when heated in H (Struve, J. pr. 79, 350); heated with NH Cl gives NaCl, NaPO,, and PCl, (Rose). The hydrated salt, Na₄P₂O_{.10}H₂O, erystallises from Na₄P₂O_{.4}Q (Clark, l_e,; von Blücher, P. 50, 542) in monocline crystals (Rammelsberg; Haidinger, P. 16, 510; Handl, W. A.B. 32, 250; Schaechi, P. 109, 365; Duffet, C. R. 102, 1327). Crystallises unchanged from Aq with NH₄ or NH₅Cl added. Solution boiled with acids gives Na₂PO₄Aq. Poggiale (J. Ph. [3] 44, 273) gives solubility; 100 parts water dissolve—

~	Na P.O.	Na_P_0,10H_0
at 0°	3.0	5.41
10	3.95	6.81
20	6.53	10.92
30	9.96	18-11
40	13.5	24.97
50	17.45	33.25
. 60	21.83	4.1.07
70	25.62	$52 \cdot 11$
80	30.01	63.40
90	35.11	77.47
100	40.26	93:11

The acid salt Na₂H₂P₂O₂; by heating NaH₂PO₄ to 190° - 204° (Graham, Gm-K. 2, 169), or by addition of alcohol to an acetic acid solution of Na₄P₂O₇ (Schwarzenberg, A. 65, 139). Crystallises from aqueous solution with 6H,O (Bayer, J. pr. 106, 501; Rammelsberg, B. 16, 21; Duffet, C. R. 102, 1327). When strongly heated gives Ta, H,P,O, (Fleitmann a. Henneberg, A. 65, 328).

Double salts.—1. Na.(NH.), P.O., xH.O., x=5 or 6 (Schwarzenberg, A. 65, 140, 142; Rammelsberg).—2. Na.K., P.O., 12H.O., and Na.P.O., Na.H.P.O., 2H.O. (S., Le.; R., Le.). Wall-salt (H.) 20, 20, 214, Na. (S., Le.; R., Le.). roth (Bl. [2] 39, 316) has described double salts with pyrophosphates of Al, Be, Bi, Cd, Ca, Ce, Cr, Co, Cu, Di, Er, La, Mn, Mg, Ni, Th, Yb, Y, Zn, and Zr. For double salts with pyrophosphates of Sn and Ti v. Wunder, J. 1870. 359; 1871. 323. Na, P.O, seems to combine with B₂O₃ by fusing Na₄P₂O₇ with boric acid (Prinvault, C. R. 74, 1219).

Strontium pyrophosphate, Sr.P.O, orystalline powder; from Sr(NO₃),Aq and Na₄P₂O,Aq; also by heating SrHPO₄ (S., Lc.). Forms acid salts (von Knorre a. Oppelt, B. 21, 769); also a double salt with Na (Baer, P. 75, 166).

Thallium pyrophosphates. Normal thallous salt, Tl.P.O.; by heating Tl.HPO. (Descloizeaux, 4. Ch. [4] 17, 329). S.G. 6.786. Crystallises Johnson, B. 22, 976).

is obtained by treating the normal with acetic | from aqueous solution with 2H.O (D., I.c.). The acid salt Tl₂H₂P₂O₇,H₂O is formed by heating TlH₂PO₈ to 250³-275⁵ (Lamy, Rammelsberg, Gm.-K. 3, 177).

Thorium pyrophosphates. Double salts with K and Na are described by Ouvrard (C. R. 105, 30).

Uranium pyrophosphates. Double salts with K and Na are described by Ouvrard (C. R. 110, 1333).

*Yttrium pyrophosphate. Johnson describes Y₄(P₂O₇)₃, formed by heating Y₂3SO₄ with HPO₃ to 316° (B. 22, 936).

Zine pyrophosphate, Zn,P,O,. By ppg. Zn salts by Na,P,O, (Stromeyer, Am.-K. 2, 832; Gladstone, ibid. 3, 16; Schwarzenberg). Forms a double salt with NH, (Bette, A. 15, 129).

Zirconium pyrophosphates. Double salts with K and Na are described by Ouvrard (C. R.

METAPHOSPHATES. Salts derived from HPO. The general methods of preparation, properties, and reactions of the metaphosphates are described at the beginning of this article (p. 106); the divisions into mono-, di-, tri-, tetra-, and hexa- metaph sphates, with the processes by which typical salts of each division are prepared, have also been described already (p. 107). It will suffice here to enumerate the salts, with an indication in each case to which division the salt is assigned by Maddrell, Fleitmann a. Henneberg (cf. Tammann's results regarding Na, di-, and tri- metaphosphates p. 107). T.'s paper in J. pr. [2] 45, 417 should also be consulted.

Aluminium dimetaphosphate, AlaPaO18. By dissolving Al2O2xH2O in H2PO1Aq, evaporating. and heating to 316° (Maddrell, C. S. Mem. 3. 373; Johnson, B. 22, 976). For hexa- salt v. T.,

373; Johnson, B. 22, 976). For hexa-salt v. T., J. pr. [2] 45, 417.

Ammonium metaphosphates. (MI₁),P₂O₃, from Cu salt by (NI₁),SAq; at 200° 250° becomes mono-salt (NH₂)PO₃ (Fleitmann, A. 72, 236). For decta-and penta-salts v. T. l.c.

Barium metaphosphates. (1)? Mono-salt BaP₂O₄; by heating BaCO₂ with H₂PO₁ to 316° (M. l.c.; F., l.c.; Rose, P. 76, 5; Birnbaum, Z. [2] 7, 139). (2) Di-salt, Ba₂P₁O₁₂-sH₂O; from Na ort NH₄ salt* and BaCl₂Aq (F., l.c.). (3) Trisalt, Ba₂P₂O₁₈-sH₂O; from Na salt and BaCl₂Aq (F. a. Henneberg, A. 65, 313). (4) Hexa-salt; (F. a. Henneberg, A. 65, 313). (4) Hexa-salt; from Na salt and BaCl₂Aq (Rose; Graham, P.

Bismuth metaphosphate. ? Tetra- salt; by Insing H.PO₄ with Bi.O₄.» H.O (F., l.c.); HPO₃Aq, Bi.NO₃ solution and NH₂Aq give a pp. (Persoz, Gm. K. 2, 832).

Cadmium metaphosphate. ? Tetra- salt (F., l.c.; Persoz, Gm.-K. 3, 54). Double s with Na and K (Ouvrard, C. R. 106, 1729). Double salts

Calcium metaphosphates. A salt is obtained by heating CaHPO,; for action of HPO, on CaCO, v. Rose (P. 76, 5), Liebig (A. 11, 262); Dissilt, Ca,P,O,,xH,O; from Na salt and CaClAq (M., l.c.; F., l.c.). Double salts.—CaAm,P,O,,x2H,O (F., l.c.); CaNaP,O, (F. a. H.,

Chromium dimetaphosphate, Cr.P.O.s. By heating CrO.H. with H.PO. to 316° (M., Lc.; Hautefeuille a. Margottet, C. R. 96, 849, 1042;

Cobalt metaphosphates. ? Mono- salt ! CoP2O4; by evaporating CoSO4 with H3PO4Aq, and heating to 316° (M., l.c.; H. a. M., l.c.). Di- salt Co.P.O.; by heating roseo-cobaltic phosphate (Braun, Ammon. Kobaltverbindungen [Göttingen, 1862]). ? In xa-salt Co. P. 10. in the Col. Aq and the Na salt (Rose). Ohto-salt (T., Le.). Double salt with Na (M., Le.).

Copper metaphosphates. Dissult Cu.P.O.; by heating CuO or Cu(NO3)2 with H3PO4 to 3160 of cally of the state of the st

NH, and Na (F., l.c.; T., l.c.).

Iron metaphosphate. Di-ferric salt Fe P.O. by heating FeCl, with H.PO, to 316° (M., l.c.; H. a. M., l.c.; Johnson, B. 22, 976).

Lithium bexametaphosphate. A double salt Li Na, P.O., is described by Tammann (l.c.).

Lead metaphosphates. Di- salt Pb.P.O.; from $Pb(NO_3)_*Aq$ and the Na salt; also by heating H_3PO_4 and $PbO(F_1, Lc.)$. Tri-salt $Pb_1P_0I_{3,1}$ from the Na salt and $Pb(NO_3)_*Aq(F, a. H., Lc.)$. Deka-salt, T. (l.c.). Double salt PhAm. P.O. (F., l.c.).

Magnesium metaphosphates. ? Mono- salt MgP₂O₆, by heating MgO with H₃PO₄ (M., l.e.). Di-salt Mg₂P₄O₁₂xH₂O; and tri-salt Mg,PaO1,xH2O; from the corresponding Na salt and MgCl2Aq (F., l.c.). Hexa-salt Mg, P12O ... (Graham, Gm. K. 2, 214). Double sults, with NH, and Na, v. F. (l.c.); F. a. H. (l.c.); M. (l.c.); Graham (l.c.); Ouvrard (C. R. 106, 1729); Tammann (l.c.).

Manganese metaphosphates. manganese metaphosphates. 11. sate Mn.P.O.; by heating a Mn salt with H.PO, to 316° (M., Le.; F., Le.); with 8H.O. by ppg. (NH.).P.Q. Aq by excess of MnCl.Aq (F., Le.). Tri-salt Mn.P.O.; H1H.O; from MnCl.Aq (not MnSO₄) and Na.P.O.; Hexa-salt Mn.P.O.; by using Na P₂O₂ (Otto, Rose, Gm. K. 2, 490; Braun, I.c.). Deha-salt Mn₁₀P₂₀O₄₀ (Tammann, J. pr. [2] 45, 417). Double salts, with NII and Na (v. F., l.c.; Rose, l.c.; T., l.c.).

Mercury metaphosphates. White pps, are formed by adding Na tri- and hexa- metaphosphate to $Hg(NO_3)_2\Lambda q$ (F. a. H., l.c.; Rose, Gm., K.

2, 754).

Nickel metaphosphates. Di-salt Ni₂P₄O₁₂; by heating Ni O3 with H3PO4 to 316° (M., l.c.; 11. a. M., l.c.). Hexa-salt Ni P12O16; by adding NiCl Aq to Na P.O. (Rose). Double salt with Na

(M., l.c.).

metaphosphates. Potassinm Mono- salt KPO,; by heating KH,PO, to full redness (M., l.c.; Graham, Darracq, Gm.-K. 2, 32). S.G. 2.2639 at 14.5° (Clarke, Am. S. (3] 14, 281). Disalt K,P,O,; by treating the Cu salt with K.SAq (F., l.c.). Hexa-salt K,P,O,; (T., l.c.). Double all with NH, (F., l.c.). Compound with BO, salt with NH, (F. 9l.c.). C (Prinvault, C. R. 74, 1249).

Silver metaphosphates. Di-salt Ag₂P₂O₀; and tri-salt Ag₃P₃O₉; from AgNO₃Aq and the corresponding Na salts (F., l.c.; F. a. H., l.e.). Heza-salt Ag, P₀()₁; from Ag, NO, heated with H₂PO, to 316³, or by adding Na₅P₂O_{1,8}Aq to AgNO,Aq (Grsham; F., Lc.; T., Lc.; Rose, Berzelius). Double salts with Al, Cr, and Fe (H. a. M., l.c.).

Sodium metaphosphates. For conditions of formation and general reactions v. p. 106. The following salts have been described: Mono- salt NaPO, (F., l.c.; M., l.c.; F. a. H., l.c.; Graham, Gm.-K. 2, 170; Jamieson, A. 59, 350; Müller. P. 127, 428); di- salt Na, P.O., 2H.O (F., l.c.); tri-salt Na, P,O, 6H,O (F. a. H., l.c.); tetra-salt Na₁P₄O₁₂ (F., l.c.); hexa-salt Na₆P₆O₁₈ (F., l.c.; T., l.c.; G., l.c.). For double salts with Na and NH , v. F. (l.c.).

Strontium metaphosphates. ? Mono- salt SrP.O.; by heating SrCO, with HaPO, (M., l.c.; ct. Rose, F. 76, 8; Scheerer, J. pr. 75, 113). For

a deka- sait, r. T. (l.c.).

Thallium metaphosphate. TIPO₃ said to exist in two forms, one insoluble in water (? disalt), and the other soluble (hamy, Gm.-K. 2, 177).

Thorium metaphosphate ThP4O12 (? di-salt, Th₂P₈O₂₁); by heating Th(SO₄)₂ with H₃PO₄ to redness (Johnson B. 22, 976). For deable salts with K and Na, v. Troost a. Ouvrard (C. R. 105, 30).

Uranium metaphosphate. Di-sall U2P8O18 (H. a. M., l.c.).

Zine metaphosphates. Di- salt Zn2P4O12; by heating ZnO with H,PO, to 350° (F., Lc.); with 4H2O by adding ZnCl2Aq to (NH1) P.O.Aq. For double satts with NH, and Na, v. F. a. H. (l.c.); Bette (A. 15, 129).

TETRAPHOSPHATES and DEKAPHOS-PHATES. Salts of the hypothetical acids H.P.O. and H.P.O. (v. pp. 106, 107).

Barium tetraphosphate Ba,P,O,, A heavy crystalline powder; by fusing Na,P,O,, with BaCl. (F. a. H., A. 65, 313).

Magnesium tetraphosphate Mg_1P_iO_15. pared similarly to the Ba salt (F. a. II., L.c.).

Silver tetraphosphate Ag_aP₄O₁₃. From the Na salt and AgNO₂Aq (Berzelius, P. 19, 331).

Sodium tetraphosphate Na,P,O,, fusing Na₆P₆O₁₈ with Na₄P₂O₇ or Na₃PO₄ (F. a. H., l.c.; Uelsmann, A. 118, 101).

Silver dekaphosphate Silver dekaphosphate $Ag_{12}P_{10}O_{31}$. From the Na salt and $AgNO_4Aq$ (F. a. H., l.c.; U., l.c.).

Sodium dekaphosphate Na₁₂P₁₀O₃₁. A glassy mass; by fusing Na, PoO18 and Na, PoO 2(F. a. II., l.c.). M. M. P. M.

PHOSPHENYL CHLORIDE v. PHENYL-di. chloro-phosphene.

PHOSPHENYLIC ACID v. PHENYL PHOS-PHITES

PHOSPHENYLOUS ACID Call PHO.OH. Benzene phosphinic acid. [70]. S. 7-23 in the PHOSPHENYLOUS ACID cold; 211 at 100°. Formed by adding water to Coll PCl2, and boiling (Michaelis, A. 181, 303; B. 10, 816). Leaflets, v. sol. alcohol. Decom. posed by heat into phenyl-phosphine, benzene, posed by heat into pnenyt-pnospnine, benzene, and HPO₃. PCl₅ forms C₆H₃PCl₂.—KA' 2aq.—SH₄A'. BaA', 4aq.—PbA'₂: amorphous pp.

Ethyl ether EtA'. Oil.

Diethyl ether C₆H₃P(OEt). (235°).

Formed from C₈H₂PCl₂ and NaOEt. Liquid with

very powerful odour.

PHOSPHIDES. Compounds of P with one other more positive element. The chief phos phides are those of Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cu, Cr, Au, H, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Pt, Ag, Na, Th, Sn, Tl, W, Zn, Zr. (Phos-

phides of H are described as Phosphorus hydrides | order to decompose the compound of the phosunder Phosphorus.) Many phosphides are formed by heating together P and the more positive element in an atmosphere of CO2 or N; phosphides are also produced by heating P with several metallic oxides or with salts in solution; also by heating metals or their oxides in PH, Phosphides are generally brittle solids; many react with water or dilute acids, evolving P hydrides; some yield basic phosphates when heated in air. For descriptions of the different phosphides v. the individual elements.

M. M. P. M.

PHOSPHINE. PH is sometimes known by this name, v. Phosphorus, hydrides or, p. 135. PHOSPHINES are the phosphorus analogues of amines, and result from the replacement of hydrogen in phosphuretted hydrogen by alkyl radicles. They may be classified, like the amines, into primary, secondary, and tertiary bases, and, in addition, quaternary compaunds are known analogous to the salts of compound ammoniums.

Methods of preparation. 1. Action of the haloid derivatives of hydrocarbon radicles on metallic phosphides. It was by this reaction that Paul Thénard (C. R. 21, 141; 25, 892) discovered the first members of the phosphine group in 1843-47. He experimented with methyl emoride and calcium phosphide, and apparently isolated trimethyl-phosphine, (CH₃)₂P₄ as an inert solid, and a substance (CH₃)₄P₂ analogous to cacodyl as a spontaneously inflammable liquid, boiling at 250°, very explosive, poisonous, and Thénard recognised the relationship unstable. of trimethyl-phosphine to ammonia, and predicted the existence of the then undiscovered organic compounds of nitrogen and antimony.

In 1855 Hofmann a. Cahours (T. 1857; A. Ch. [3] 61, 5) investigated the action of methyl iodide on sodium phosphide, and obtained tetramethyl-phosphonium iodide in addition to trimethyl-phosphine and the phosphorised encodyl of Thénard. They found that the method was dangerous, and furnished mixtures the separation of which presented enormous difficulties.

Berld (J. pr. 66, 73) about the same time obtained very small quantities of triethyl-phosphine by the action at a very high temperature of ethyl iodide on sodium phosphide obtained by heating sodium and phosphorus together in rock oil.

Cahours in 1859 (C. R. 49, 87; J. 1859, 430) prepared tetrethyl-phosphonium iodide by the action of ethyl iodide on crystallised zinc phosphide (obtained by heating the metal in phosphorus vapour at 180°).

In 1882 Letts a. N. Collie (Tr. E. 30 pt. i. 181) investigated the action of benzyl chloride on sodium phosphide, and found that tetra-benzylphosphonium chloride was produced in abundance.

2. Action of organo-metallic bodies on tri-chloride of phosphorus. The action of zine alkyls on phosphorus trichloride was first investigated by Hofmann a. Cahours (A. Ch. [3] 51), and was further studied by Hofmann (A. Ch. [3] 62; 63 · 64). By this method tertiary phosphines are exclusively formed: 3R.Zn + 2PCl. = 2R₃P + 3ZnCl₂. It is necessary to treat the product of the reaction with caustic potash, in

phine with zinc chloride. By this reaction Hofmann a. Cahours obtained PMc, and PEt, and showed that they resemble the corresponding amines in many respects, especially in the readiness with which they combine with alkyl iodides to give quaternary compounds. On the other hand, they proved that, unlike the amines, tertiary phosphines readily combine with oxygen to give very stable compounds of the general formula R,PO.

3. Action of alcohols on phosphonium iodide; and Action of alkyl iodides on phosphonium iodide and exide of zinc (Hofmann's methods). In the year 1871 Hofmann again took up the study of the phosphines (B. 4, 205), and by the action of alkyl iodides on phosphuretted hydrogen obtained not only tertiary and quaternary compounds, but also primary and secondary bases. Hofmann took advantage of the fact that phosphonium iodide when heated with alcohol yields phosphuretted hydrogen, ethyl iodide, and water. When phosphonium iodide (1 mol.) is heated with alcohol (3 mols.) for 8 hours at 180, the crystalline product is a mixture of PEt.HI and PEt.I. and, on addition of caustic soda, friethyl-pho-phine separates as a clear liquid, while the solution gives, on evaporating, beautiful crystals of tetrethylphosphonium iodide. If the tubes are heated for four hours only, two layers of liquid are visible on cooling, and the tubes show great pressure when opened. It may be taken for granted, then, that the reaction occurs in two phases, in the first of which Etl is liberated, which then acts upon PH, in the same way as it acts on ammonia. Hofmann employed this method successfully in the methyl (B. 4, 209), ethyl (B. 4, 205), propyl (B. 6, 292), butyl (B. 6, 296), and amyl (B. 6, 297) series. Hofmann (B. 4, 372) endeavoured to prepare the primary and secondary bases according to the equations:

 $PH_{1}I + C_{1}H_{2}O = C_{2}H_{2}PII_{2}M + H_{2}O$ $PH_{1}I + 2C_{1}H_{2}O = (C_{2}H_{2})_{2}PIIIM + 2H_{2}O_{2}$ by altering the proportions of phosphonium . iodide and alcohol, but without success, the tertiary base being produced alone or mixed with the quaternary compound, while with the proportions required for the second equation the tubes invariably exploded.

In the meantime Orechsel a. Finkenstein (B. 4.352) believed that they had succeeded in obtaining the primary bases by saturating EtI or MeI with PH, and allowing the solutions to remain for some time at the ordinary temperature, or by heating them at 100°, and also by heating an ethereal solution of ZnI. saturated with PH, together with MeI. Hofmann (B. 4, 372) repeated these experiments, and showed that only tertiary and quaternary derivatives were formed. The idea then occurred to him of heating the alkyl iodide with phosphonium iodide ein presence of a metallic oxide, with the happiest results; for on heating a mixture of phosphonium iodide (2 mols.) with ethyl iodide (2 mols.) and zine oxide (1 mol.) in scaled tubes at 150° for from six to eight hours, a complete reaction occurred. the tubes when cold containing a crystalline mass consisting exclusively of the hydriodates of the primary and secondary bases, the former being the chief product, while the latter was only

formed in small quantities. The addition of water to the product of the reaction liberated the primary phosphine alone, which was distilled off in a hydrogen atmosphere, while the secondary phosphine was subsequently set at liberty by the action of an alkali. By means of this general method Homann prepared methyl (B. 4, 430), ethyl (B. 4, 605), propyl (B. 6, 292), butyl (B. 6, 296), amyl (B. 6, 297), and benzyl

(B. 5, 100) phosphines.
4. Michaelis's methods. methods, although of excellent service for obtaining the phosphines of those radicles which form alcohols, could not be employed in the preparation of phosphines containing purely arounatic radicles (B. 5, 100). Michaelis, on the other hand, not only succeeded is obtaining all the phenyl-phesphines, but also in discovering a fairly general method for the production of primary phosphines. The substance forming the starting-point for the preparation of phosphines by these methods is trichloride of phosphorus. One atom of chlorine is first replaced in that body by one or other of the following processes :-

(a) The mixed vapours of a hydrocarbon and the trichloride are repeatedly passed through a red-hot tube. Thus when benzene is employed 'phosphenyl' chloride is obtained: $PCl_3 + C_9H_6 = (C_6H_5)PCl_2 + HCl$.

(a) A mercury alkyl is heated with the trichloride under pressure : PCl, + (C, H,), Hg

 $= (C.H.)PCl_0 + Hg(C_0H_1)Cl_1$

(c) By digesting a hydrocarbon with the trichloride and aluminum chloride, the reaction being the same as (1). Other substances besides hydrocarbons—yield—substituted—phosphorus chlorides when submitted to this reaction. Thus a mixture of acctone, PCl3, and aluminium chloride react spontaneously, according to the equation:

2(CH₃)₂CO + PCl₃ - 2HCl + (CH₃ CO.CH₃)₂PCl.

By means of these different reactions Michaelis and his pupils have obtained a considerable number of substituted phosphorus chlorides, among which are: Phenyl phosphoruschloride by methods 1, 2, and 3 (B. 6 [1873], 601; 8 [1875], 922; 12 [1870], 1009). Tolyl phose phorus-chloride by method 3 (B. 13, 653). Xylyl phosphorus-chloride by method 3 (A. 212, 203, 209). Ethyl phosphorus-chloride by method 2 (B. 13, 2174). Propyl phosphorus-chloride by method 2 (B. 13, 2174). Naphthyl phosphorus-chloride by method. 2 (B. 9, 1051). Acctonyl phosphorus-chloride by method 3 (B. 17, 1273). The substituted chlorides resemble PCl₃ in properties. As a rule they are fuming liquids, combining readily with chlorine to give solid compounds analogous to pentachloride of phosphorus; treated with water, they yield phosphinous (phosphinic) acids. Thus phenyl phosphorus-chloride gives phenyl phosphinous (benzene phosphinic) acid: $(C, H_3)PCL_+ 2H_2O = (C, H_3)PH_2O_2 + 2HCl$. The products of addition which they form with oblorine react with water to give phosphinic (phosphonic) acids: (C₄H₃)PCl₄+3H₂O = (C₄H₃)PH₂O₂+4HCl. Michaelis was unable to obtain more than mere traces of the primary phosphine by the action of nascont hydrogen on the substituted chlorides. When gaseous HI is passed into the chloride,

chlorine is gradually displaced by iodine; $C_6H_3PCl_2+3HI=C_8H_3P1_2HI+2HCl$. From this iodide Michaelis obtained phenyl-phosphine by the action of alcohol: $3C_aH_1PI_2HI + 9C_2H_aO$ = $C_aH_3PII_1 + 2C_6H_3PO_3H_2 + 3H_aO + 9C_2H_3I$. In later experiments he employed a simpler method, namely the destructive distillation of the phosphinous (phosphinic) acid which, as already stated, is produced by the action of water or alcohol on the substituted chloride: 30, H.PO, H. = C.H.PH. + 2C.H.PO.H. From phenyl phosphorus chloride Michaelis obtained diphenylphosphine by the following reactions: (1) The chlorido is digested with mercury diphenyl at

 $(\mathbf{C}_{\mathbf{a}}\mathbf{H}_{\mathbf{a}})\mathbf{PCl}_{\mathbf{a}} + \mathbf{Hg}(\mathbf{C}_{\mathbf{a}}\mathbf{H}_{\mathbf{a}})_{\mathbf{a}} = (\mathbf{C}_{\mathbf{b}}\mathbf{H}_{\mathbf{a}})_{\mathbf{a}}\mathbf{PCl} + \mathbf{HgCl}(\mathbf{C}_{\mathbf{a}}\mathbf{H}_{\mathbf{a}})$ (B. 8, 1304); or it is heated for some time at 280', when the following reaction occurs: $H(C_0H_5)PCl_2 = (C_0H_5)_2PCl + PCl_3$.

(2) Diphenyl phosphorus chloride when heated with water or dilute soda solution decomposes in the following manner: 2(C, H,),PCI+2H,O $= (C_n H_s)_2 PH + (C_n H_s)_2 HPO_s + 2HCl$ (Michaelis a. Gleichaffan, B. 15, 801). He also obtained the tertiary base; at first by acting upon a mixture of phenyl-phosphorus chloride and bromo benzene with sodium: (C,H,)PCl, +2C,H,Br+3Na

2NaCl+NaBr+(CH,),P, but later this method was modified in a remarkable way, by substituting for phenyl phosphorus chloride, phosphorus chloride alone, the reaction occurring quite easily and very energetically at ordinary temperatures according to the equation:

 $P(T_a + 3(C_aH_a)Br + 6Na = 3NaCl + 3NaBr + (C_aH_a)_aP_a$

5. Action of alcohols on a mixture of phos-phoras and phosphorus iodide. Letts a. Blake (Tr. E. pt. 2) have shown that very remarkable reactions occur when benzyl alcohol acts upon a mixture of phosphorus and phosphorus iodide (in the proportions employed for obtaining phosphonium iodide by the action of water), whereby a number of the phosphorus derivatives of benzyl are obtained. The action occurs spontaneously at ordinary temperatures, and, although its mechanism was found difficult to investigate, the following equations account for the formation of the different products:-

(1) $PI_2 + C_7H_7OH + H_2O = (C_7H_7)H_2PO_2 + HI + I$ (2) $PI_2 + C_1H_1OH + 2H_2O + I = (C_1H_1)H_2PO_3 + 3HI$ (3) $PI_2 + 2C_1H_1OH = (C_1H_1)_2HPO_2 + HII + I$ (1) $PI_2 + 3C_1H_2OH + HII = (C_1H_1)_2PO + 2H_2O + 3I$ (5) $PI_2 + 4CHOH + 4HI = (CH_1)_1PI + 4H_2O + 5I$ (6) PI₂ + 2H O (7) PI₂ + 4H O + 3I $= H_3PO_2 + HI + I$ = $H_3PO_4 + 5HI$ (S) 2HI + C, H, OH $= \mathbf{C} \mathbf{H}_n + \mathbf{H}_2 \mathbf{O} + \mathbf{I}_2$ (9) P + L2 = PL

All the products indicated by the above equations were obtaine in quantity, especially benzyl phosphinic acid, di-benzyl phosphinic acid, and tri-benzyl phosphine oxide, and the method is un loubtedly the easiest and best for the preparation of those substances. Whether other alcohols behave in a similar manner to benzyl alcohol with a mixture of phosphorus and its iodide has not yet been ascertained.

General proporties of the primary phosphines. The following primary bases have been obtained;

• Name		Condition	Boiling-point	
Iso-amyl n-Octyl	phine 1 2 3 4 5 6 7 8	Gas Liquid ,,	-14° 25° 41° 62° 106° 184°-187° 160°-161° \$80183°	
p-Tolyl	,, •	Solid at 14°	178°	

- Hofmann, B. 4, 209.
- Hofmann, B. 4, 432,
 Hofmann, B. 6, 296,
 Moslinger, B. 9, 1005,

- Hofmann, B. 4, 209. Hofmann, B. 6, 292. Hofmann, B. 6, 297. Michaelis, B. 7, 6, 1688. Hofmann, B. 5, 100; Let's a, Elske, Tr. E. 35 pt. 2. Michaelis a, Panek, A. 212, 233.

Most of the primary bases are liquids, insoluble in water, but soluble in ether. They fume in the air, and grow very hot, their vapour igniting spontaneously at times. The products of this oxidation appear to have been investigated only acid when boiled with water is decomposed, in a few cases, and chiefly in the aromatic series. Phenyl phosphine (Michaelis, B. 10, 807) and tolyl phosphine (Michaelis a. Panek, 1, 212, 234) both absorb a molecule of oxygen, and are converted into phosphinous (phosphinic) acids, which are monobasic, and therefore probably have the constitution RPH(OH):O. These acids are readily decomposed by heat, giving the primary phosphine, and the corresponding phosphinic (phosphonic) acid 3RPH2O2 RPH2 + 2RPH2O3 a reaction analogous to that which gives rise to phosphoretted hydrogen and phosphoric acid when hypophosphorous and phosphorous acids are heated. Letts and Blake (Tr. E. 35, pt. 2) find that benzyl phosphine yields a mixture of benzyl phosphinous (phosphinic) and benzyl phosphinic (phosphonic) acids with some phosphoric acid. Submitted to the action of strong nitric acid, many of the primary phosphines (and probably all) absorb three atoms of oxygen, and are converted into phosphinic (phosphonic) acids. This has been shown by Hofmann (B. 5, 110) to be the case in the methyl, ethyl, isopropyl, isobutyl, and isoamyl series.

The phosphinic acids are solid substances, which, with the lower members of the fatty series, can be distilled unchanged (Hofmann, B. 6, 303). But in some other instances a different reaction occurs: thus phenyl phosphinic (benzene phosphonic) acid when heated slowly to 200° gives a pyro-acid, while when rapidly heated to 250° it decomposes into benzene and metaphosphoric acid: $C_aH_aPH_2O_3 = C_6H_6 + HPO_3$. The phosphinic (phosphinic) phonic) acids are all dibasic, and no doubt have the structure RPO(OH). All the primary phosphines have distinct alkaline properties. They combine readily with hydracids forming crystalline compounds, which can, as a rule, be volatilised (with dissociation more or less complete), and which resemble the compounds of phosphoretted hydrogen in being instantly decomposed by water with liberation of the phosphine. The hydrochlorides combine with chloride of platinum to give chloroplatinates. The salts of the primary bases with oxyacids have been scarcely at all investigated. The action of halogens on primary phosphines has not been sufficiently investigated.

phosphine take fire when they come in contact with chlorine or bromine (Hofmann, B. 4, 433, 609). Benzyl-phosphine yields with bromine a mixture of its own hydrobromide and substitu-tion-products (Letts a. Blake, Tr. E. 35, pt. 2). Sulphur acts on the primary bases. With

the methyl and ethyl derivatives, compounds have been obtained but not investigated (Hofmann, B. 4, 433, 610). With phenyl phosphine sulphur acts slowly in the cold, rapidly at a high temperature (Michaelis, B. 10, 810). Two substances are produced, one, a thick liquid, soluble in other, having the composition (C,H,)PH2S, the other a crystalline product to which Michaelis assigns the formula $(C_oH,P)_aS$. The first of these bodies decomposes when heated in the following Anner:

2C, H, PH, S = C, H, PS + C, H, PH, + H, S, When benzyl phosphine is warmed with sulphur

the following reaction occurs (Letts a. Blake, l.c.): $2C_1H_1PH_2 + 6S = (C_1H_2)_2P_2S_1H_2 + H_2S$ and the resulting pyro-benzyl-thiophosphinic

yielding mono-thio-benzyl phosphinic acid: $(C_2H_2)_2P_2S_3H_2+4H_2O=2C_3H_2PS(OH)_2+3H_2S_4$ In view of the analogies existing between nitrogen and phosphorus, considerable interest is attached to the action of carbonyl chloride and bisulphide of carbon on the primary phosphines. Bisulphide of carbon acts upon both methyl and ethyl phosphine (Hofmann, B. 4, 433, 610), but the products have not been investigated. Michaelis a. Dittler (B. 12, 338) have studied the action of both reagents on phenyl phosphine. When carbonyl chloride is passed slowly into that substance, an energetic reaction occurs in the following manner:

2COCl₂ + C₆H₃PH₂ = C₆H₅PCl₂ + 2CO + 2HCl₂Phenyl phosphine and bisulphide of earbon act upon each other when heated in a scaled tube at 150°, and sulphuretted hydrogen is liberated. The product of the reaction is a resinous body (CaHaPHCS)2S, and the reaction itself proceeds according to the equation

 $2C_6H_5PH_2 + 2CS_2 = (C_6H_3PHCS)_3S + H_3S_2$ Michaelis a. Dittler were not successful in their attempts to prepare a phosphorised mustard oil Lom this compound.

They were equally unsuccessful in obtaining phosphorised carbylamine by the action of chloroform and caustic potash on phenyl phosphine. It is true that a reaction occurs, but its course is completely different from that which takes place with an amine, viz. :

 $C_8H_8PH_2 + 4KHO + CHCl_3 = C_8H_8PHKO_2 + 3KCl + CH_3OH + H_2O.$

It thus appears that, in their behaviour with carbonyl chloride and a mixture of caustic potash and chloroform, primary phosphines behave in an entirely different manner from the corresponding amines, though there is a certain degree of analogy as regards the action of both on bisulphide of carbon. This difference is no doubt due to the strong affinity of phosphorus for electronegative elements, such as the halogens, oxygen, and sulphur. Chloracetic and bromacetic acid react with benzyl phosphine. and chloroformic ether appears to form a product of addition (Letts a. Blake, l.c.). Probably other physphines act in a similar Methyl and ethyl manner with these reagents.

Primary phosphines readily combine with ! alkyl iodides to give hydriodides of secondary phosphines.

General properties of the secondary phosphines. The followings secondary phosphines have been obtained:

Name	Condition	Boiling-point
Dimethyl phosphine	in Liquid .	25°
Di-ethyl , •		85°
Di-isopropyl ,,	,,,	118
Di-isobutyl ,		1532
Di-isoamyl ,,		210°-215°
Di-phenyl ,,		280° (about)
Methyl-isopropyl.,	,	78°_80°
Iso-propyl,	, "	
isobutyl "	·	139°-140°
,		Decomposes
Di-benzyl "	? .	when boiled

- Hotmann, B. 4, 610
 Ibid, B. 6, 294
 Ibid, B. 6, 298
 Ibid, B. 6, 295
 Letts a. Blake, Le.

All the secondary phosphines obtained as yet are liquids, having a powerful odour. They are insoluble in water, but soluble in other &c.

 Hold, B. 6, 296.
 Michaelis, B. 15, 801 v. • Hofmann, B. 6, 300.

They have as a rule a strong attraction for oxygen, fuming and growing hot on exposure to the air, and often inflaming spontaneously. In some cases they appear to have even a greater affinity for oxygen than the primary bases. This is so according to Hofmann with all the secondary phosphines of the fatty series which he obtained. But apparently it is not the case with diphenyl phosphine. The products of this spontaneous oxidation do not appear to have been examined except in the case of dibenzyl phosphine, which yields dibenzyl phosphinic (phosphonic) acid and possibly the oxide also (C,H,)₂PO (Letts a. Blake, l.c.). But the products of their oxidation by nitric acid have been investigated, chiefly by Hofmann (B. 5, 104; 6, These are in all cases phosphinic acids, R₂PHO₂, which are monobasic, and no doubt have the constitution R.P(OH) O.

These acids are probably also produced when the chlorides R.PCl are oxidised by nitric acid. Such is at least the case with (CoH2)2PCL Some of them can be distilled unchanged, e.q. dimethyl phosphinic acid; others, e.g. diphenyl and dibenzyl phosphinic acid, lose water, and give pyroacids.

Secondary phosphines combine with acids, the resulting salts being far more stable than those of the primary bases. Thus in most cases they are not decomposed by water, though some are (e.g. salts of diphenyl phosphine). Comparatively little is known regarding secondary phosphines, and very few of their compounds have been investigated.

Sulphur acts upon them, and in the case of diethyl phosphine, according to A. W. v. Hofmann a. Mahla (B. 25, 2436), triethyl phosphine sulphide and diethyl dithiophosphinic acid. PEt2SSH are formed, together with a third substance which probably has the composition PSEt, S.S.PSEt, Bisulphide of carbon also acts upon them, but the products do not appear

to have been investigated. They readily combine with alkyl iodides, giving hydriodides of tertiary phosphines.

General properties of tertiary phosphines. The following tertiary bases have been obtained:

		a contract c		
Name	Condition	Boiling-point		
Trimethyl phosphine	Liquid	40°-42°		
Tri-ethyl ,,	- 1	1270		
Tri-isoptopyl ,	3 ,,	?		
	4	215°		
	٥) ;;	about 300°		
	Solid	above 360°		
	h. ,,			
Ethyl-isopropyl-	1 "	. "		
	Liquid	about 190°		
Methyl-diphenyl	·	284°		
Ethyl-diphenyl "	" "	293°		
Di-ethral-pnenyl "		2200		
Di-methyl-ethyl ,		83"_85°		
Di-cthyl-methyl "		110°-112°		
Di-ethyl-propyl , 1		· 146°-149°		
Di-ethyl-isoamyl ,	1 ,	185° 187°		
Di-ethyl-benzyl ,,		252°-255°		
Ethyl-dibenzyl "		320°-330°		
Dimethyl p-tolyl ,	7	210°		
D:	. "	240°		
Discontinui marini I	"	230°		
Diethol volul	, ''	260°		
meniyi xyiyi ",	"	200		

- * Hofmann a, Cabours, A. Ch. [3] 51, 35.

- Hofmann a, Cahours, A. Cr. [3] 51, 50.
 Hofmann, B. 6, 292, 304.
 Michaelis, B. 15, 801.
 Michaelis, B. 15, 801.
 Michaelis a, Link, A. 107, 210.
 Michaelis a, Link, A. 107, 210.

The tertiary phosphines hitherto obtained are, with the exception of triplienyl and tribenzyl phosphine, liquids at ordinary temperatures, having a powerful odour. They are insoluble in water, but soluble in ether &c. As a rule, they oxidise rapidly in contact with the air, fuming and growing hot, and in some cases igniting spontaneously. The product of this oxidation is a tertiary phosphine oxide of the formula R₃PO, and, no doubt, of the constitution R₂P:O. The final products of the oxidation of phosphuretted hydrogen, and of primary, secondary, and tertiary phosphines, are therefore respec-tively: H₃PO₄, RH₂PO₅, R₂HPO₅, R₃PO, the amount of oxygen absorbed by the phosphine decreasing in a regular manner as the series is ascended.

The oxides of tertiary phosphines are solid substances of remarkable stability. They can in the majority of cases be distilled, and even boiled with nitric acid, without change. By no means as yet discovered can they be reduced. Hydracids combine with them, and they give crystalline compounds with a number of metallic salts, such as the cl. orides of platinum, zinc, mercury, iron, cobalt, &c., also in some cases with chloride of acetyl, bromine, and sulphur.

Tertiary phosphines also combine with the elements of the sulphur group, forming compounds analogous to the oxides.

The salts of tertiary phosphines are readily obtained by dissolving the bases in acids. They are stable, and are not, as a rule, decomposed by water. Their compounds with hydracids have been chiefly studied; those containing oxyacids have not been investigated (with very few exceptions). The haloid salts dissociate to a greater or less extent on heating. Their hydrochlorides combine with chloride of platinum to give chloroplatinates of normal composition.

Some of the tertiary phosphines combine with chloracetic acid to give hydrochlorides of phosphorised betaines. At present only two or three of these substances have been obtained - trimethyl phosphorus betaine by Meyer (R. 4, 734), the corresponding ethyl derivative by Hofmann (Pr. 11, 530), and in addition to these two the closely allied compound, tri-methyl phosphorus benzo-betaine hydrochloride, by flichaelis a.

Ozimatis (B. 15, 2018), (CH₃)₃PCl.C₈H₄.COOH.

The compounds of these phosphorised betaines are stable and well-defined substances. Letts (Tr. E. 30, pt. 1, 285) has investigated the reactions and decompositions of the ethylated body,

which are of some interest.

The hydrate and the salts of this betaine lose carbonic anhydride when heated, and give rise to the hydrate or salt of methyl-tri-ethyl-phosphonium

 $(C_2H_b)_3PX.CH_2.COOH = CO_2 + (C_2H_5)_3PX.CH_3$ a reaction which is entirely analogous to that occurring when the corresponding sulphur compounds(thetines) are heated: (CH,) SX.CH, COOH = CO₂ + (CH₃)₂SX.CH₃. While it is perfectly different from that which the true (nitrogen) betaines experience, as they either dissociate into the original trialkyl-amine and the group X.CH, COOH (or the products of its decomposition), or distil unchanged (Brühl, A. 177, 214).

Treated with caustic potash, all the salts of tri-ethyl phosphorus betaine yield tri-ethyl phosphine oxide: $(C_2H_1)_3PX.CH_2.COOH + 2KHO$ = $(C_2H_2)_3PO + KX + CH_3.COOK + H_2O$. Several of the tertiary phosphines combine

directly and energetically with a molecule of bisulphide of carbon to give highly characteristic compounds, usually of a red colour, and possibly having the constitution, R₃P<S. So characteristic and so readily formed is this compound in the case of tri-ethyl phosphine, that its production may be employed as a test either for bisulphide of carbon or for the phosphine itself. As yet these (bisulphide) compounds have been obtained only with methyl, ethyl, and iso-propyl phosphine, and with those of the aromatic phosphines containing ethyl or methyl groups.

According to Czimatis (B. 15, 2016) these mixed phosphines combine very easily with bisulphide of carbon if they contain methyl, tho readiness with which combination occurs diminishing, however, in proportion to the molecular weight of the aromatic radicle, while, if they contain ethyl, combination occurs only slowly and with difficulty. Hofmann (Tr. 1860, 431 has somewhat exhaustively studied the compound of tri-ethyl phosphine and the bisulphide, which forms with explosive violence. Among its properties are the following: It is insoluble in water, difficultly soluble in ether, but easily dissolves in hot alcohol, from which it separates on cooling in red needles like chromic anhydride. From an ethereal solution it is deposited by spontaneous evaporation in large deep-red monoclinic crystals exhibiting dichroism, which melt

at 95° and volatilise at 100°. It is soluble in strong hydrochloric acid, and if the solution is mixed with platinic chloride, a yellow amorphous compound is produced, 2(C.H.), PCS, PtCl. When heated with silver oxide or nitrate, it is decomposed as follows: (C2H4)2PCS2+2Ag2O = Ag₂S + Ag₂ + CO₂ + (C₂H₅)₃PS, and moist air produces a similar change. But if is heated with water to 100°C., the following reaction occurs:-

 $\begin{aligned} &4(C_{a}H_{\bullet})_{a}PCS_{a}+2H_{\bullet}O\\ &=2(C_{a}H_{\bullet})_{a}PS+(C_{a}H_{\bullet})_{a}PO+(O_{a}H_{\bullet})_{\bullet}(CH_{\bullet})POH+3CS_{a}. \end{aligned}$

Heated with sulphuretted hydrogen, it suffers the following change: 3(C,H,),PCS2+H2S

 $= 2(C_2H_3)_3PS + (CH_2S)(C_2H_3)_3PCS_2 + CS_2$ The action of halogens upon tertiary phosphines has not been very fully studied. Probably direct addition would occur in all cases. This has been proved to take place with tri-ethyl phosphine if the halogen is allowed to act very gradually upon it. The chloride (C₂H₅)₄PCl₂ thus obtained is crystalline, melting at 100° and volatilising readily, though its boiling-point is high. Similar compounds of bromine and iodine have been obtained.

Compounds of tri-methyl and tri-ethyl phosphine with mustard oils are formed easily, and give crystalline hydrochlorides. They, no doubt, have the constitution, S:C:NR:PR_s.

[Note.—Some of the aromatic tertiary phosphines, especially tri-phenyl phosphine, have properties which differ materially from those of other tertiary phosphines. Thus tri-phenyl phosphine is a crystalline solid having scarcely any odour, and it does not oxidise spontaneously. It is remarkably stable, and is not attacked by chlorine even when heated. The hydriodide and hydrochloride are formed when it is dissolved in the warm concentrated hydracids, and are crystalline, but on adding water they dissociate. By treating the phosphine with bromine and an alkali, or by oxidising it with hydrochloric acid and chlorate of potash, the hydrate (C, H,), P(OH), is obtained as a crystalline solid. This when heated to 100° readily loses water, and is converted into the oxide, a substance which is not acted upon by bromine, oxygen; sulphur, &c. By dissolving the phosphine in fuming nitric acid a nitrate of the formula (CaHa) P(NO3)2 is obtained.]

Tertiary phosphines, apparently without exception, unite with alkyl iodides to form phosphonium salts.

General Properties of Quaternary Compounds (Phosphonium Salts). So many of these bodies have been obtained that a list appears inad-It would include derivatives of the visable. series C_nH_{m+1} to the 5th term, one or two of the series C₁H_{2n-7}, and a large number of mixed phosphoniums containing various radicles, among which are vinyl, allyl, and ethylene.

The phosphonium salts are the most stable of all organic phosphorus compounds. None are decomposed by water, and most of them can be obtained readily in the crystalline state by evaporating their solutions.

As a rule, they are soluble in water and in alcohol. They are readily prepared from their . iodides, either by double decomposition with a silver salt, or by first obtaining their hydrates (by the action of meist oxide of silver), and

subsequently neutralising the solution with the acid.

The hydrates R.POH are solid substances, having a powerful alkaline reaction and many properties similar to those of an alkali. Indeed. in the case of tetrethyl phosphonium hydrate, the only remarkable point of difference between it and caustic potash (so far as its reactions with metallic salts &c. are concerned) is that, when added to a zinc or aluminium salt, the zinc or aluminium hydrate, which is at first precipitated, is insoluble in an excess. Phosphonium hydrates are decomposed when heated, and in some cases, when their solutions are boiled or at the moment of production, into a tertiary phosphine oxide and a hydro-carbon,

$$R_3POH = R_3PO + R - H$$
.

The action of heat upon the salts of the phosphoniums has been investigated in a number of cases, partly by Letts and N. Collie (Tr. E. 30, part 1, 213; P. M. August 1886), and partly by the latter chemist alone.

As regards the haloid salts, the chlorides decompose almost quantitatively into a hydrocarbon and a tertiary phosphine hydrochloride (Collie), furnishing an excellent method for retrograding' from quaternary to tertiary

When the phosphonium chloride contains several ethyl groups, then if more than one of the latter is present, ethylene is always formed, e.g. $(C_2H_5)_3(C,H_7)PCl = (C_2H_5)_2(C,H_7)P.HCl + C_2H_1.$ But when only one ethyl group is present, then, although ethylene is still formed, two decompositions occur, e.g. (1)

 $2(C_2H_5)(CH_3)_3PCl = 2(C_2H_5)(CH_3)_2P.HCl + C_2H_4$ (2) $(C_2H_5)(CH_3)_3PCl = (CH_3)_3P.HCl + C_2H_4$. If we compare the decomposition by heat of phosphonium chlorides with the decomposition of any of the compound ammonium salts, it must be with the hydroxides and not with the corresponding chlorides' (Collie, C. J. 1888, 636, 711), e.g.

$$\begin{array}{lll} (C_2H_3)_2POI &= (C_2H_3)_3P.IICI + C_2H_4 \\ (C_2H_3)_4NOH &= (C_2H_3)_2N + C_2H_4 + II_2O \\ (C_2H_3)_4(C_3H_3)POOH) &= (C_2H_3)_2PO + C_3H_4 \\ (C_2H_3)_2(CH_3)NCI &= (C_2H_3)_3N + CH_2CI. \end{array}$$

The effect of heat on phosphonium salts derived from oxyacids is completely different. In the case of the ethyl series at all events, they suffer, as a rule, at least two, and occasionally three, different and distinct decompositions. In one of these the molecule splits up into three new groups, consisting respectively of carbonic anhydride, a (paraffin) hydrocarbon, and the tertiary phosphine. In the other, two hydrocarbons are formed-namely, an olefine and a paraffin-in addition to carbonic anhydride and the tertiary phosphine. Whilst in the third, a totally different change occurs, in which only two products are formed-namely, the oxide of the tertiary phosphine and a ketone,

(1)
$$\operatorname{Et_2P} < \frac{\operatorname{C_2H_3}}{\operatorname{OOC_1}\operatorname{R}} = \operatorname{Et_2P} + \operatorname{CO_2} + \operatorname{C_2H_3R.} \bullet$$

(2)
$$Et_{2}P < \frac{C_{2}H_{4}}{OOC}H_{2} = Et_{2}P + CO_{2} + C_{2}H_{4} + RH$$

It is possible, if not indeed probable, that the third reaction occurs subsequently to the first, and that it really depends upon the reducing action of the triethylphosphine upon the carbonic anhydride, at the high temperature at which the decomposition usually occurs, whereby carbonic oxide is liberated, which combines with the hydrocarbon radicle in statu nascendi, forming

$$\begin{aligned} & \text{Est}_3 \text{P} + \text{CO}_2 + (\text{Et}) + (\text{R}) = \text{Et}_3 \text{PO} + \text{EtCOR} \\ & \text{(or Et}_3 \text{P} + (\text{OCO} - \text{R}) + (\text{Et}) = \text{Et}_3 \text{PO} + \text{EtCOR}). \end{aligned}$$

If we merely consider the third kind of decomposition alone, it appears to be, to a certain extent, analogous to the decomposition which a sulphine compound suffers when heated, the difference depending on the greater attraction which phosphorus has for oxygen, compared with that of sulphur for the same element. In both cases a hydrocarbon group is detached from the molecule, and also the residue of the acid, but while with the sulphur compounds these two simply combine (forming a compound ether), and leave a hydrocarbon sulphide, in the case of the phosphonium salt the acid residue is reduced by the tertiary phosphine, and the group thus left combines with the hydrocarbon radicle, forming a ketone.

$$Et_{2}S < \frac{Et}{OOCR} = Et_{2}S + EtOOCR.$$

$$Et_{3}P < \frac{Et}{OOCR} - Et_{3}PO + EtOCR.$$

A result of this kind is in perfect harmony with the views expressed by Crum Brown and Letts (Tr. E. 28, 371; Letts, Tr. E. 30, 285) regarding the analogies and differences existing between phosphorus and sulphur and their compounds.

When the phosphonium salts contain ethylene they suffer a different decomposition under the influence of heat; at least this has been ascertained to be the case with the bromide of bromo-ethylene-triethylphosphonium, and the bromide of hydroxy-ethylene-triethyl phosphonium, which decompose as follows (Hofinann) :-

 $C_aH_aBr.P(C_aH_a)_aBr = HBr + (C_aH_a)(C_aH_b)_aPBr$ $C_2H_1(OH).P(C_2H_2)_3Br = H_2O + (C_2H_3)(C_2H_3)_3PBr$ and also in that of the hydrate of ethylene-hexethyl diphosphonium, which decomposes according to the equation: $C_2H_1(P(C_2H_3)_3OH)$ $= C_2H_1 + (C_2H_3)_3P + (C_2H_3)_3PO + H_2O.$ Masson and Kirkland (C. J. 1889, 126) have

studied the action of bromine and chlorine on the salts of tetrethyl phosphonium, the results showing a very close similarity between the polyhaloid derivatives of tetrethyl phosphonium and those of trimethyl sulphine and of tetramethyl ammonium previously described by Dobbin and Masson (C. J. 1885, 56; 1886, 846). The tendency to form solid poly-haloid compounds is, however, more marked. For the able, containing a list of the new substances, the methods of forming them, and their chief properties, the original memoir should be consulted.

Organic Phosphorus Compounds which cannot be placed in any of the above Groups. A phorphorised cacodyl (CH₁),P₂ (the methyl analogue of liquid phosphoretted hydrogen) was obtained by Thénard (C. R. 21, 144, 25, 829) by the action of chloride of methyl on phosphide of calcium, and is interesting not alone as being the sole representative (as yet prepared) of its class, but also as having been probably the first phosphine obtained. Thénard describes it as a colourless, highly refractive liquid, of an odour recalling that of cacodyl itself, insoluble in water, and boiling at about 250°. It inflames spontaneously in contact with air, but if exidised slowly gives a crystalline acid (CH₁), P₂H₂O₄= (CH₃)₂PHO₂ (dimethyl phosphinic acid?), analogous to cacodylic acid. Treated with an excess of hydrochloric acid, it is converted into trimethyl phosphine, and a solid yellow substance (CH₂), P₂ (which is also formed in the original reaction), and which Thénard regarded as the methyl analogue of solid phosphide of hydrogen.

Michaelis (B. 10, 807) obtained a substance, which he named diphosphenyl or phosphospersene, ch., P.P.C.H., (corresponding to axobenzene), by the action of phortyl phosphorous chloride on monophenyl phosphine C.H., PCl. + C.H., PH. = (C.H.), P. + 2 + 2 + C.H. It is a pale-yellow powder, insoluble in water, alcohol, and ether, but readily soluble in hot benzene, and is slowly oxidised by the air to (C. H.), P.Q. Treated with chlorine, phenyl phosphorous chloride is regenerated. With nitric acid it is oxidised to phenyl phosphinious (benzene phosphinic) acid C.H., PH.O. if the acid is dilute, but to phenyl phosphinic fonzene phosphonic) acid C.H., PH.O. if the acid is strong. Treated with hydrochloric acid, it reacts so as to regenerate the substances from which it is formed.

Michaelis (B. 7, 499) also obtained a substance, which he called di-phospho-benzene hydrate C.H. P.P.OH, by the action of spontaneously inflammable phosphoretted hydrogen on phenyl phosphorous chloride. It is a yellow powder, soluble with ease in bisulphide of carbon, taking fire on exposure to air, and oxidised by nitric acid to phenyl phosphinic (benzene phosphonic) and phosphoric acids. In addition to the above, Michaelis (B. 11, 885) obtained a phenylated solid phosphide of hydrogen (C,H,)HP, by treating phenyl phosphorous chloride with a quantity of water insufficient for complete decomposition (for instance, by keeping it in a badlystoppered bottle). It is a dark-yellow amorphous body, having a faint odour of phenyl phosphine, soluble in hot bisulphide of carbon, but insoluble in water, alcohol, and ether. Treated with chlorine it reacts as follows: (C₄H₅)HP₄+6Cl₂= 8PCl₂ + (C₅H₂)PCl₂ + HCl. Nitric acid oxidises it to a mixture of phenyl phosphinic (benzene phosphonic) and phosphoric acids.

The action of phosphonium iodide on aldehydes has been studied by Girard (A. Ch. [7] 2, 50), while that of phosphoretted hydrogen and hydrochloric acid on the same bodies and on ketonic acids has been investigated by Messinger and Engels (B. 21, 328, 2019). Girard obtained products of addition containing four molecules of the aldehyde (valerte, propionic, salicylic, and benzoic) to one of phosphonium iodide.

Messinger and Engels obtained similar bodies

Messinger and Engels obtained similar bodies by acting on the aldehydes with hydrochloric acid and phosphoretted hydrogen. The compounds thus formed are for the greater part solid, crystalline, and fairly stable. By treatment with water they are decomposed, and the aqueous solution gives the reactions of hydrochloric acid and phosphoretted hydrogen. Their constitution is probably represented by the formula (B.CHOH), PCI. Chloride of tetra-hydroxyethylidene phosphine (C,H,O), PCI is decomposed by caustic potash into the free phosphine (C,H,O), PC,H,O and the hydrate (C,H,O), P(OH). Benzaldehyde and its mono-nitro-derivative give compounds which differ from those obtained in the fatty series in that they contain no hydracid.

Messinger and Engels have summarised the results of their researches as follows: (1) Phosphoretted hydrogen does not act on an aldehyde alone, but is absorbed if at the same time a hydracid is present. The absorption occurs more completely if the aldehyde is largely diluted with ether. (2) The aldehydes of the fatty series combine with a molecula of phosphoretted hydrogen and a molecule of hydracid, while those of the aromatic series combine with phosphoretted hydrogen only, though in order that the compound shall be formed the presence of the hydracid is necessary. (With benzoic aldehyde the compound has the formula $(C_0H_1COH)_1PH_2$.) (3) The phosphorised derivatives of the fatty series have an unpleasant smell, and are decomposed by water, while those of the aromatic series have no odour, and are nearly insoluble in water. All are soluble with difficulty in ether, and in some cases are insoluble.

By the substitution of a ketonic acid for an addehyde in the above reaction, compounds are produced in certain cases. Thus levulic acid gives an oil, and pyruvic acid a solid compound,

either
$$(CH_3\cdot CO.CO)_3P$$
 or $(CH_3-C-C=0)_3P$,

which is a well-defined crystalline body, having neither busic nor acid praperties, soluble in alkalis with decomposition, and also decomposed when heated with acids. It dissolves, however, without change in glacial acetic acid, and crystallises cout on cooling. Boiled with water, it is decomposed into the substances from which it was originally produced. It forms crystalline compounds with aniline, phenyl hydrazine, and toluene diamine. E. A. L.

PHOSPHINIC ACIDS. The name oxy-ethylphosphinic acid has been given to the acid CHMe(OH).PO(OH),, which is got from aldehyde by successive treatment with PCl, and water. A more appropriate name for this acid is, however, oxy-ethane-phosphonic acid, the term phosphinic acid being reserved for acids R'P(OH)₂ containing trivalent phosphorus.

PHOSPHINO-BENZENE C.H., PO. Phosphenylic anhydride. [100°]. Formed from phosphenylic acid and POCI, (Michaelis a. Rothe, B. 25, 1747). White crystalline powder, v. sol. water, being reconverted into phosphenylic acid.

PHOSPHINO. \$\psi\$-CUMENE C_6H_Me_PO_[216]. Formed from C_6H_Me_PO(OH), and C_H_Me_POCl_4 (Michaelis a. Rothe, B. 25, 1749). Plates (from benzene), v. e. sol. chlosform. Converted by hot water into \$\psi\$-cumene phosphonic acid.

PHOSPHINO-TOLUENE C. H. Me. PO.: Tolus phosphonic anhydride. [101°]. Formed one phosphonic anhydride. [101°]. Formed from C.H., PO(OH), and C.H., POCl, (Michaelis a. Rothe, B. 25, 1748). Converted by water into toluene phosphonic acid.

PHOSPHITES. Salts of the acid H.PO.; v.

PHOSPHORUS, OXYACIDS OF, p. 151.

PHOSPHO -. Use of this prefix applied to inorganic compounds; for phospho-acids, phosphosalts, &c., v. the acids, salts, &c., to which phospho- is prefixed. Thus, phosphomolybdic acid and phosphomolybdates are described under MOLYBDENUM, ACIDS OF, AND THEIR SALTS.
PHOSPHO-AMIDO-BENZENE SULPHONIC

ACID PO, H, NH.C, H, SO, H. The chloride C, H, NSPO, Cl, [158] is formed from p-amidobenzene sulphonic acid and PCl, (Laar, J. pr. [2] 20, 250). It is converted by McOII and alcohol into Me₃A''' [114°] and Et₂A''' [102°] re-

spectively.

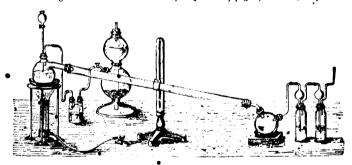
PHOSPHOBENZENE CaHaP:PCaHa. [150°].
Formed by slowly adding CaHaPRa to CaHaPCl. in a current of H (Köhler a. Michaelis, B. 10, 812). Yellowish powder, insol. water, alcohol, and ether, sol. benzene. On exposure to air it is oxidised to $(C_aH_3P)_2O$. Dilute HNO3 oxidises to phosphenylic acid. Chlorine, diluted with CO₂, forms C₆H₂PCl₂. Conc. HClAq forms phenyl-phosphine and C₆H₂PO₂H₂.

PHOSPHONIUM COMPOUNDS. PH, combines with the halogen acids HX to form com-

20 atmos. pressure at 14°, or by cooling to -25° under ordinary pressure (Ogier, C.~R.~89,.705). Skinner (Pr. 1887, 283) found the critical temp. to be 48° under 95 atmos.; and the maximum vapour-pressure line to be below those of HCl and PH, at all temperatures; from - 80° to 10° the line was normal, above 10° combination began; at temperatures near the critical the volume of liquid PH,Cl formed was nearly half that of the liquid constituents.

PH₄ is strongly compressed in presence of water the PH, liquelies and floats on the water. If the pressure is now suddenly decreased, white crystals are formed; these crystals are probably PHOH (no analyses have been made). The production and dissociation of the crystals occur at definite pressures and temperatures. No formation occurs above 28° at any pressure. The crystals can be distilled from one part of the tube to another by gently warming (Callletet a. Bordet, C. R. 95, 58). When equal volumes PH, and CO, are compressed in presence of water, below 22°, the gases disappear and white crystals are formed, which C. a. B. (l.c.) take to be a mixture of PH.OH and the hydrate CO...8H.O

discovered by Wroblewski (С. R. 94, 954). Рноврномим попик РН.І. Н.Г. [Р.Н.І.] = 29,500 (solid PH,I from H, solid P, and solid I); [PH3,HI]=24,100 (solid PII,I from gaseous PH, and HI) (Ogier, C. R. 89, 705). This com-



pounds PH,HX. The reactions of these compounds are most simply expressed by regarding them as salts of the radicle PH; following the analogy of the ammonium compounds, the bodies PH,X are called phosphonium compounds. The mol. weights of these compounds have not been determined.

PHOSPHONIE M BROMIDE PH.Br. $[PH^3,HBr] = 23,000$; $[P,H^4,Br] = 44,100$ (solid PH Br from H, solid P, and liquid Br) (Ogier, C. R. 89, 705). Colourless cubes; melts at 30. V.D. 27.7 corresponding with that required by PH, + HBr (Bineau, A. Ch. [2] 68, 431). Deliquesces in air; decomposed violently by water to PH, and HBrAq. Prepared by bringing together PH, and HBr (Serullas, S. 64, 233); by leading PH, into cold conc. HBrAq (Ogier, C. R. 89, 705); by heating conc. HBrAq with P to 100°-120° (Damoiseau, C. R. 91, 883).

PROSPHONIUM CHLORIDE PH.Cl. Formed in solourless crystals, melting at c. 25°, by subjecting a mixture of equal volumes HCl and PH, to eapacity, and to this solution, kept cool, 680 g.

pound was discovered by Labillardière and Gay-Lussac (A. Ch. [2] 6, 304), and more fully examined by Serullas (S. 64, 238) and H. Rose (P. 24, 151; 46, 636).

Formation .- 1. By bringing together PH. and HI as gases or in conc. aqueous solutions .-2. By the action of gaseous PH, on I (Hofmann, A. 103, 355).—3. By the action of red Pon conc. HIAq at 160° (Oppenheim, Bl. [2] 1, 163).—4. Along with P2I, by the action of HI gas on P at ordinary temperatures (Damoiseau, C. R. 91, 883). - 5. By the action of a little water on PI, (v. Preparation).- 6. By the reaction of HI on 11, PO, and warming the product in CO, (Lissenko, B. 9, 1313).

Preparation.—P and I are combined in CS. solution, and the product is decomposed by a little water (Baeyer, A. 155, 269; Hofmann, B. 6, 286). Hofmann (l.c.) gives the following directions: 400 g. P are dissolved in the same weight of dry CS, in a retort of 1 litre I are added by small portions. The whole of the QS, is then distilled off on a water-bath, an operation which takes 9 or 10 hours. The retort is then connected with a long wide condensing tube, and a two-necked globular receiver, from which a connecting tube passes to two condensing bottles, the first containing dilute HIAq, the second water (see fig.). Heat is then applied to the retort, gently at first, and 240 g. water are slowly added through the drop-funnel. . PH,I and HI are formed; the HI collects in the con-densing bottles, and the PH, I forms a crust, chiefly in the tube, and in smaller quantity in the globular receiver, which, to prevent stoppage, should be connected with the long tube by a wide tube. To prevent the liquid in the condensing-bottles from being forced back in consequence of the rapid absorption, a slow stream of CO, is passed through the apparatus during the whole operation. A well-conducted sublimation may be completed in 8 or 9 hours. When it is finished one end of the long condensing tube is closed with a cork, and the PH.I is detached by means of a stout wire bent and sharpened at the end. Hofmann expresses the reaction thus: $18P + 9I + 21H_{0}O = 7PH_{1}I + 3H_{4}P_{2}O_{7} + 2HI$. The PH,I may be sublimed in dry HI.

-Properties. - Large, clear, lustrous, pyramidal crystals; boils at c. 80°; may be sublimed in HI.

Reactions.—1. With carbon compounds reacts as a very energetic reducing agent, and is much used in preparing phosphines &c. (v. Phosphines).—2. Decomposed rapidly by water or alkali solution, evolving non-inflammable PH, (v. Phosphorus tranvorder, Preparation 2, p. 136).

S. With alcohol forms Etl and PH,; if the reaction is conducted in a scaled tube PEt, and PEt, I are produced.—4. With phosphorus trichloride forms P,I, HCl, PH,, and solid P,H (de Wilde, B. 16, 217).—5. PH,I is inflamed by contact with many cone acids, e.g. 11NO₃, HCl, HBr, HI.

Phosphonium sulphate. When PH₃ is passed into H₂SO₂ at ordinary temperatures much heat is produced, S separates, and SO₂ is formed. The reaction is much slower if the acid is cooled by ice and salt; if the H₂SO₃ is cooled to -20° or -25° (by rapid evaporation of CH₃Cl) a syrupy liquid is formed, from which a white, crystalline, very deliquescent solid separates; this solid seems to be phosphonium sulphate [?(PL₃),SO₃] (Bosson, C. R. 109, 644). Exposed to air, H₃PO₃, and H₃PO₂ are formed with SO₂, S, and a little H₂S; dissolves in water with hissing noise and evolution of PH₃, but no reduction of the H₂SO₄. M. M. P. M.

PHOSPHORIC ACIDS. In this article are described the three acids, H₁PO₄, HPO₃, and H₄P₃O₇; the salts of these acids are described under Phosphates (p. 106); for the other oxyacids of P and their salts v. Phosphorus, OXYACIDS OF, AND THEIR SALTS (p. 149). The oxide P₂O₅ is the anhydride of three acids: cold water added to P₂O₅ forms HPO₃, the long-continued action of moist air on HPO₅ produces H₄P₄O₇, and H₂PO₄ is formed by boiling for some time an aqueous solution of HPO₅ or H₄P₂O₇. The three acids may be formulated as P₂O₅. H₄O, P₂O₅. 2H₄O, and P₂O₅. 3H₄O (cf. Phosphates, p. 106).

Obthophosphoric acid. Phosphoria acid. Tribasic phosphoric acid.) S.G. 1-88 (Schiff, A. 113, 183). Melts at 41.75°; liquid solidifies at 38°, temperature rising to 40.5° (Berthelot, Bl. [2] 29, 8). H.F. [P,O',H'] = 302,600 (formation of solid acid); 300,080 (formation of molten acid); [P,O',H',Aq] = 305,230 (Th. 2, 225). Heat of fusion = -2520 (Th., l.c.). One mol. w. of the molten acid in grams occupies 52.02 c.c. (Th., l.c.). \(\mu_1\): 3584, \(\mu_1\): 3585, \(\mu_1\): 365, \(\mu_1\): 3746, for H,PO,Aq. S.G. 1·11 (=29 p.c.) (Gladstone, C. J. [2] 8, 101, 147). Affinity in aqueous solution = c. 25 (HNO₂ = 100) (Ostwald).

Formation.—1. By oxidising P, by long exponents

sure to moist air (Leeds, A. 200, 286; Wenzell, Ph. [3] 14, 24), or by HNO, HClO, HClO, SO, NO2, &c.; phosphates are formed by treating P with many metallic oxides, and with alkali carbonates.—2. By oxidising H.PO,Aq or H.,PO,Aq by ClAq, BrAq, or IAq, HClOAq, HNO,, or by Ag.O or HgO; H.,PO,Aq is oxidised to H.,PO,Aq by standing in air.—3. By reaction of boiling water with P₂O₃, HPO₃, or H₄P₂O₅,—4. By burning PH, in moist air or O .- 5. By reaction of water with POCl3, or much water with PCl3.-6. By oxidising, by HNO,Aq, the mixture of H,PO,Aq and H,PO,Aq obtained in making HI by the action of P, I, and H,O (Pettenkofer, A. 138, 57).—7. By decomposing many phosphates, e.g. $Ca_3P_2O_8$, by H_2SO_4 ; $Pb_3P_2O_8$ decomposed by H.S in presence of water gives H.PO.Aq. For production from bones v. DICTIONARY OF APPLIED CHEMISTRY .- 8. By decomposing (NH,)H,2PO, by warm cone. HClAq, separating NH,Cl after cooling, and evaporating with HNO, till all NH, salts and HCl are expelled (Joly, C. R. 102, 316).

Preparation .- One part P is mixed with 10-12 parts HNO, Aq (free from H2SO,) S.G. 1.2 (the acid must not be more cone than this) (Kranthausen, Ar. Ph. [3] 10, 410) in a large retort, the beak of which passes loosely into a receiver placed in cold water; about 3 to 6 gently warmed until the P has completely dissolved. Should any liquid distil over, it is returned to the retort. Oxidation proceeds more regularly, and at a lower temperature, when a little I is present than when HNO, Aq alone is used (Horn, Ph. [3] 10, 468; Ziegler, D. P. J. 258, 239). If I is not added, and the acid is more cone, than S.G. 1.2, violent explosions may occur. Von Schrötter recommends the employment of amorphous P and acid more conc. than When the P is all dissolved, the con-S.G. 1.2. tents of the retort are boiled, and 5-7 parts of the liquid are distilled off (the distillate is HNO, Aq, S.G. 1.1 to 1.14). During this part of the process copious evolution of NO2 often occurs, due to the oxidising action of INO, on H.PO,. According to Reinsch (J. pr. 28, 385) little NO, but much N, is formed during the oxidation of P by HNO, at boiling temperature in absence of air, but much NO is produced in an open vessel at low temperatures. The liquid in the retort is evaporated in a basin until the fumes cease to turn blue litmus red. During this operation NO. is often freely given off (especially if little or none of this gas has been produced in the retort), as the oxidation of H_sPO_s is not alwaysecom-pleted until the liquid has been evaporated; ahould no gas be evolved it is advisable to add a little cone. HNO₂Aq to the liquid in the basin after concentration, and again evaporate till acid fumes cease to come off. The liquid in the basin is diluted with water, saturated with H₂S, kept in a warm place for 24 hours, and filtered from As S₃ (and Sb₂S₃); which may separate (ordinary P generally contains As). The filtrate is then evaporated, at a temperature not above 150°, until it becomes a thick syrup on cooling, and the cold liquid is placed over H₂SO₄, when it slowly solidities. By evaporating the syrup in vacuo over H₂SO₄, crystalline tablets of H₂PO₄ are obtained; a fragment of these placed in acid S.G. 1.8 (or more cone.) immediately causes crystallisation (Huskisson, B. 17, 161).

Properties.—A thick semi-solid mass, S.G. 1788 (Schiff, A. 113, 183); also obtained in crystalline tablets by evaporation of the syrup S.G. 1788 in vacuo over H.SO., According to Berthelot (Bl. [2] 29, 3) crystals of H.PO., melt at 47.75°; the liquid solidifice at 38°, with a rise of temperature to 40.5°. H.PO., is tribasic, forming salts M'H.PO., M'.1HPO., and M'.1PO. in aqueous solution is about 25 (HNO. = 100) (Ostwald). Both crystalline and syrup-like H.PO. deliquesee in air. The acid dissolves readily in water; Hager (in his commentary to the Pharmacopacia Germanica) gives the adjoining table.

According to Sieber (Ph. [3] 9,598), H,PO,Aq containing 5 p.c. acid (or even less) stops putrefaction.

Reactions. - 1. Heated to c. 213°, H.P.O, is formed; at a higher temperature HPO, begins to be formed, and at full red heat only HPO, is produced .- 2. Is not decomposed by electric current, according to Luckow (Fr. 1880.1); by electrolysis of H₁PO₁Aq, using C poles, Bartoli a. Papasogli (G. 11, 239, 468; 12, 113, 117, 125) obtained a substance containing C and P, which they called phosphomellogen. Molten H.PO., on electrolysis, gives off H and O, and forms H,P,O,, then HPO₃, and then II₃PO₃, and inflammable P hydride (Janecek, C₂ C. 1888, 273).—3. It is not certain whether water forms hydrates with HaPO, when the acid is dissolved in water (v. Crompton, C. J. 53, 116). -4. By adding alkali solutions to H₃PO,Aq till neutral, salts M₂HPO, are formed; addition of considerable excess of alkali produces M3PO4. For connection between quantity of alkali added and electrical conductivity of the solution, v. D. Berthelot (C. R. 113, 851) .- 5. Reacts with phosphorus pentachloride at ordinary temperatures to form POCl, and HCl; with phosphorus oxychloride when hot to form HPO3 and HCl, or H,P2O, and HCl, according to the relative quantities of H,PO, and POCI,; with phosphorus trichloride to form HPO, H,PO, and HCl; and with metaphosphoric acid to form H,P,O, (Geuther, J. pr. [2] 8, 359). For reactions of salts of H,PO, v. Phosphates, p. 107. For nitriles of H.PO, v. PHOSPHAM (p. 104), and PHOSPHORUS OXYNITRIDE (p. 144); for amide and imido amide .v. Phosphamides (p. 105) and PHOSPHAMIDO-IMIDE (p. 105). For thio-amide v. PHOSPHORUS SULPHOCHLORIDE, Reaction(p. 148).

PYROPHOSPHORIC ACID, H₄P₂O₇.

Preparation.—1. An impure acid, containing some E.PO, and HPO,, is obtained by heating H,PO, to 218° until a little dissolved in cold

l					
Sp. gr.	Per cent. P.O.	Per cent. H.PO.	Sp. gr.	Per cent.	Per cent.
1.809	68	93-67	1.325	35	48.21
1.800	67.5	92.99	1.819	84.5	47.52
1·792 1·783	67 66·5	92·30 91·61	1·314 1·308	34 33·5	46.84
1.775	66	90.92	1.303	83	46.15
1.766	65.5	90.23	1.298	82.5	44.77
1.758	65	89.54	1.292	32 -	44.08
1·750 1·741	645 •	88·85 88·16	1·287 1·281	81. 5 31	43·89 42·70
1.733	63.5	87.48	1.276	30·5	42.01
1.725	63	86.79	1.271	30	41:33 40:64
1·717 1·709	$\frac{62.5}{62}$	86.10	1.265	29.5.	
1.703	61.5	85·41 84·72	1·260 1·255	29 28·5	39·95 39·26
1.693	61	84.03	1.249	28	38.57
1.685	60.5	83.34	1.244	27.5	37.88
1.677	60 59·5	82.65	1·239 1·233	27	37.19
1.669 1.661	59	81·97 81·28	1.228	26· 5 26	36·50 35·82
1.653	58.5	80.59	1.223	25.5	35.13
1.645	58	79.90	1.218	25	34.44
1.639 1.629	57·5 57	79·21 78·52	1·213 1·208	$24.5 \\ 24$	33·75 33·06
1.621	66·5	77.83	1.208	23.5	32.37
1.613	56	77.14	1.198	23	31.08
1.605	55.5	76.45	1.193	22.5	80.99
1·597 1·589	. 55 54·5	75·77 75·08	1·188 1·183	22 21·5	30·31 29·62
1.581	54	74.39	1.178	21.5	28.93
1.574	53.5	73.70	1.174	20.5	28.24
1.566	53	73.01	1.169	20	27.55
1·559 1·551	52·5 52	72·32 71·63	1·164 1·159	19·5 19	26·86 26·17
1.543	51.5	70.94	1.155	18.5	25.48
1.536	51	70.26	1.150	18	24.80
1.528	50.5	69.57	1.145	17.5	24.11
1·521 1·513	50 49·5	68:88 68:19	1·140 1·135	17 16·5	23·42 22·78
1.505	49	67.50	1.130	16	22.04
1.498	48.5	66.81	1.126	15.5	21.35
1·491 1·484	48	66.12	1.122	15	20.66
1.476	47·5 47	65·43 64·75	1·118 1·113	14·5 14	19·97 19·28
1.469	46.5	64.06	1.109	13.5	18.60
1.462	46	63.37	1.104	13	17.91
1·455 1·448	45·5 45	62·68 61·99	1·100 1·096	12·5 12	17·22 16·53
1:441	44.5	61.30	1.091	11.5	15.84
1.435	44	60.61	1.087	11	15.15
1·428 1·422	43·5 43	59.92	1.083	10.5	14.46
1.415	42.5	59·23 58·55	1·079 1·074	10 9·5	13·77 13·09
1.409	42	57.86	1.070	9	12.40
1.402	41.5	57.17	1.066	8.5	11.71
1·396 1·389	41 40·5	56·48 55·79	1.062 1.058	8 7·5	11·02 10·33
1.383	40.5	55.10	1.053	7	9.64
1.377	39.5	54.41	1.049	6.5	8.95
1.371	39	53.72	1.045	6	8.26
1·365 1·359	38·5 38	53·04 52·35	1·041 1·037	45 ·5 5	7·57 6·89
1.354	37.5	51.66	1.033	4.5	6.20
1.348	37	50.97	1.029	4	5.51
1·342 1·336	36·5 36	50·28 49·59	1·025 1·021	8·5 8	4·82 4·18
1.330	35· 5	48-90	1.021	2.5	8.14
- 300		00			

water gives a white pp., without a trace of yellow Ag, PO,, with AgNO, Aq, after neutralisation by NH, Aq. -2. Péligot (A. Ch. [2] 73, 286 obtained crystals of H.P.O, by allowing glacial HPO, to stand in moist air in a bottle for some years. Crystals of H₃PO₄ formed at the top of the bottle, a liquid S.G. 1.7 in the middle, and the bottle, a liquid S.G. 1.7 in the middle, and erystals of H₁P₂O₂ at the bottom.—3. An aqueous solution of H₂P₂O. is obtained by decomposing Pb₂P₂O₂ suspended in water by H₂S, filtering from PbS, and allowing the H₂S to evapocate at the ordinary temperature (Geuther, J. Jr. [2] & 559).—4. By heating together H₁PO₄ and HPO₃ in the ratio HPO₃:H₂PO₄.—5. By the reaction of H₂PO₄ and POCl₃ in the ratio 5H₃PO₄:POCl₃ (G., Le.).

Properties and Reactions—A classification

Properties and Reactions. - A glass-like solid; Péligot (A. Ch. [2] 73, 286) obtained the acid in non-transparent crystals resembling loaf-sugar. Dissolves readily in water; dilute solutions remain unchanged at ordinary temperatures (Graham), when heated H,PO,Aq is formed. The solution, neutralised by NH,Aq, gives a white pp. of Ag.P.O. with AgNO.Aq. H.P.O. is tetrabasic; for description of salts c. Phosphates, p. 107. When heated with 70. PROSPIATES, p. 107. When heated with the problem of the proble HPO, and HCl (G., l.c.). For the amic acids of H,P,O,, and other amic acids derived from hypothetical condensed pyrophosphoric acids, v. Рнозримис астов (р. 105).

Метарновий асто HPO3 (Graham, T. **1833. 253).**

Preparation.-1. H.PO.Aq or II.P.O.Aq is evaporated to dryness and the residue heated to full redness until H₂O ceases to be evolved. - 2. PbP₂O₄ is suspended in water and decomposed by H₂S, the filtrate from PbS is evaporated to dryness and heated to full red heat .- 3. By the ting together H₂PO₄ and POCl₂ in the ratio 2H₂PO₄:POCl₃, or H₁P₂O₇ and POCl₂ in the ratio 2H₂P₂O₇:POCl₃, or H₄P₂O₇ and PCl₃ in the ratio 3H, P,O,: PCl, (Geuther, J. pr. [2] 8, 359).—4. By reacting on H.PO.Aq with Cl or Br .- 5. A solution of P2O, in a little cold water contains HPO.

Properties and Reactions.—According to Tammann (J. pr. [2] 45, 417), two varieties of HPO, exist; one is a soft, silky mass, formed by heating HaPO, until one molecule of H.O is removed; the other is obtained by heating H,PO, until it sets to a glassy mass on cooling. A transparent, colourless, glass-like solid. Ordinary glucial phosphoric acid is impure HPO,, generally containing considerable quantities of Na salts, and some H₂PO₄ or H₁P₂O₇. Very hygroscopic, soon deliquesces in air. Volatilised completely at bright-red heat (H. Rose, A. 76, 2, 13; 77, 319). Not dehydrated by heat nor by the action of dehydrating agents. Heated with PCl, forms POCl, and HCl, HPO, Aq is changed to H, PO, Aq. forms slowly at ordinary temperatures, more rapidly by boiling or by adding HClAq or HNO,Aq. (For rate of change v. Sabatier, C. R. 106, 63; 108, 738, 804.) HPO, is monobasic; several series of metaphosphates, some polymeric and some isomeric, exist (v. Phosphates, p. 106).
M. M. P. M.

PHOSPHORIC ETHER v. TRI-STHYL-PHOS PHATE

PHOSPHOROUS ACID H.PO. v. PHOSPHORUS,

OXYACIDS OF, p. 149.
PHOSPHOROUS ETHER v. ETHYL PHOS-PHITES

PHOSPHORSELLIC ACID v. vol. iii. p. 782. PHOSPHORUS P. At. w. 30-96. Mol. w. 123-84 and 61-92 (v. infra). The following data apply to ordinary crystalline P. Melts at 44-92 (Schrötter, P. 81, 299); at 44-22 (Desains, C. R. 23, 149). Boils at 290° (Felletier, A. Ch. 4, 8); at 250° (Heinrich, Gm.-K. [6th ed.] 2, 102); at 287-3° at 762 mm., 165° at 120 mm. (Schrötter J. 1847-48). S. C. 1.8367 at 0° 1.8328 at 20° J. 1847-48). S.G. 1.8367 at 0°, 1.8232 at 20° 1 8068 at 40° (Pisati a. de Franchis, B. 8, 70). S.G. at b.p. 1-485 (Ramsay a. Masson, C. J. 39, 50). V.D. 62-7 to 65-1 at 500°-1000° (Dumas, A. Ch. [2] 49, 210; Mitscherlich, A. 12, 137; Deville a. Troost, C. R. 49, 211). V.D. at 1700° Deving a. 17008; C. R. 49, 211). V.D. 81 1700°. C. 45 (Biltz a. V. Meygr, B. 22, 725). S.H. solid, -78° to 10°=-1699, 7° to 13°=-1884 (Hegnault, A. Ch. [3] 26, 286); 13° to 36°=-202 (Kopp, T. 155, 71); liquid = 2015 (Person, A. Ch. [3] 21, 295). S.V.S. c.17; at b.p. c. 21 (Ramsay a. Young, C. J. 39, 50). S.V. of P in PCl, and PBr, = 253. C.E. '0003674+'000000211t from 50° to 280°; C.E. liquid P from 50° onwards = '0005167+ 0.0000037 (t = 50) (Graham-Otto, 1831. II. 2, 283; v. also Kopp, A. 93, 129; Pisati a. de Franchis, B. 8, 70; Leduc, C. R. 113, 259).

Refraction-equivalent $\binom{\mu-1}{d}$. At. w.) 14.93;

spec. refractive power for H line a=4816 (Haagen, P. 131, 117). H.C. $[P^2, O^3]=369,900$, $[P^2, O^3, Aq]=405,500$, $[P^2, O^3, Aq]=250,000$ (Th. 2, 408). Crystallises in dodecahedra and octahedra (Trantwein a. Buchner; Whewell, C. N. 39, 144; Story-Maskelyne; Mitscherlich, B. B. 1855, 409; Hermann, B. 6, 1415). For spectrum, v. B. A. 1884. 434.

The following data apply to red amorphous P. S.G. 2-106 at 17 (Schrötter, J. 3, 262), 2-19° (Hittorf); in powder S.G. = 1-964 at 10° (S), 2-6 (H.). S.H. 15° to 98° = 1698 (Regnault, P. 89, 496). S.V.S. c.15. E.C. (Ag at 0° = 100) 00000123 at 20° (Matthiessen, P. 103, 428). H.C. [P2, O3] = 362,820 (Troost a. Hautefeuille, C. R. 78, 748).

The following data apply to crystalline metallic P. S.G. 2:34 ct 155°. S.V.S. c. 13:2

(Hittorf, P. 126, 193).

Historical .- In the early part of the seventeenth century a substance was prepared by heating heavy spar with combustible organic matter. e.g. egg-white and charcoal, and this substance glowed in the dark (Kopp, Geschichte der Chemie, iv. 42). From this time the name phosphorus was given to any substance which emitted light in the dark without being ignited $(\phi \omega \sigma \phi)^{\rho} \rho \sigma$ = light-bearer). The substance now known as phosphorus was prepared for the first time about 1670: Brand seems to have been the discoverer, but the discovery is sometimes attri-buted to Kunkel or to Boyle (for details v. Kopp's Geschichte der Chemie, iii. 327).

For a long time P was prepared in very small quantities; it was obtained by evaporating urine, mixing the residue with sand, and heating in a very hot fire. In 1737 charcoal was mixed with the sand and urine-residue. The discovery of phosphates in bones by Scheele in 1771, and in minerals by Gahn in 1780, led to the preparation of P on a comparatively large scale. The discovery of P played an important part in the development of the phlogistic theory. Phosphorus was supposed to be a compound of phlogiston with the acid which was formed when P was burnt; this acid was composed of phlogiston and muriatic acid according to Stahl. and of vitriol and muriatic acid according to Hofmann. Marggraf in 1743 determined that P increased in weight when burnt, and that P was obtained by heating phosphoric acid with combustible matter. In 1777 and 1780 Lavoisier showed that P was a constituent of phosphoric acid (cf. Kopp, l.c.).

Occurrence.-P is not found uncombined. Phosphates of Al and Ca occur in large quantities in many rocks; phosphates of Fe, Pb, Mg, and NH, &c. are also widely distributed minerals. Coprolites (the fossilised excrements of former land-animals) and guano (the excrement of certain birds) consist very largely of Ca phosphate. Phosphates also occur in some kinds of coal (Carnot, C. R. 99, 154). Phosphates of Ca and Mg are found in the ashes of plants and the bones of animals; P occurs in combination with C, H, and N in the yolk of eggs, in blood, in semen, and in nerve and brain matter.

Formation.—Ordinary phosphorus is formed: 1.—By heating CaPO, with powdered

charcoal, $3\text{Ca}(\text{PO}_3)_2 + 10\text{C} = 4\text{P} + 10\text{CO} + \text{Ca}_3(\text{PO}_4)_2$; or wicharcoal, $2\text{Ca}(\text{PO}_4)_2 + 10\text{C} + 2\text{SiO}_2$ or with SiO2 and

= $4P + 10CO + 2CaSiO_3$.—2. By reducing $Pb_3(PO_4)_2$ with charcoal (Donovan, P. M. [4] 2, 202; Foureroy a. Vauquelin, Gmelin's Handb. [6th edit.] i. 2, 95).—3. By decomposing a strongly-heated mixture of Ca₃(PO₃)₂ and C by HCl (Cari-Montrand, C. R. 38, 864).

Red phosphorus is formed: 1. By the action of light, heat, or electricity on ordinary P, whether the P be solid or in solution, dry or P, whether the P be sold or in solution, any or moist, at ordinary temperature or at -14° (Schrötter, W. A. B. 1, 130; C, 241; 9, 414; Corenwinder, A. Ch. [3] 30, 242; Lallemand, C. R. 70, 182; Hittorf, P. 126, 193; V. Meyer, P. 15, 267; Clear C. 7, 16, 260, 2, 38; Perset B. 15, 297; Grove, C. J. 16, 269).—2. By heating common P with a little I. One part of I suffices to transform c. 100 parts of P into the red variety, by melting the P, mixing in the I, and heating again; the mass becomes red at 100°, at 120°-130° a red powder separates, at 200° a more or less explosive action occurs and the change is complete (Brodie, J. pr. 58, 171).-3. By adding a little I to a solution of common P in CS, evaporating to dryness, adding water, and washing with CS, (Corenwinder, A. Ch. [3] 80, 242; Lallemand, C. R. 70, 182; Brodie, J. pr. 58, 171). Rüdorff (P. 128, 463) supposed the red substance thus formed to be a hydride of P.

1. Crystalline ordinary phosphorus is formed: 1. By heating red Pina vacuous scaled tube to 447° (Hittorf, P. 126, 193).—2. By dissolving ordinary P in molten lead and crystal-

lising therefrom (H., l.c.).

Preparation.—1. The details of the preparation of ordinary phosphorus from boneash are described in DICTIONARY OF APPLIED CHEMISTRY, vol. iii. Ordinary P frequently contains notable quantities of As, derived from the H2SO, used; this can be removed only by repeated treatment with dilute IINO, Aq. S.G. 1.1, a process which involves the loss of about 5 of the P (Herz a. Bärwald, B. B. 32, 2, 133; cf. Dulk, ibid. 34, 1, 247; also Wackenroder, J. pr. 2, 340; and Liebig, A. 11, 260). Traces of red P may be removed by shaking in a closed vessel with cone. K Cr.O.Aq and H.SO. (Wöhler, A. 45, 249). Lockver (C. N. 40, 101) found that a specimen of dry P gave off considerable quanti-ties of H when heated in vacuo.

2. Red or amorphous phosphorus.-A small flask of hard glass is fitted with a good cork carrying a short tube and an exit-time which dips just beneath the surface of a little Hg; the entrance tube is fitted with a stopcock. Dry CO. is passed through the apparatus for some time; a dry stick of common P is then placed in the flask, and the stream of CO₂ is continued for a little, after which the stopcock is closed, and the flask is heated on a sand-tray or in an oil-bath, to 240°-280°, for 50-60 hours. After cooling, a layer of red P is found at the bottons of the flask, generally covered by a mixture of the two kinds of P. The ordinary P is melted by running in a little water at 50°-60°; the water and melted P are poured off; the resi dual red P is washed repeatedly with CS₂ (addition of CaCl₂Aq, 38°-39° Beaume, causes the CS2 solution to rise to the surface; Nickles, C. R. 42, 646), or with boiling KOHAq S.G. 1.3, and then with water containing a little HNO,; the red P is finally washed with water. and dried at c. 100° (Schrötter, W. A. B. 1, 130; 8, 241; 9, 414).

The change of common into red P occurs in ten minutes by heating the former to 300° in scaled tubes of thick glass, from which the air has been pumped out (Hittori, P. 126, 193; V. Meyer, B. 15, 297).

3. Crystalline metallic phosphorus. Hittorf (P. 126, 193) claimed to have formed a distinct variety of P by heating red P in sealed tubes of hard glass to c. 417° (in vapour of S): and also by dissolving common P in molten lead and crystallising. A wide tube of hard glass is closed at one end, filled to 4 with common P and then filled with pieces of lead; the open end is narrowed, and the air is pumped out of the tube, which is then sealed. The tube is embedded in calcined MgO, placed in an iron tube, and heated above the melting-point of Pb for 8-10 hours. After cooling, the Pb is dissolved in HNO, Aq, S.G. 1.1, and violet-black crystals of P remain; these crystals have not, however, been obtained quite free from lead.

Properties. - P exists in three, and perhaps in more than three, modifications.

1. Ordinary, octahedral, or stick phosphorus is a semi-transparent, colourless. or stick crystalline solid, with a very distinct smell. The smell is very probably due to a mixture of ozone and P2O3, formed by the oxidation of the P (Schönbein, P. 65, 377; Thorpe a. Tutton, C. J. 57, 573). When melted and cooled quickly P is opaque; when cooled slowly it is nearly as clear as water. P must be kept under water; if the water is free from air the P remains transparent (Baudrimont, C. R. 61, 857). In ordinary water

P becomes covered with a whitish film, but this again becomes transparent at-c. 50° (H. Rose, P. 27, 563; Baudrimont, l.c.). According to Marchand (J. pr. 20, 506) the white film contains from 4 to 7 p.c. water; Pelouze (A. Ch. [2] 50, 88) regarded this substance as a hydrate of P, and Mulder (J. Ph. 23, 20) as a compound of oxide with hydride of P. When melted in large quantity and allowed to cool slowly, fairly large dodecahedral and octahedral crystals separate (Hautwein a. Buchner, Kastn. Arch. 10, 127, 504; Whewell, C. N. 39, 144; Hermann, B. 6, 1415). At ordinary temperatures P is as soft as wax; when cooled it becomes brittle. Exposed to light, P soon becomes yellow and then red on the surface. In a vacuum tube, or in a tube filled with an indifferent gas, P easily sublinies in colourless, transparent, very lustrous crystals (Hermann, B. 6, 1415; Mitscherlich, B. B. 1855. 409; Blondlot, C. R. 63, 397; Desains, C. R. 23, 149). Melted P often remains liquid many degrees below its m.p.; this is shown especially when P is melted by warming with alcoholic KOH solution, or when a solution of P in CS₂ is gradually evaporated under water (H. Rose, P. 32, 469; Kallhofert, J. pr. 50, 1). In some cases P remains liquid at c. -15°. P may be obtained in finely-divided particles by melting it under water, and shaking carefully in a flask until the P solidifies; if pure P is melted mass until the r solutions; if pure r is metted under a solution of sugar, gum, dextrin, NH₂Cl, (NH₃)₂CO₃, &c., and shaken until it solidities, the P is obtained in a state of extremely fine division (Casaseca, J. Ph. 16, 202; Blondlot, J. 1865, 126; Schiff, A. 118, 88; also A. Suppl. 4, 37). P is slightly sol. water, alcohol, ether, ethereal and fatty oils, and hot conc. acetic acid (Vulpius, Ar. Ph. [3] 13, 38). Water shaken with P loses the smell and taste of P, and ceases to glow in the dark when it has been exposed to air for a time (Müller, B. 3, 84). P is very soluble in CS2, S2Cl2, and liquid P2S.

P volatilises in water-vapour, even at the ordinary temperature; when P is distilled in steam and the distillate is cooled rapidly, the P is obtained as a white snow-like mass (Remsen a. Kaiser, Am. 4, 459); it is also often obtained in this form by distilling crude H1Aq containing

P (Hell, J. 1883. 312).

P oxidises very easily; slowly when exposed to low temperatures, and more rapidly as the ignition temperature, 60°, is approached. When P is burnt in air or O it emits very bright yellow-white light, and much heat is produced. But if H is passed over slightly warmed P, or if a stream of the warm gas is charged with a very little P, the issuing gas glows with a very feeble greyish white light, scarcely visible in daylight; the temperature of this flame is very low: if the H is ignited an emerald-green cone appears in the interior of the H flame (for spectrum of this green cone v. Christofle a. Beil-stein, C. R. 56, 399; Salet, A. Ch. [4] 28, 56). The glowing of P in the dark was formerly supposed to be due to the evaporation of the P (Corne, J. Ph. [5] 6, 17; Marchand, J. pr. 50, 1). It was shown that P glows in an indifferent gas only when small quantities of O are present; also that P neither oxidises nor glows in pure O at the ordinary pressure, but only when the O is diluted with an indifferent gas or the pressure is

diminished; and also that the glowing is stopped by the presence of H.S. PH., SO., CS., Br. Cl., N.2O., NO., &c. (Fischer, J. pr. 85, 842; 39, 48; Schrötter, J. pr. 58, 158; Müller, B. 3, 84; Joubert, C. R. 78, 1853; Deschamps, C. R. 52, 355; Müller-Erzbach, B. 12, 2130; Chappuis; Bl. [2] 35, 419; cf. Thorpe, 'On the Glow of Phosphorus,' N. 41, 523). Much work has been done to determine whether ozone or H.O., or both, is formed when P oxidises in moist air; the question is not yet finally settled (McLeod, C. J. 37, 118; Kingzett, Č. J. 37, 792); Leeds (N. Y. Acad. of Sciences, 1, 363, and 3, 150) has given a full index to the memoirs on the subject. Schmid (J. pr. 98, 414) determined that ozone is not formed when P oxidises in dry O. P is extremely poisonous; the lethal dose for adults is from 2 to 5g. Burns with P are very dangerous; the parts should be rapidly and thoroughly washed with dilute bleaching powder solution.

The atomic weight of P has been determined, (1) by ppg. Ag and Au solutions by P and determining the ratio of Ag:P and Au:P (Berzelius, G. A. 53, 433; P. 8, 17); (2) by finding the Ag needed to ppt. Cl from PCl₂ (Pelouze, C. R. 20, 1047; Dumas, A. Ch. [3] 55, 174); (3) by oxidising red P in O to P₂O₃ (Schrötter, J. pr. 53, 435); (4) by analysing and determining V.D. of PCl₃, PF₃, &c.; (5) by measuring S.H. of P.

Determinations of the S.G. of P vapour made by Dumas, Mitscherlich, and Deville a. Troost at temperatures from 500° to 1000° gave numbers agreeing with the molecular wt. P₄=124. Biltz a. V. Meyer (B. 22, 725) obtained the values 52·5 at 1480°, 46·7 at 1680°, and 45·5 at 1700° for V.D. of P, showing that at a white heat the mol. formula is probably P₂ (V.D. = 31).

The mol wt. of ordinary P in solution in C_1H_3 was determined by Paterno a. Nasini (B. 21, 2153) by the cryoscopic method; values were obtained between P_2 and P_4 . Hertz, using the same method and the same solvent, obtained the value $124 = P_4$ (Z. P. C. 6, 358). Beckmann also found $124 = P_1$ for P in solution in CS_4 by the method of raising of boiling-point of the solvent (Z. P. C. 5, 76).

The action of light, heat, or electricity on P changes it into allotropic red P. Light affects the change whether the P be in air or another gas, or in vacuo, whether water be present or not (Schrötter, W. A. B. 1, 130, 8, 241; 9, 414), at temperatures as low as -14° , and whether the P be solid or dissolved in CS₂ (Corenwinder, A. Ch. [3] 30, 242; Lallemand, C. R. 70, 182). For an account of the action of tropical sunlight on P in CS, v. Pedler, C. J. 57, 599. The action of heat begins at c. 215° at the ordinary pressure; diminution of pressure causes a slackening of the rate of change, and the action stops at 393 mm. pressure, temp. being 215°. The change is complete by heating to 260° for c. 8 days; at 800°, in a scaled tube, it is finished in a few minutes (Schrötter, *l.c.*; Hittorf, P. 126, 193; V. Meyer, B. 15, 297; cf. Dissociation, vol. ii. p. 891). The change is accomplished by electricity by passing the current through a little P in a closed tube with Pt wires fused into the ends (Grove, C. J. 16, 269; Geissler, P. 152, 171). Hittorf (P. 126, 198) regards the action as due

to the heating of the P vapour by the current. Certain reagents also effect the change: c.g. heating with a very little I (Brodie, J. pr. 58, 171); or heating a solution of P in CS, with I (Corenwinder, A. Oh. [8], 30, 242; Lallemand, C. R. 70, 182), but Rüdorff (P. 128, 463) says the product is a hydride of P. In the change of 62 g. ordinary P into red P c. 7,100 g.-units of heat are produced; and there is a contraction of volume (v. Petersen, Z. P. C. 8, 601).

2. Amorphous of red phosphorus is a dull, dark carmine, odourless, tasteless powder, which becomes darker on heating, and black when boiled with KOHAq. It is brittle, and shows no trace of crystalline form. Amorphous P is heavier, and conducts electricity much better, than crystalline P, although its conductive power is very small compared with the metals (v. data at beginning of this article). Amorphous P does not melt when heated to redness in a sealed tube (Hittorf, l.c.); vapour is formed in the tube, and on cooling this solidifies as crystalline P, but the unvapourised portion remains amorphous. When distilled, amorphous P becomes crystalline; the action begins at c. 260° (Schrötter, l.c.). The process, like the reverse change of crystalline into amorphous P, is essentially one of dissociation (v. Dissociation, vol. ii. pp. 391-3). Amorphous P takes fire at c. 250°-260° (Hittorf, Schrötter, l.c.), but active combustion begins at c. 300°; it does not oxidise in dry air, but in presence of moisture oxidation proceeds slowly, with the smell of ozone and the formation of an acid liquid (Personne, C. R. 45, 113; Wilson, Ph. 17, 410; Pedler, C. J. 57, 599). Red P does not glow in the air; it is not poisonous (De Vrij. J. 1851, 313). This variety of P is insoluble in the menstrua which dissolve ordinary P; boiling turpentine, and a few liquids of high Soiling-points, dissolve a fittle and change it into ordinary P.

3. Crystalline metallic phosphorus is described by Hictorf (P. 126, 193) as forming long, black, thin, rhombohedral crystals which appear red in transmitted light; S.G. 2:34 at 15:6°; less volatile than amorphous P; heated in a sealed tube drops of ordinary P appear at c. 358°. It is doubtful whether this is a distinct variety of P; it does not seem to have been obtained free from Pb (for preparation, v. ante). According to Troost and Hautefeuille (C. R. 78, 748), the S.G. and heat of combustion of red P change continuously with temperature; at 580° ruby-red crystals appear, which have the S.G. of Hittorf's metallic P.

Thénard observed that P became black when heated and suddenly cooled (Gm. K. [6th ed.] i. 2, 102); some experimenters claim this to be a special variety of P (v. Reichardt, Ar. Ph. [3] 9, 442; P. Thénard, C. R. 95, 409); according to others it contains fogeign substances. Blondlot obtained it only when a trace of Hg was present (C. R. 70, 856; 78, 1130); Ritter found the presence of As necessary (C. R. 78, 192).

(C. R. 70, 856; 78, 1130); Ritter found the presence of As necessary (C. R. 78, 192).

Napoli (C. R. 25, 369) thought that a special yellow modification of P was produced by keeping freshly-melted ordinary P under water.

The atom of P is trivalent in most gaseous molecules, e.g. PCl₂, PH₂, PF₃, &c.; it is pentavalent in the gassous molecule PF₂. P acts as a non-metallic element; its oxides are acidic, although Vot. IV.

some of them combine with less acidic oxides to form salt-like compounds. P is closely related to As, Sb, and Bi, and also to N, V, Nb, Di, Er, and Ta; those elements form Group V. For a detailed consideration of the chemical relations of P v. Nithoorn Group of Elements, vol. iii. p. 571. The specific volume of P at its b.p. is 20-21 (Pisati a. de Franchis, B. 8, 70; Ramsay a. Young, C. J. 39, 50); the specific volume of P in combination is c. 25-3 (Thorpe, C. J. 37, 233).

Reactions and Combinations .- 1. P combines with oxygen to form P.O, P.O., and P.O.; the reaction begins at ordinary temperature with crystalline P, and at c. 250'-260° with amorphous P. (For more details v. Phospical's, exides of, p. 138.) P does not combine with pure O at the ordinary pressure, but only when an indifferent gas is present, or the pressure is diminished (for references v. Properties of P, p. 128). The combination of P in O is arrested in proportion to the dryness of the O (Baker, C. J. 47, 349; Pr. 46, 1). Amorphous P does not oxidise in dry air, but the oxidation proceeds slowly in moist air. Ordinary Poxidises readily in moist air; it is not yet finally settled whether or not ozone is produced (v. McLeod, C. J. 37, 118). In moist air HaPOs is formed; this maybe a direct product of oxidation, or it may result from the reduction of H_sPO₄ formed by the direct oxidation of the P (v. Schönbein a. Bohlig, J. 1863. 167; Blondlot, C. R. 66, 851; Stiassay, D. P. J. 199, 414).-2. P is easily changed to P2O3 by oxidising agents, e.g. HNOn Cro, KNO, &c. A mixture of P and KClo explodes violently when struck or rubbed; the explosion is less violent with amorphous P. Amorphous P is inflamed when rubbed with Amorphous P is infinited with CrO₃, PbO₂, Pb₃O₄, HgO, K₂Cr₂O₇, or Ag₂O, and when heated with MnO₂, CuO, or KNO₃.—
3. P combines with sulphur, the halogens, and many non-metals when heated with these. reactions occur at lower temperatures, and more rapidly, with ordinary than with amorphous P, yet amorphous P combines with Br and Cl at the ordinary temperature .- 4. P decomposes solutions of salts of copper, silver, and some other metals, with separation of the metal, which often combines with the P .- 5. Boiling water is slightly decomposed by P in presence of air, with formation of PH3, H3PO3Aq, and H3PO4Aq (Cross a. Higgin, C. J. 35, 254); at 250° the reaction is more rapid (Schrötter); with amorphous P the action is slow (C. a. H.). - 6. Concentrated hydrochloric acid is decomposed by P at 140°, with formation of PH, and H.PO.Aq (Oppenheim, Bl. [2] 1, 163).-7. Hydriodic acid reacts with P to form PH I and PI; hydrobromic acid reacts at 100°-120° to produce PH,Br (Damoiseau, C. R. 91, 883).—8. Chlorosulphonic acid [SO, OH.Cl] reacts explosively with ordinary P at 25°-30°, and more slowly and at a higher temperature with amorphous P, to form SO₃, HCl, and H₂PO₄ (Heumann a. Köcklin, B. 15, 416) .- 9. Sulphuryl chloride [SO,Cl,] produces PCl, and SO₂; the reaction is violent, even with amorphous P (H. s. K., B. 15, 1736).—10. Adie (C. J. 59, 230) describes the action of sulphur trioxide on P as producing \$P_0_280_.—11. With boiling solutions of alkalis P forms PH, and alkali salts of H_PO_ P left for a long time in

contact with ammonia solution probably forms P hydride and NH, phosphite (v. Blondlot, C. R. 57, 1250; Commaille, C. R. 68, 263; Flückiger, 71, 1200; Commande, C. R. 03, 200; Pittanger, 1, 1863, 171). Red P is not acted on by NH₂Aq (F., L. c.),—12. Heated with the alkaline earths P forms phosphides and phosphates.—13. When P is strongly heated with anhydrous alkali carbonates C is separated. For an account of the technical applications of P v. DICTIONARY OF APPLIED CHEMISTRY; for description of the methods of testing for P and estimating it a manual of analysis must be coffsulted.

Phosphorus, acids of. The phosphoric acids are described under that heading (p. 124), the other soids under the heading Phosphorus, oxy-ACIDS OF, AND THEIR SALTS (p. 149). For phosphamic acids v. p. 105, and for thiophosphamic acids v. Thiophosphoryl Chloride, Reaction No. 7, p. 148.

Phosphorus, bromides of P and Br combine violently; two products of the reaction have been isolated, PBr, and PBr. These formulæ are probably molecular.

PHOSPHORUS TRIBROMIDE, PBr. (Phosphorous bromide). B.P. = 172.9° at 760.2 mm. (Thorpe, C. J. 37, 835). S.G. 292311 (T., l.c.). Does not solidify at -18.6°. A colourless liquid, with very penetrating odour; fumes in the air. PBr. is formed by the direct union of P and Br. If P is added to Br, the Br must be kept in a freezing mixture, and the P must be added in extremely small pieces until a colourless liquid is obtained; the process is dangerous. Lieben (A. 146, 314) recommends to pass CO, through slightly warmed Br, to lead the gas over small pieces of dry P, and to distil the liquid thus produced after it has stood for some days. Schorlemmer uses amorphous P. The P is placed in a flask connected with an inverted condenser, and having a dropping funnel passing through the cork. Br is added drop by drop from the funnel: the first few drops combine, with a production of flame, but after a little the Br may be added more freely; the PBr, is distilled from the excess of P (v. also Pierre, A. Ch. [8] 20, 5; Kekulé, A. 130, 16; Löwig, Gm.-K. i. 2, 334).

PBr, is not acted on by O; reacts with S to form PSBr, (Gladstone, P. M. [3] 35, 345); Cl forms PCl, and Br; HgCl, forms PCl, and HgBr.; H₂S produces P₂S₂ and HBr. PBr, is decomposed slowly by cold water, rapidly at 25°, to HBrAq and H₃PO₂Aq (Löwig, *l.c.*). P and I dissolve in PBr.

PHOSPHORUS PENTABROMIDE, PBr, (Phosphoric bromide. Perbromide of phosphorus). Produced by adding excess of Br to PBr, stirring well with a glass rod, and after a time removing the excess of Br by warming very gently in a stream of dry CO₂. Also formed by action of Br on FOL, in presence of a little I (Gladstone, P. M. [8] 53, 345). PBr, forms a citron-yellow solid; fumes in the air; melts to a red liquid when gently warmed, which solidifies again to rhom-boidal crystals, which are yellow if cooling has been rapid, and red if cooling has been slow. The red crystals become yellow when rubbed (Baudrimont, Bl. 1861. 118); at a higher temperature (below 100°) gives red vapours that condense to yellow needles. PBr, is separated at c. 100°

into PBr, and Br, which re-combine on cooling. (Ogier, C. R. 92, 83) gives the following heats of formation: [P,Brs] = 63,000 from liquid Br; Br; in each case solid PBr, is formed.

Reactions.—1. Heated to 200° in oxygen,

PBr, inflames with formation of P₂O₃ (Baumstark, A. 140, 75).—2. Neither hydrogen nor sulphur reacts in the cold with PBr₂.—3. Chlorine forms PCl, and Br; iodine produces PBr, and IBr. -4. In moist air, POBr, is formed (q. v.).-6. A little water produces HBr and POBr.; with much water HBr and H3PO, are formed.--6. PBr, reacts with hydroxides to substitute OH by Br; the reaction is similar to, but not so energetic as, that of PCl₃.-7. Hydrogen sulphide forms PSBr₃ and HBr.- 8. Phosphorus hydride forms at first PBr, and then also P and HBr.-9. Hydriodic acid has no action a dry boric acid forms some BBr. (Gustavson, B. 3, 426); dry oxalic acid produces POBr, HBr, CO, and CO. 10. Antimony sulphide produces SbBr, and PSBr, (Baudrimont, Bl. 1861. 118) .- 11. With many metals at high temperatures. PBr. produces phosphides and bromides.

Combination. - With ammonia to PBr, 9NH, Prepared by passing dry NH, into a solution of PBr, in CCl, (Besson, C. R. 111,

Phosphorus, bromochlorides of. compounds of P, Br, and Cl are formed by the reaction of PCl₂ with Br. PBr₂Cl₃, PBr₄Cl₄, or PBr₈Cl₄ is produced according to the relative quantities of PCl, and Br used; and from one or other of these the compounds PBr,Cl₂ and PBrCl, are obtained. According to Stern (C. J. 49, 815) PBr.Cl. is formed, and on addition of . more Br the compound PBr, Cl, is produced, and unites with Br to form PBr, Cl2; the whole of the Cl in PCl, cannot be thus replaced by Br (Michaelis, B. 5, 9, 411; Wichelhaus, A. Suppl. 6, 277; Stern, C. J. 49, 815; Geuther, J. Z. 10, 128; Michaelis a. Geuther, J. Z. 6, 242; Prinvault, C. R. 74, 868). Michaelis regarded PBr.Cl. and PBr,Cl, as compounds of PBr,Cl, with Br, and 3Br, respectively; Prinvault looked on PBr,Cl, as PBr,Cl, EPCl, and PBr,Cl, and PBr,Cl, as PBr,SBrCl and PBr,BrCl, respectively. Against Prinvault's view it was urged by Michaelis that if the compounds contain PBr, they must whereas the products are POCl₃, SBr, and Br; but Geuther showed that POBr₃ reacts with BrGl to give POCl, and Br. Geuther regarded the compounds as containing trivalent Br atoms.

PHOSPHORUS DIBROMOTRICHLORIDE, PBr,Cla Yellow-red crystals, melting at 35°; obtained by gradually adding 160 pts. Br to 187.5 pts. PCl. and keeping in a closed tube in a freezing mixture for some time (M.). Addition of 18 pts. water reacts thus (G. a. M.): 3PBr.Cl, +3H.O = 2POCl, + POBr, +3HCl +3HBr. It 8O, is passed into the contents of the tube, SBr. and POCI, are formed (M.)

PHOSPHORUS TETRABROMOTRICHLORIDE PBr,Cl. Large dark-red crystals with a blue sheen; formed by adding Br slowly to PCl, till two layers are produced, the lower of which is dark and oily, and then adding PBr.Cl, until the lower layer solidifies (G.). Also produced by warming PBr, with PCl, to 40°;

 $4PBr_a + 6PCl_a = 5PCl_a + 5PBr_aCl_a$ (G.), when heated PBr.Cl, melts and separates into two layers, which unite again on cooling. A little H₂O produces POCl₂, POBr₂, HCl, HBr, and Br: much H.O forms H.PO., HCl, HBr, and Br; SO, produces POCl, SBr, and Br.

PHOSPHORUS OCTOBROMOTRICHLORIDE PBr.Cl. Brown needles, melting at 25°. Formed by adding 42 pts. Br to 1 pt. PCl, (i.e. in the ratio 8Br: PCl,), heating to 65°, and allowing the oily liquid to cool to c. 4° much heat is produced in the reaction (P.). Geuther (I.c.) says the compound is also produced by adding BrCl to PBr, in the ratio PBr. : 3BrCl.

PHOSPHORUS HEPTABROMODICHLORIDE PBr, Cla. Prismatic crystals. Obtained by rapidly distilling the preceding compound at a little above 90° (P.); also by dropping PCl, into Br until two layers are formed, and allowing to stand. Soluble in PCl3.

PHOSPHORUS MONOBROMOTETRACHLORIDE

PBrCl. According to Prinvault (l.c.) this compound is obtained, as yellow crystals, by heating to boiling a solution of the preceding compound in PCl₃, also by the reaction of PCl₃ with BrCl. P. says that PBr₈Cl₃ and PCl₃ react in accordance with the equation PBr,Cl, + PCl, = PBr,Cl, + PBrCl,.

Phosphorus, bromofluoride of, PBr.F. liquid, which fumes in the air, and is violently decomposed by water; also decomposed easily by heat to PBr, and PF,; formed by passing PF₃ into Br (Moissan, C. R. 100, 1348).

Phosphorus, bromonitride of, PBr.N. This compound is said to be formed by heating the product of the action of NH, on PBr, in a sealed tube, to 250°-275°, with twice its weight of PBr, for twelve hours, and then heating the resulting aubstances under reduced pressure, when PBr_s sublimes, and then at 200° a white crystalline sublimate of PBr_N is formed; the compound is purified by resubliming in vacuo. The crystals melt at 1880-190°; sublime at 150° in vacuo; sol. ester, less sol. CS₂ or CHCl₂, insol. water (Besson, C. R. 114, 1479).

Phosphorus chlorides of. P and Cl com-

bine directly and easily, with the production of light and much heat. Two compounds are thus produced, PCl, and PCl,; these formula are molecular. According to Donny a. Mareska (C. R. 20, 717), and Dumas (A. Ch. [3] 55, 172), liquid Cl surrounded by solid CO2 combines with P.

PHOSPHORUS TRICHLORIDE PCl, (Phosphorous chloride). Mol. w. 13707. Boils at 75.95° at 760 mm. (Thorpe, C. J. 37, 333; v. also Pierre, A. Ch. [3] 20, 5; Haagen, P. 131, 122). S.G. ⁰⁰/_{x0} 1·61275 (Thorpe, l.c.); V.D. 70·6 (Dumas, A. Ch. [8] 55, 172). S.H. of vapour 1347, equal weight of air = 1; 64, equal vol. of air = 1 (Regnault, J. 1863. 85). μ for H line a = 3222; $\frac{\mu - 1}{d}$. Mol. w.

= 44.3 (Haagen, P. 131, 122). H.F. [P,Cl*] = 75,300 (Th. 2, 408; formation of liquid PCl, Regnault (J. 1863, 65) gave the vapour pressures of PCl, in mm. of Hg as follows:—87.98 at 0°, 62.68 at 10°, 100.55 at 20°, 155.65 at 30°, 233.78 at 40°, 841-89 at 50°, 485-63 at 60°, 674-23 at 70°.

Formation.—1. By direct union of P and Cl.

2 By reaction of P with HgCl, FeCl, CuCl,

ICl., S₂Cl., or SeCl. (Gm.-K. 1. 2, 390).—3. By reaction of Cl or HgCl. with PBr, or PI, (l.c.).— 4. By decomposing PCl, by heat sided by H, P, PH, I, HI, S, or one of several metals. 5. By heating HPO, with NaCl (*Gm. K.*, *l.c.*).—6. By heating Na, HPO, with NH, Cl (H. Rose).—7. By heating P with conc. HClAq (Oppenheim, Bl. [2] 1, 163).—8. By passing POCl, through a tube filled with glowing charcoal (Riban, C. R. 95, 1160).

Preparation. About 500-600 g. P, in pieces about 1 inch long, are dried quickly, twice, between filter-paper, and placed in a dry retort of c. 1 litre capacity, through the neck of which a stream of dry CO₂ is kept passing. The beak of the retort is now passed into a well-cooled receiver, and the tubulus is connected with an apparatus which is evolving dry Cl. The tube through which the Cl passes into the retort is fixed somewhat loosely in the cork, so that it may be moved up or down easily. The retort is placed in warm water until the P is melted: after the action has fairly begun, the heat produced suffices to keep the P molten. A large basin with cold water is kept beneath the retort in case the latter should break. The reaction is regulated by moving the tube from the Cl apparatus near to, or away from, the surface of the P; if this tube is too near the P, the heat of the reaction vaporises much of the P, which then condenses in a reddish layer in the upper part of the retort; if the delivery-tube is too far from the P, solid PCI, forms and deposits on the upper part of the retort in yellow crystals. As the reaction proceeds, pieces of red P appear here and there in the retort. Towards the end much red P is formed; this must be heated carefully with a lamp, a process in which the retort is apt to be cracked. The distillate is digested with a little P for a few days, to decompose any PCl,, and then redistilled from a retort heated on a water-bath (Donny a. Mareska, C. R. 20, 717; Dumas, A. Ch. [3] 55, 172). Thorpe (C. J. 37, 333) recommends to heat red P in dry Cl; he says that the reaction is very regular, and that large quantities of PCl, may be prepared thus with great ease and rapidity; the red P should be washed with water, then with alcohol, then with ether, and dried at a gentle

Properties .- A clear, colourless, highly refractive, liquid, which can be vaporised without decomposition in absence of moisture; fumes in air with decomposition; does not redden dry blue litmus paper; vapour has an acrid smell and excites tears. Does not solidify at -115° (Natterer, P. 62, 133). Does not conduct electricity. Dissolves P; also I (Gladstone, P. M. [3] 35, 345). Mixes with C.H., Et.O. CHCl. and CS2. In a gas-flame or alcohol-flame, PCl, burns brightly. Sinks in water and then begins to decompose to H,PO,Aq and HClAq; if a little warm water is used, amorphous P separates. Slowly decomposes in the dark to PCl, and P (Casselmann, A. 83, 247). Combines with Cl to form POl. Not acted on by O at ordinary temperatures; POCl is slowly formed at b.p. of PCl. POCl, is formed by action of ozone and various O compounds which readily part with O (v. Reactions).

Testing PCL, for POCL .- PCl, has little ac-

tion on zinc-dust at ordinary temperatures; POCl₁, produces P₂O₂ and Zn phosphide, which is decomposed by H₂O, giving inflammable P hydride. To apply this reaction, a few drops of the liquid are added to a little zinc-dust in a test tube, and then a few drops of water; if POCl₂ is present, small bubbles of gas are given off, and take fire in the air (Deniges, Bl. [3] 2, 787).

Reactions.—1. Water produces H₂PO₃ and

HCl; the reaction proceeds somewhat slowly. If a little warm water is added to PCl, amorphous P separates at the product of a secondary reaction —3 H₁PO₂Aq + 2PCl₁ = 3HPO₃Aq + 6HClAq + 2P (Michaelis, B. 8, 704); but cf. Geuther, J. Z. [2] 3, 2nd Suppl. 116) .- 2. Oxygen does not react at ordinary temperatures, but POCl₃ is slowly formed at b.p. of PCl₃ (Michaelis, J. Z. 6, 93; Remsen, Am. S. [3] 11, 365).—3. Ozone rapidly forms POC1, (Remsen, Lc.).—4. Polarsium, chlorate produces POC1,—5. Sulphfir trioxide reacts violently, forming POC1, and SO. (Michelis, J. Z. 6, 239; 7, 110; Armstrong, J. pr. [2] 1, 255; cf. Rose, P. 44, 304).—6. Selenion dioxide produces POCl, and Se at 110°; if the SeO, is in excess, SeCl, and P.O. are also formed; SO, has no action at 140° (M., l.c.). -7. Heated in a closed tube at 130° with arsenious oxide, forms As, AsCl₃, and P₂O₃ (Michaelis, l.c.). --8. Thionyl chloride forms PCl₃, POCl₃, and PSCl₃. Chromyl dichloride produces POCl, P2O, PCl, and CrCl, 9. Nitrogen trioxide or pentoride reacts with strongly cooled PCl₃ to form NOCl, P₂O₅, POCl₃, and P₂O₅Cl₄ (Geuther a. Michaelis, B. 4, 766). 10. Many metallic oxides withdraw Cl from PCl. forming metallic chlorides; PbO forms Pb and Pb(PO₃) besides PbCl₂—11. Many metallic sulphides when heated with PCl₃ react to form P₃S₂ and metallic chlorides; e.g. K₂S, BaS, CaS, Sb₂S₃, PbS, &c. (v. Gm.-K. i. 2, 320). - 12. Sulphur reacts at c. 130° with production of PSCI, (Henry, B. 2, 638).—13. Antimony forms SbCl, and P (Gm.-K., l.c.).—14. Red-hot iron filings produce Fe phosphide and FeCl, (Gm.-K.).

15. Zinc, at 100°, forms ZnCl, and P (Most, B.
18, 2029).—16. Platinum and silver are not acted on by PCl_s (Gm.-K.).—17. Sulphuric acid reacts slowly in the cold, rapidly when hot, to form SO₂, HCl, P₂O₃, and SO₂, OH, Cl (Michaelis, J. Z. 6, 239).—18. Phosphorous acid produces P.O. (Nacquet's Chem. German ed. 1868. p. 218). 19. Hydriodic acid reacts at the ordinary temperature, forming PI, and HCl (Hautefeuille, Bl. [2] 7, 198, 200, 203). 20. PSCl₂ and PCl₃ are formed by heating for some hours at 160° with sulphur chloride. - 21. Iodine pentabromide is said to form ICl, and PBr, -22. Phosphorus hydrids produces HCl and solid P₂H (Besson, C. R. 111, 972). SbH, is said to be without action (Mahn, Z. [2] 5, 729).—23. Heated with hydrogen sulphide, HCl and P.S. are formed (Baudrimont, A. Ch. [4] 2, 5).—24. Anmonia seems to form various compounds which have not been fully examined (v. Phospham, p. 104).— 25. Passed over heated ammonium chloride, phospham (q. v.) is formed.—26. With many carbon compounds containing hydroxyl, PCl,

reacts to substitute Ol for OH.

Combinations.—1. With chlorine, to form PCl, (q. v.).—2. With bromins to form several bromochlorides (q. v.).—3. With iodine

to form PLCl, (v. PHOSPHORUS IODOCHLORIDE, P. 138).—4. With titanium chloride to form PCl, TiCl, (Bertrand, M. S. [8] 10, 1331); also with a few other metallic chlorides, e.g. AuCl.—5. With dry ammonia to form PCl, 5NH, (Rose; Besson, C. R. 111, 972).

PHOSPHORUS PENTACHLORIDE PCl. (Phosphoric chloride. Phosphorus perchloride). Mol. w. 207-81. Melts at 148° under pressure; boils at 160°-165°, with partial decomposition to PCl, and Cl. V.D. varies with temperature; c. 103 in un atmosphere of PCl. (v. Properties). H.F. [P.Cl.] = 104,996 (Th. 2, 408).

Formation.—1. By combining PCl, with Cl,

Formation.—1. By combining PCl, with Cl, or by the action of excess of Cl on P.—2. By reacting with PCl, on PH, S.Cl., or SOCl.,—3. By the action of SbCl., on PH, (Mahn, Z. [2] 5, 729).

Preparation.—PCl, may be prepared by the

action of Cl on P, but the PCls is apt to retain pieces of unchanged P, the presence of which may lead to violent explosions; it is, therefore, better to prepare PCl, from PCl, PCl, is placed in a strong flask with a wide neck; the flask is surrounded by a freezing mixture, and dry Cl is passed in by a wide tube which reaches almost to, but does not touch, the surface of the liquid. As the contents of the flask get semi-solid they must be thoroughly broken up by a glass rod. The whole of the PCl, is not changed to PCl, until Cl has passed for a considerable time; the change is not complete until, after closing the flask, shaking thoroughly, and allowing to stand for some time, the presence of greenish-yellow gas in the flask is quite apparent. Excess of Cl is finally removed by the long-continued passage of a slow stream of dry CO₂ (Müller, Z. 1882.

295; Gräbe, Ar. Sc. [3] 5, 477).

Properties. - A white, or slightly yellow, crystalline solid with a strong odour; crystallines in rhomble plates; fumes in moist air, with decomposition; sublimes without melting under 100°, but melts at c. 148° under considerable pressure; boils at c. 160°-165°, with partial dissociation to PCl, and Cl, which re-combine on cooling. PCl, does not conduct electricity (Gm.-K.i. 2, 390). Decomposed by O at c. 300°. Burns in a candle-flame.

Vapour density.—The S.G. of the vapour obtained by heating PCl, is less than that calculated for PCl,, and it decreases as temperature increases until it is equal to half the calculated value. Wanklyn a. Robinson (C. R. 56, 547) showed that the vapour contained free Cl, by diffusing into CO₂, and that PCl₃ was present in the residue. Deville noticed that the vapour showed the colour of Cl, and that the intensity of colour increased as temperature rose (A. 141, 147). The V.D. was determined by Cahours at different temperatures, with the following results (A. 141, 42; v. also Gibbs, Am. S. [3] 18, 277,

1):		
Temp.	S.G. (air = 1)	P.c. Dissociation
182°	5.08	41.7
190	4.99	44.3
200	4.85	48.5
23 0	4.80	67.4
250	4.00	80.0
274	8.84	87.5
288	3.67	96.2
*289	8.69	9597
800	8-65	Q7-R

The temperature whereat 50 p.c. is dissociated is c. 202°. Wurtz (B. 3, 572) showed that, making certain assumptions, the S.G. of PCl, vapour formed in an atmosphere of PCl, is c. 74-6.8, which agrees with that calculated for PCl_s, viz. 7.2.

Reactions .- 1. Heat dissociates PCl, into PCl, and Cl, which recombine on cooling (v. ante).-2. PCl, is decomposed by water to HClAq and POCl, and finally to H,PO,Aq with some HPO, Aq (Gm.-K. i. 2, 390). Thomsen gives [PCP, Aq] = 123,440 (Th. 2, 322).-3. Boric acid and antimonic hydrate react similarly to water (Gerhardt, A. 87, 66, 290; Schiff, A. 102, 111; 106, 116). Boric oxide when heated with PCl_s forms B.O., P.O., and BCl_s (Gustavson, B. 3, 426).— 4. Hydroxides generally, including carbon compounds which contain the group OH, exchange OH for Cl, with production of POCl, and chloride of the radicle before in combination with OH.— 5. Compounds containing the group SII generally react similarly to OH compounds; e.g. SH.H gives OH and PSCl₂.—6. Oxides generally exchange O for Cl.; carbon compounds containing the group CO generally also react in this way. -7. Oxygen reacts with vapour of PCl, at c. 300°, producing POCl₃, P₂O₅, and Cl (Gm.-K. i. 2, 390; Wanklyn a. Robinson, C. R. 56, 547) .-8. PCl, vapour mixed with hydrogen and passed through a red-hot tube produces HCl, PCl, and P (Baudrimont, Gm.-K. i. 2, 394) .- 9. Heated with phosphorus PCl, is produced.-10. The compound PS,Cl, is formed by distilling PCl, with 8 parts of sulphur (Gladstone, C. J. 3, 5). 11. Selenion produces Se.Cl₂ and PCl₃.—
12. Iodine forms PCl₃, and ICl which combines with part of the PCl, to produce PCl, ICl (Gm.-K., l.c.). - 13. PCl3 reacts with many metals to form metallic chlorides and PCl,; sometimes P and metallic phosphides are formed (Baudrimont, J. pr. 87, 300; 88, 78; Casselmann, A. 98, 213). Among the metals which react with I'Cl, are Al, As, Cd, Au, Fc, Pt, K, Na, Sn, and Zn. The metallic chloride formed often combines with the undecomposed PCl₃; this occurs, e.g., with AlCl₃, FeCl₄, HgCl₂, PtCl₄, and SuCl₄ (Wöhler, B. 13, 875; cf. Goldschmidt, C. C. 1881. 489) .-- 14. Phosphorus hadride produces PCl, and HCl; with excess of PH3, HCl, and are formed.-15. Antimony hydride forms PCl, SbCl, and HCl; silicon hydride acts similarly but more slowly (Mahn, Z. [2] 5, 729; ammonia forms phospham (q. v., p. 104) and nitrogen phospham (q. v., p. 104). phochloride (vol. iii. p. 570); also phosphamidoimide (q. v., p. 105; cf. also Besson, C. R. 114, 1364). 16. Sulphur dioxide produces SOCl₂ and POCl₃ (Schiff, A. 102, 111; 106, 116; Persoz a. Bloch, C. R. 28, 86; Kremers, A. 70, 297).-17. Sulphur trioxide forms S2Cl2O, and POCI, (Schiff, l.c.; Michaelis, J. Z. 6, 235, 240, 292; Williamson, Pr. 7, 11).-18. Selenion dioxide when distilled with PCI, forms POCI, SeCl., and P₂O, SeOCI, being formed as an intermediate product (Michaelis, Z. [2] 6, 465).— 19. Phosphoric oxide produces POCl, 20. Boric oxide reacts slowly when heated to c. 140° with PCl,; BOCl, is probably formed, and on heating more strongly BCl, and B,O,P,O, remain (Gustavson, B. 3, 426).—21. Nitrogen dioxide produces NOCl and POOl, (Gm.-K. i. 2, 390).—
22. Silicon dioxide forms POCl., and SiOl, which

combines with the excess of PCl, (Weber, P. 107, 875) .- 23. Vapour of PCl, reacts with many metallic oxides, when these are strongly heated, to form POCl,, and metallic chlorides which frequently combine with undecomposed PCI,. The following react in this way—Al₂O₃, As₂O₄, and As₂O₅ (Hurtzig a. Geuther, A. 111, 159; Michaelis, J. Z. 6, 239), [no reaction with Sb.O.; Schiff, A. 102, 111], CdO, Cr.O., Fe.O., MnO., MoO., Schiff, l.c.), SnO, TiO., (Weber, P. 107, 375; Tittscheff, A. 141, 111), WO., (Gerhardt a. Chiozza, C. R. 36, 1050; Schiff l.c.).—24. Phosphorus sulphide forms PSCl, (Weber, P. 107, 375; Gm.-K. i. 2, 390) .- 25. Carbon disulphide does not react at 100° (Hofmann, A. 115, 264); at 200° PSCl, 'a produced (Carius a. Fries, A. 112, 193), and CCl. (Rathke, Z. [2] 6, 57). - 26. Many metallic sulphides when heated are decomposed by vapour of PCl, with formation of PSCl, S.Cl, and metallic chloride; the following react in this way—sulphide of As, Ba, Bi, Cd, Ca, Pb, Na, Sn. Zn (Weber, *l.c.*; Baudrimont, *l.c.*).— 27. Antimony selenide and lead selenide form SeCl, which forms a double compound with the excess of I'Cl₅. - 28. Hydriodic acid produces I'Cl₃, HCl, and I (Wurtz, Gm.-K., l.c.); hydrobromic acid is without action (Gladstone, C. J. 3, 5); syrupy phosphoric acid solution reacts slowly, the vapours of this acid do not act (Gerhardt, A. 87, 66, 290; Schiff, A. 102, 111; 106, 116; Persoz a. Bloch, C. R. 28, 86).— 29. Conc. nitric acid reacts energetically, forming POCl3 and HCl.-30. Sulphuric acid forms SO. OH.Cl, HCl, and HPO, and Scl.O, as the result of a secondary reaction (Michaelis, J. Z. 6, 235, 240, 292; Williamson, Pr. 7, 11; Baumstark, A. 140, 75) .- 31. Many metallic salts react with PCl,; KNO, gives NOCl and POCl, (Nacquet, Bl. 1860); sulphites form SOCI, (Buchanan, B. 3, 485); Agl produces AgCl and probably a fluoride of P (Pfaundler, W. A. B. 46, 258); KClO, gives POCl.; KSCy forms PSCl., S.Cl., and PCl.; Na.HPO, gives H.,PO, and HCl; haloid salts of the alkalis, and also KCy and K, FeCy, are not acted on by PCl,

Combinations. -1. With iodine chloride to form PCl, ICl (Gm.-K. i. 2, 390). - 2. With selenion tetrachloride to form SeCl., 2PCl. -3. With many metallic chlorides (cf. Reactions, Nos. 13 and 23). These compounds are solids, which sublime with partial decomposition when heated, and are decomposed by water (Baudri-mont, J. pr. 87, 300; 88, 78; Weber, ibid. 77, 65; Casselmann, A. 83, 258) .- 4. With ammonia to form PCl, SNH,; produced by slowly passing dry NH, into a solution of PCl, in CCl, (Besson, C. R. 111, 972; 114, 1264).

Phosphorus, chlorobromides of, v. Phosphorus

Phosphorus, chlorofluoride of, PCl₃F₂. 175 07. V.D. 78. Poulenc (C. R. 113, 75).

Preparation .- Tw stoppered flasks of c. 500 c.c. capacity are connected by a bent tube, which passes through the stoppers; one flask is filled with dry Cl, and the other with dry PF.; that containing PF, is connected with a bulb full of Hg. which can be caused to flow into the flask and so force the PF, into the flask full of Cl. The PF, is slowly driven into the other flask, and the PCl.F, thus formed is kept in contact with Hg for some days (without being shaken

with the Hg, else some PF, may be decomposed) to remove traces of Cl.

Properties — A colourless gas, with very irritating odour; incombustible; liquefied at -8° at ordinary pressure; absorbed and decomposed by water; heated to c. 250° gives PF₂ and PCl₃, also decomposed in the same way by electric sparks.

Reactions.—1. Heat produces PF, and PCl,; the action proceeds at c. 250°.—2., Electric sparks also produce PF, and PCl,.—3. Heated with sulphur to c. 115°, PSF, and S₂Cl₂ are formed.—4. Heated with phosphorus to c. 120° PF, and PCl₃ are formed.—5. Several metals when heated to c. 180° produce metallic chloride and PF, e.g. Al, Fe, Pb, Mg, Ni, and Sn; Hg exerts a slight action at ordinary temperatures, and acts rapidly at 180°; Na seems to absorb PCl₃F₂ entirely.—6. Water reacts rapidly; if a little water-vapour is mixed with PCl₄F₂ the products are POF, and HCl; it the gas is passed into water, H,PQ,Aq, HClAq, and HFAq varo formed.—7. Absorbed by alcohol, with formation of a compound not yet examined.—8. Ammonia is absorbed at ordinary temperature, forming a white solid, which is probably PF₃(NH₂)₂.

Phosphorus, chloro-iodide of, v. Phosphorus

"дороспьовире, р. 138.

Phosphorus, chloronitride of, v. Nitrogen Phosphoculoring, vol. iii. p. 570. Besson (C. R. 114, 1479) recommends to prepare PCl₂N by forming a layer of PCl₃ on the sides of a large flask, by acting on PCl, with Cl, then to heat the PCl, with NH, till it is superficially saturated, and then to heat under reduced pressure.

then to heat under reduced pressure.

Phosphorus.compounds of, with hydrogen and oxygen. Those compounds of P, H, and O, which are acids, are described in the articles Phosphoric ACIDS (p. 124), and Phosphorus, oxyacids of, and THEIR SALTS (p. 149); but two compounds which have been described by Gautier will find a place here. Gautier (C. R. 76, 49) says that the compound P.HO is formed by heating crystallised H.PO, with 5 or 6 times its weight of PCl, to 79°, washing with water, and drying at -10° ; at between 80° and 100° the products of the reaction are H₂PO₄, HCl, and amorphous P. This compound is described as an amorphous yellow powder; unchanged in air when dry, but oxidised slowly when moist; insoluble in most menstrua: burns when heated in air to c. 260°: burns explosively when heated with CuO; unchanged at 240°-250° in CO, but evolves PH. at 265°, and at 350°-860° ordinary P distils off not acted on by dilute acids; oxidised by ordinary HNO₂Aq; conc. H₂SO₄ evolves SO₂ at c. 200°; decomposed by H₂O at c. 170° to H₂PO₂Aq, H₂PO₃Aq, and PH₃; reacts with dilute alkali solutions; NH, combines to form a very unstable brown substance. Gautier (C. R. 76, 173) described another compound P_bH₃O; obtained by adding PI2, little by little, to H2O at 80°-90° allowing the yellow solution to deposit a flocculent pp., washing this with warm water, and drying in vacuo. If water is added slowly to PI₂ the products are HIAq, H₂PO₂Aq, and H₂PO₂Aq. P₂H₃O is described as a pure yellow solid; amorphous, or perhaps showing traces of crystalline form; tasteless and odourless; insoluble in all menstrua; oxidises in air when n.oist, when dry oxidises slowly at 100°; oxidised

violently by HNO.Aq; evolves SO. from H.SO.; gives off PH, when heated to 185° in CO., and ordinary P at 850°; decomposed by dilute alkali solutions to PH, H, H, KPO., and HK.PO.; combines with NH, to form a brown very unstable substance.

Phosphorus, cyanide of, v. Cyanogen phosphide, vol. ii. p. 358.

Phosphorus, fluorides of. Two fluorides of P are known, PF, and PF,; these formulæ are molecular. The compounds are gases at ordinary temperatures.

PHOSPHORUS TRIFLUORIDE PF. (Phosphorous fluoride.) Mol. w. 87-96. V.D. 43-7 (Moissan, A. Ch. [6] 6, 433).

Formation.—1. By the reaction of PbF₂ with Cu phosphide (M., l.c.).—2. By adding AsF₃ to PF₂ (M., l.c.).—3. By the reaction of PbF₂ with PCl₃ or POCl₃ (Güntz, C. R. 103, 58).—4. By adding PBr₃ to genly heated ZnF₂ (M., A. Cl₃ [6] 19, 286).

Preparation.—1. AsF₃ is dropped into perfectly dry PCl₂; the gas is shaken with a little water, and dried over H₂SO₄ (M_{*}, C. R. 100, 272).

2. A mixture of well-dried Cu₂P₂ and PbF₂ free from SiO₂ is heated in a brass tube to dull redness, the gas is passed by a leaden tube through two very small bottles (2 or 3 c.c. capacity) containing H₂SO₄, then through pumice soaked in H₂SO₄, and is then collected over Hg.—3. PBF₃ is gradually added to warm ZnF₂, the gas is washed by passing through water, then dried by passing over pumice soaked in H₂SO₄, and collected over Hg (M. A. Ch. [6] 19, 286).

Properties.—A colourless gas, condensed to a colourless liquid at -10° and 40 atmos. pressure. The gas is not liquefied at 24° under a pressure of 180 atmos., but liquefaction occurs when the pressure is suddenly reduced to 50 atmos. (Moissan, l.c.). PF, does not fume in the air; it is very slowly decomposed by water, with formation of H₂PO₂Aq and HFAq; burns when mixed with 0; decomposed by heat; also by electric sparks.

Reactions and Combinations .- 1. Decomposed by heat; in a glass apparatus P and SiF, are formed; in contact with Pt black a gas is formed, probably containing F (Moissan, C. R. 102, 763).—2. Electric sparks slowly decompose PF₃, forming PF₃ and P (Moissan, C. R. 102, 763).—3. Burns when mixed with pure oxygen and ignited; a mixture of 1 vol. PF, and 1 vol. O explodes violently when sparked, with formation of POF, (M., C. R. 102, 1245).-4. Very slowly decomposed by water, with formation of H3PO,Aq and HFAq; more rapidly decomposed by steam at 100°.-5. According to Berthelot (A. Ch. [6] 6, 358) potash solution produces a fluophosphorous acid probably analogous to fluoboric or fluosilicic acid; Moissan (C. R., 99, 655) says that a fluoride and a phosphite are formed.-6. Absorbed rapidly by bromine with formation of PBr₂F₃ (v. Phosphorus bromoriuoride, p. 181), also by chlorine, with formation of PCl₂F₃ (v. Phosphorus chlorofluoride, p. 133).—7. Decomposed rapidly by solutions of chromic acid or potassium permanganate.-8. Decomposed by hot sodium, copper, boron, and silicon (M., C. R. 99, 655).—9. Combines with ammonia to form white, flocculent compound, which is decomposed

by water (M., I.c.).—10. Combines with fluorine to form PF, (Moissan, Bl. [8] 5, 454).

Determination of composition. — The compound was analysed by Moissan (C. R. 100, 272) by heating a known volume in a glass vessel, measuring the volume of SiF, formed, dissolving the P deposited in HNO Aq, and estimating as Mg-NH, phosphate.

PHOSPHORUS PENTAFLUORIDE PF, (Phosphoric fluoride). Mol. w. 125'96. V.D. 68'2 to 65'1 (Thorpe, A. 182, 201; Moissan, C. R. 102, 763;

103, 1257).

Formation .- 1. By passing PF, into Br at -15°, PBr.F., is formed, and when heated this gives PF, and PBr. (Moissan, C. R. 101, 1490).

2. By the reaction of AsF, with PCl., -3. By direct combination of PF, with F (M., Bl. [3] 5, 454).

Preparation. - AsF, is added gradually to PCl. surrounded by a freezing mixture; the gas which comes off is passed through PCl, contained in a tube which is kept cold, and is collected over

Hg (Thorpe, A. 182, 201).

Properties and Reactions. — A colourless, strongly-smelling gas, which fumes in air and rapidly attacks the membranes of the mouth and the bronchial tubes. Condensed at 15° and 46 atmos. to colourless liquid which does not act on glass (Moissan, C. R. 101, 1490); on partially releasing pressure the liquid solidifies, but soon again becomes liquid (M., I.c.). Decomposed by powerful electric sparks (150 200 mm. long) to PF, and F (M., C. R. 103, 1257), but not by ordinary sparking (Thorpe, l.c.). Incombustible and does not support combustion. Not acted on by heating with phosphorus to dull redness, nor with sulphur vapour at 440°, nor iodine at 500° (M., l.c.). In presence of trace of water acts on glass, forming SiF, and POF, Passed over gently heated spongy platinum is partially de-composed to PF, and F; when the Pt is heated to dull redness a compound of Pt with P and F, probably PF_s.PtF₂, is formed (M., Bl. [3] 5, 454). Phosphorus, fluobromide of; v. Phosphorus

BROMOFLUORIDE, p. 131 Phosphorus, fluochloride of; v. Phosphorus

CHLOROFLUORIDE, p. 133.

Phosphorus, haloid compounds of. P combines readily with the halogens, with production of much heat, to form compounds PX, and PX,; besides these, the compound PL is also known. Several compounds of the type PX, and at least one of the type PX, (viz. PF,), have been gasified, so that the formulæ are molecular. The haloid compounds of P are decomposed by water, the fluorides only very slowly, with formation of oxyacids of P and halogen acids; these compounds also combine with many other haloid compounds, both of metals and non-metals, to form double salts.

Phosphorus, hydrides of. P and H do not resplaces, hydraes of. P and H do not combine directly; but hydrides of P are produced by evolving H in contact with phosphites or hypophosphites. Three hydrides of P have been isolated; PH., PH. (or P.H.), and P.H (or P.H.). Janssen (Repert. Chim. app. 8, 393) obtained a crystalline, explosive substance by the reaction of milk of lime with P, to which he care the formula PH. gave the formula P.H. At the ordinary temperature and pressure the first hydride is gaseous, the second siquid, and the third solid. The formula PH is molecular; Croullebois (C. R. 78, 496)

said that the V.D. of the liquid compound shows the mol. w. to be P.H., but no details are given; the mol. w. of the solid compound is unknown. The liquid hydride takes fire in contact with air; the gas inflames in air at c. 150°, and the solid at c. 200°; the processes for preparing gaseous PH, generally also produce more or less liquid P.H., the resultant gas is therefore spontaneously inflammable. PH, resembles NH, in its reactions, but it is much less decidedly alkaline; phosphonium compounds, c.g. PH,I, similar to ammonium compounds, are known

PH. PHOSPHORUS TRIHYDRIDE phoretted hydrogen. Phosphine). Mol. w. 88.96. Liquefies - 90°; solidifies -133.5°; melts at 2-132-15°; boils c. -85° (Olszowski, M. 7, 371). S.G. (air = 1) 1-185. V.D. 17°2. H.F. [P,H'] = 36, 600 (Ogier, C. R. 87, 210). S. 112 (Dy-

browski, J. 1866, 735).

Formation. - The gas obtained by the following methods is never pure PH_1 ; it contains more or less P_2H_1 , and generally also H; it is usually spontaneously inflammable. 1. By evolving H in contact with phosphites or hypophosphites in solution; phosphates are not reduced (Gm.-K. i. 2, 138; Fresenius, Fr. 6, 203; Herapath, Ph. 7, 57). P and H do not combine directly (Fourcroy a. Vauquelin, A. Ch. 21, 202; Dusart, C. R. 43, 1126).—2. By heating solutions of phosphites or hypophosphites (Gm.-K., l.c.). 3. By the action of boiling alkali solutions on P (H. Rose, P. 6, 199; 8, 191; 14, 188; 24, 109, 295; 32, 467; 46, 633).—4. By heating P with syrupy H₃PO,Aq, or with HClAq, HBrAq, or HIAq (Oppenheim, Bl. [2] 1,163).—5. By heating P with water to 200° (Oppenheim, l.c.).— 6. By long-continued heating P with blood to 35°-41° (Dybrowski, J. 1866. 735).-7. By the action of the electric current on moist molten P (Groves, C. J. 16, 268).—8. By heating P with H₂O to c. 200°.—9. By decomposing Zn phosphide by dilute acids, or boiling alkali solution Schwarz, D. P. J. 191, 396). According to Lüpke $(C.\ C.\ 1890.\ {
m ii}.\ 642)$, the gas obtained by acting on phosphide of Mg, Sn, or Zn with dilute acid is not spontaneously inflammable. - 10. By treating Cu phosphide with KCN and a little 80 p.c. alcohol (Gm.-K. i. 2, 138).—11. By decomposing phosphides of the alkali or alkaline earth metals by water or dilute acids.

Preparation .- 1. A small flask carrying an exit tube is nearly filled with a conc. solution of KOH in 80 p.c. alcohol; small pieces of P are dropped in, and the flask is heated; the gas is passed through a CaCl, tube to absorb alcohol vapour, and collected over water. The gas thus prepared does not contain more than c. 45 p.c. PH. (Hofmann, B. 4, 200); it is generally free from the spontaneously inflammable hydride. The gas prepared by the action of KOHAq on P contains some P2H, and much H; it is spontaneously inflammable in air. The simplest way of preparing this gas is to place a few small pieces of P in a little flask which carries a cork with two tubes, one fitted with a stopcock and passing just through the cork, and the other bent like an ordinary gas-delivery tube and dipping under water in a basin; the flask is nearly filled with conc. KOHAq; the tube with the stopcock is attached to the gas-supply, the cork is fitted loosely into the flask, and a stream of coal gas is passed

through the apparatus for a few minutes, after which the cork is fitted tightly into the flask, the estopcock is closed, and the flask is heated. During this process the end of the delivery-tube is kent under the surface of the water in the basin. After a few minutes gas is evolved, and each bubble takes fire as it comes into contact with the air after passing upwards through the water in the basin. If the whole of the air is not driven out of the apparatus before the flask is heated, serious explosions may occur.—2. The best way of preparing pure PH, is to decompose PH,I by KOHAq. A small flask is fitted with a caoutchouc cork, which carries a tube furnished with a bulb and stopcock and an exit-tube; pieces of PH,I about the size of peas are placed in the flask along with several small pieces of glassrod, KOHAq (c. 1 pt. KOH in 2 pts. H2O) is allowed to drop from the bulb-tube very slowly on to the PH I in the flask. Pure PH, is evolved without heating; if the KOHAq is added too rapidly the gas may contain a little P.H. and be spontaneously inflammable (Hofmann, B. 4, 200; Rammelsberg, B. 6, 88). About 1 litre PH₃ is obtained from 7-7½ g. PH₄I (for preparation of PH,I v. Phosphonium compounds, p. 123).

Properties .- PH, is a colourless gas, with a very disagreeable smell like that of onions mixed with decaying fish; very poisonous; slightly soluble in water (v. beginning of this article). The solution glows in the dark, and deposits amorphous P when exposed to light and air; on boiling, PH, is given off. PH, is slightly soluble in alcohol, ether, ethereal oils, and blood; it is completely absorbed by solution of bleaching powder, also by Cu,Cl, in HClAq (v. Combinations, No. 4). PH, combines with the halogen acids to form salts similar to those of NH₄ (v. Phosphonium compounds, p. 123); the H of PH₃ is replaceable by organic radicles (v. Phosphines, p. 116). PH, reduces solutions of salts of heavy metals. PH, free from P,H, takes fire in air at The gas prepared as mentioned under Formation takes fire immediately on contact with air; it loses this spontaneous inflammability by exposure to sunlight, by passage through a U-tube cooled to -10° , by mixing with small quantities of Al_2O_3 , wood charcoal, various gases, &c. (v. Graham, P. M. 5, 401). These processes remove P,H, to the presence of which the ready inflammability of the gas is due. Addition to PH, of 1 of its weight of P,H, causes the gas to become inflammable in air; the presence of $\frac{1}{1000}$ to 1 or NO produces the same effect (Graham, l.c.; cf. Landolt, A. 116, 193). The gas prepared by the action of KOHAq on PH.I (v. Preparation, No. 2) is described by Hofmann as taking fire when gently warmed, and being sometimes inflamed by the friction of the stopper of the bottle in which the gas may be kept. According to Rammelsberg (B. 6, 88), the gas prepared in this way is sometimes spontaneously inflammable. The gas prepared in this way takes fire when passed into conc. AgNO,Aq (Poleck a. Thümmel, B. 16, 2442).

Reactions.—1. PH, is decomposed by heat; when passed through a red-hot tube, lustrous, amorphous P is deposited (Merz a. Weith, B. 18, 718).—2. Decomposed by electric sparks to

P and H; the process takes place with regularity, 20 c.c. are decomposed in 5-6 mins, with production of P and 30 c.c. H (for description of an apparatus for lecture purposes v. Hofmann, B. 4, 204) .- 3. PH. burns in air at c. 150° with production of P2O, and H2O; if a cold substance is brought into the flame, yellow red specks of amorphous P are deposited .- 4. No reaction occurs when pure PH, free from P,H, is mixed with oxygen, but the mixture explodes if the pressure is suddenly lowered; explosion is said to occur after some hours at the ordinary pressure (Labillardière; v. Gm.-K. i. 2, 144).— 5. Bubbles of PH, burn explosively to PCl, and HCl if passed into a vessel filled with chlorine; if the Cl is diluted with CO, the action is slower, and some P separates.—6. Bromine and iodine react similarly to Cl; if PH, is heated gently with iodine, some PHI is formed .- 7. Heated with sulphur, H.S and P sulphide are formed (Jones, C. J. [2] 14, 148).—8. Salts of the alkali metals and of the alkaline earth metals decompose PH₃, producing phosphites and hypophosphites (Winkler, P. 111, 443).—9. Solutions of salts of heavy metals generally decompose PH, with production of metallic phosphides, which sometimes combine with the excess of the metallic salts (v. Kulisch, A. 231, 327). AgNO, Aq forms a yellow compound (? Ag, P.3AgNO,), and then black Ag, P which is quickly reduced to Ag (Poleck a. Thümmel, B. 16, 2442); HgCl, Aq, according to Ashan (Chem. Zeitung, 10, 82, 102), forms a yellow compound $3 Hg_1 P_2$.7HgCl₂, a red compound 4Hg₃P₂.5HgCl₂, and a brown compound Hg₃P₂.HgCl₂; PtCl₁ is said to form Pt.PH₂ (Gavazzi, B. 16, 2279); chlorides of Cr, Co, Cu, Au, Fe, and Ni are reduced, with formation of phosphides of the metals, or of metal and P. 10. Potassium permanganate solution is reduced by PH, to Mn₂O₃, K₂HPO₄ being also formed (Gavazzi, B. 16, 2279).—11. PH₂ is decomposed by many oxides, acids, and salts, e.g. by H.S, SO, NO, N₂O, PCl₃, HNO₃ (no reaction at -25°; Besson, C. R. 109, 644), H₂SO₄ (v. Besson, l.c.), SbCl₃, &c., also by certain metals, e.g. Sb, Cu, Fe, K, and Zn (v. Gm.-K. i. 2, 138).—12. With haloid compounds of arsenic PH, reacts to form haloid acid and phosphide of As (Besson, C. R. 110, 1258). -13. With an ethereal solution of bismuth bromids forms a black lustrous body, probably PBrH(BiBr₂)₂ (Cavazzi a. Tivoli, G. 21,

Combinations.—1. With the halogen acids to form compounds of the type PH,X (X = CI, Br, or I); combination with HI and HBr occurs at the ordinary temperature and pressure, with HCl combination occurs at -30° to -35° under the ordinary pressure, or at 14° under a pressure of 20 atmos. (Ogier, Bl. [2] 32, 483; v. also Skinner, Pr. 42, 283). At very low temperatures PH, seems to combine with H,SO, (v. Phosphonium sulphare, p. 124). "The compounds PH,X are described under Phosphonium compounds, p. 123.—2. When PH, is strongly compressed in presence of water, the gas liquefies and floats on the water. If the pressure is now suddenly released, a white crystalline solid is formed, but this decomposes again when the pressure is reduced below a certain amount (Cailletet a. Bordet, C. R. 95, 58; v. Phosphonium compounds, p. 123).—8. White compounds, assily

decomposed on removing pressure, are said to be formed by compressing PH, with carbon divide, and with carbon disulphide, in presence of water (C. a. B., l.c.).—4. A solution of cuprous chloride in HClAq absorbs PH, rapidly; a white crystalline mass of Cu.Cl., 2PH, is formed, but this liquefies as more PH, is passed in (? with formation of Cu.Cl., 4PH,); the crystals Cu.Cl., 2PH, are decomposed by warming, or by addition of water, to PH, HCl, and Cu.P; the liquid compound loses PH, in a stream of an indifferent gas, with production of the crystalline compound (v. Riban, Bl. [2] 35, 385). This behaviour of PH, towards Cu.Cl. gives a method for preparing pure PH, and also for estimating PH, in a mixture of gases.

PHOSPHORUS DIHYDRIDE PH, or P.H. (Liquid phosphoretted hydrogen). Mol. w. said to be 65-92, corresponding with V.D. c. 33, but no details given (Croullebois, C. R. 78, 496). Gattermann a. Hausknecht (B. 23, 1174) failed to determine V.D. as the compound always decomposed. A spontaneously inflammable gas containing P and H was obtained by Gengembre in 1783 (Crell's Ann. 1789. 450). The fact that this gas lost its inflammability by standing over air containing water was explained by Dumas (A. Ch. [2] 31, 113) by supposing that the gas was a mixture of two hydrides of P, one only of which was spontaneously inflammable; to one of these Dumas gave the formula PH, and to the other the formula PH₃. In 1832 H. Rose (P. 6, 199; 8, 191) thought that the two gases had the same composition, but were isomeric one with the other. After Graham (P. M. 5, 401) had examined the conditions under which spontaneous inflammability was removed from or bestowed on the gas, Le Verrier (A. Ch. [2] 60, 174) came to the conclusion that the gas consisted chiefly of PH, but that it contained also a very inflammable compound PH, which was decomposed by light into PH, and a solid hydride PH. In 1845 P. Thénard made a fuller study of the subject (A. Ch. [3] 14, 5); he showed that spontaneously inflammable phosphoretted hydrogen, when passed through a tube cooled to under 10°, deposited a liquid having the composition PH2, which liquid was extremely inflammable, and that this liquid decomposed in light into gaseous PH, and a solid to which he gave the formula P.H. In 1874 Croullebois said that the V.D. of the liquid hydride corresponds with the formula P₂H₄, but no details were given (C. R. 78, 496); in 1890 Gattermann a. Hausknecht attempted to determine V.D., but found that the compound decomposed (B. 23, 1174).

Preparation.—Impure Ca phosphide is prepared by heating dry CaO to bright redness in a crucible, and adding dried P little by little, the lid being replaced after each addition of P. The crucible should be arranged so that the P is brought under the strongly-heated CaO; this may be done by placing a few pieces of P in a crucible, filling up with dry CaO, covering tightly (but leaving one small hole), placing the crucible in a furnace arranged so that the lower part of the crucible projects downwards through the bottom of the furnace, heating the upper part of the erucible to bright redness, and then warming the lower part so as to vapourise the P. Small quantities are prepared by placing a dry piece of

P in the closed end of a tube of hard glass, partly filling the tube with dry CaO, arranged so that there is a little space between the CaO and the P, placing the tube in a combustion furnace, heating the CaO strongly, and then warming the P. The CaO is transformed into a mixture of Ca phosphide and phosphate; the phosphide is nearly black : the unchanged CaO is picked out when the action is over, and the phosphide is at once placed in a stoppered bottle. (For modifi-cation of process v. Gattermann a. Hausknecht, B. 23, f174.) A three-necked bottle of about 2 litres capacity is filled three-quarters with water: one of the necks carries the tube from a H apparatus, which tube dips considerably under the water, the middle neck carries a piece of tubing about 15 mm. internal diameter, dipping 2 or 3 cm. under the water, and the third neck carries an exit tube in communication with a condenser; between the condenser and the three-necked bothle is placed a test tube, to collect part of the water vapour coming over. The condenser consists of a tube about 100 mm. long and 30 mm. diameter, narrowed so that the lower end forms a tube about 40 mm. long by 12 mm. wide; this condenser is closed by a cork through which pass the entrance tube from the threenecked bottle and an exit tube, which is bent downwards and dips under the surface of water; these two tubes are cut off obliquely just below the cork. The condenser is placed in a deep vessel full of cold water which contains sufficient ice to keep the temperature at 0°. H is passed through the apparatus until all the air is driven out, the three-necked bottle is placed in a waterbath until the contents are warmed to 60°, and Ca phosphide, in pieces the size of peas, is dropped down the wide tube in portions about 2 g. at a time and at a rate such that 50 g. are added in 15 to 20 minutes. Gaseous P hydride passes off and bubbles up through the water, and the liquid hydride collects in the condenser, about 1-2 c.c. being obtained for 50 g. Ca phosphide used (Hofmann, B. 7, 531; Gattermann a. Hausknecht, B. 23, 1174; the many precautions to be taken in working with this compound are described by G. a. H.).

Properties and Reactions.—A colourless, highly refractive liquid; insol. in water; burns in air, with bright flame to P₂O, and H₂O; does not solidify at -10°; boils 57°-58° at 735 mm. (G. a. H., Lc.). S. G. 1-007 to 1-016 (G. a. H.). Decomposed by light into PH, and solid P₂H; the liquid may he kept for a short time in sealed tubes, but decomposition soon begins, and the tubes explode violently (G. a. H.). The same decomposition is effected by conc. HClAq, air mixed with CO₂, &c. Passage of the gas prepared as described above through a little conc. HClAq removes every trace of PH₂, and hence causes the gas which issues to be non-inflammable. If CO₂ is passed through the U-tube containing liquid PH₂ a nearly invisible greenish light appears at the end of the tube; this flame is not hot enough to ignite a candle (v. Hofmann, B. 7, 531; Thénard, A. Ch. [3] 14. 5; Bonet a. Bonfil, J. pr. 55, 247; Gattermann a. Hauskecht, B. 23, 1174). The composition of PH₂ was determined by Thénard by decomposing a known quantity by direct sunlight in a graduated tube filled with Hg: 100 parts liquid phos-

phide gave 61.8 parts gaseous PH, and 38.2 parts solid P₂H; -i.e. 1 molecule P₂H was produced for 8 mols. PH₃, hence the equation 5PH₄ = P₂H + 3PH₃. This equation was confirmed by G. a. H., who made also direct estimation of H by burning with PbCrO₄ in a current of CO₂ (B. 23, 1174).

DIPHOSPHORUS HYDRIDE P_2H or P_4H_2 . Mol. w. unknown. H. F. $[P^2,H] = 17,700$ (Ogier, C. R.

89, 707).

Formation.—1. By decomposing phosphide of Ca or K (Magnus, P. 17, 52) by HClAq.—2. By the action of light, HClAq, Cl (Le Verrier, A. Ch. [2] 60, 174), and various other reagents, on PH.—3. By the decomposition of PI₂ by water (Rüdorff, P. 128, 473). Hittorf (P. 126, 193) obtained only amorphous P by this process.

Preparation. — A two-necked bottle is arranged with an exit tube dipping under water, and a wide entrance tube, down which is passed the delivery tube of a H-apparatus; conce HClAq is placed in the bottle, H is passed through until all air is driven out the H apparatus is removed, and small pieces of freshly-prepared Ca phosphide (for preparation v. Preparation of phosphorus dihydride, p. 137) are dropped slowly into the bottle. The P₂H which forms in the bottle is rapidly washed with cold water, and dried in vacuo (P. Thénard, A. Ch. [3] 14, 5).

Properties.—A yellow flocculent powder, which comes orange-yellow in light; tasteless and odourless. When dry may be heated to c. 200° before taking fire; ignited by a blow of a hammer.

Reactions.—1. Ignited by heating in air to c. 200°; also by a blow of a hammer.—2. Slowly decomposed in moist air, especially it in sunlight, to P₂O₃ and H.—3. Distillation in hydrogen produces PH₃ (Thénard, l.c.).—4. Chlorine forms PCl₃ and HCl.—5. Dissolves in dilute nitric acid; oxidised with ignition by conc. HNO₂Aq.—6. Alcoholic solution of potash produces PH₃ and H; addition of water to the reddish solution ppts. yellow flocks of? amorphous P or a lower oxide of P.—7. Explodes when mixed with potassium chlorate, silver oxide, mercuric oxide, or cupric oxide, and struck or warmed.
S. Ppts. metallic phosphides from solutions of salts of many heavy metals (Le Verrier, l.c.).

Determination of composition.—The quantity of P in the solid hydride was determined by Thénard by heating with a weighed quantity of PbO, and weighing the mixture of PbO and Pb phosphate thus produced; the H was determined by decomposing by red-hot Cu, and collecting the H set free. Rüdorff decomposed the hydride by heat, and collected and analysed the mixture of PH, and H thus formed; he also oxidised the compound by HNO₂Aq, and estimated P as Pb phosphate.

Phosphorus, iodides of. P and I combine directly, even at -24°; two iodides, PI₂ and PI₃, have been isolated, and the existence of a third, PI₃, is probable.

PHOSPHERUS DI-TODIDE PI₂ or P₂I₄. Mol. w. not known. H.F. [P,I²] = 9,880 from solid P and I; 20,680 from solid P and gaseous I (Ogier, C. R. 92, 88).

C. R. 92, 88).

Formation.—1. By adding I to P Combination occurs even at -24°, with production of much heat, and ignition of the excess of P if air is admitted; amorphous P is produced be-

sides PI, (v. Wurts, A. Ch. [8] 42, 129).—2. By the reaction of I with PH; also of I in acetic acid on PCl, (Hofmann, A. 103, 805; Ritter, A. 95, 210).

Preparation.—One part by weight of P is dissolved in CS, and St parts of I are added little by little. When the colour of the dark brownish-red liquid thus produced has changed to orange it is cooled to 0° for some hours, when the vessel becomes filled with crystals; the crystals are freed from CS, by heating in a water-bath, while a stream of dry air is passed over them (Coreawinder, A. Ch. [3] 30, 242). The crystals may also be obtained by evaporating the solution in CS, in a stream of CO, (Borthelot a. Luca, C. R. 39, 748). Corenwinder says that from 2 to 3 g. P, and 60 to 75 c.c. CS, are convenient quantities to use.

Properties and Reactions.—Large orange-coloused prisms, melting at 110° (Gorenwinder, l.c.). Heated in O gives P₂O, and I (Berthelot, C. R. 86, 628, 787, 859, 920; 87, 875, 667). Decomposed by H₂O to H₂PO₃Aq, PH₃, HIAq, and a yellow flocculent solid supposed to be amorphous P (Hittorf, P. 126, 193), regarded by Rüdorff as solid P₂H₂ (P. 128, 473), and said by Gautier (C. R. 76, 49, 173) to be P₃H₃O.

Phosphorus Tri-iodde PI, (Phosphorous iodiale). Mol. w. 410-55. H.F. [P,I] = 10,900 (Ogier, C. R. 92, 83). This compound is obtained in large red prisms by dissolving one part of P in CS₂, adding a solution of 12½ parts of I in CS₂, concentrating much out of contact with air, and then placing in a freezing mixture. As the crystals are very sql. CS₂, they should be at once freed from mother-liquor, and dried in a stream of dry air at c. 50°. The crystals melt at 55°, and boil at a higher temperature, with evolution of I. PI₂ is very deliquescent; moist air decompeses it at once to H,PO,Aq and HIAq (Conenwinder, A. Ch. [3] 30, 242).

Phosphorus Perta-todde PI₄ (Phosphoric

PHOSPHORUS PENTA-IODIDE PI₈ (Phosphoric todide). Isolation doubtful. Hampton (C. N. 42, 180) obtained a dark-crimson, very deliquescent solid, giving numbers on analysis agreeing with 80 p.c. PI₈ + 20 p.c. PI₈, by dissolving P in a little CS₂ in a stream of pure dry N, adding rather more than enough I to form PI₈, distilling off CS₂ (in a N stream) at 45° under reduced pressure, and then warming to 50°; at 55°, under the reduced pressure, I began to sublime.

Phesphorus, iodo-chloride of, PLCl. Produced by adding much I to a little PCl. allowing to stand in moist air for some days, drying the crystals in a stream of air, dissolving in CS, and crystallising: large, red, six-sided crystals, very hygroscopic; decomposed by water to H.PO.Aq, HClAq, and HIAq (Moot, B. 13, 2029).

Phosphorus, nitride of. No compound of Pand N has been isolated with certainty. A substance supposed to be a flitride by Rose (P. 24, 303; 28, 529) and Wohler a. Liebig (A. 11, 139) was found to contain H. Briegleb a. Geuther (A. 123, 236) think that a compound P.N. is perhaps produced by the reaction of PCl, on hot Mg,N, in an atmosphere of N. Phosphorus, oxides of. P and O combine

Phosphorus, oxides of. P and O combine very readily, with production of much heat; four compounds are produced according to the conditions: P.O. P.O. P.O. and P.O.; the V.D.

of the second of these shows that its mol. formula as a gas is P₄O₅. The oxides P₂O₅ and P₂O₅ are anhydrides; the former reacts with water to produce the acid H.PO,, and the latter to produce three acids, HPO, H,PO, and H₄P₂O₇; the oxide P₂O₄ is not the anhydride of a corresponding acid—with water it produces the two acids H₂PO₄ and H₂PO₄.

The only oxide formed when P glows in air at ordinary temperature is P₁O₃, but P₂O₄ is formed by drawing air over P without the latter glowing (Thorpe a. Tutton, C. J. 57, 573); at 50°-50° small quantities of P₂O₄ are produced, and this oxide is produced in larger quantities when the P is actually ignited; at moderately high temperatures and with a limited supply of air the oxide P.O is formed in addition to P.O. and P2O2. If the products of the slow burning of P in dry air are heated together in CO2, the oxide P2O4 is formed, along with some P4O. The products of burning P in a limited supply of dry air generally contain small quantities of P; this may be removed by sucking the products through a tube heated by steam (Thorpe a. Tutton, C. J. 49, 833).

PHOSPHORUS SUBOXIDE P.O. Mol. w. uncertain. Some doubt still remains concerning the composition of the lowest oxide of P; but the evidence is in favour of the existence of a definite oxide P.O. Le Verrier (A. 27, 167) obtained a yellowish solid by exposing P in PCl, or in ether to air, warming the solid thus formed with water, and drying over H2SO. A similar product was obtained by the incomplete combustion of P in air, or by the action on P of such oxidisers as iodic or periodic acid in presence of water (v. Gm.-K. i. 2, 107). This substance was generally looked on as an oxide of P; Le Verrier gave it the formula P₄O; Schrötter (W. A. B. 8, 246) thought it was only a mixture of ordinary and amorphous P. Reinitzer a. Goldschmidt (B. 13, 845) obtained the oxide P₄O by heating POCl, with P to 200°-250°, also by heating POCl, with Zn, Mg, or Al, at 100°. Thorpe a. Tutton (C. J. 49, 833) found that P₄O is one of the products of burning P in a limited supply of air at moderately high temperatures, and that it is formed when the products of the slow burning of P in dry air are heated to c. 300° in CO... The experiments of R. a. G. indicate the existence of two varieties of P₄O; one of these reacts with hot alkali solutions, evolving PH,, and reduces salts of Au and Ag and mercurous salts, and the other is not acted on by alkalis, and does not reduce salts of Au, Ag, or Hg.

Preparation and Properties of P.O which reduces salts of Ag, Au, and Hg.—1. Thin plates of pure Zn are heated with POCl, in a sealed tube in a water-bath at 100° for some hours, the liquid, with suspended solid matter, is poured off, the solid is allowed to settle and the liquid is decanted off; the solid is heated as before for some time with POCl, (to remove any Zn present), the liquid is poured off, the solid is washed with CHCl, to remove POCl, then with HClAq and finally with water; the solid is then dried for some days in vacuo (Reinitzer a. Goldschmidt, B. 13, 849); the other products of the reaction are ZnCl, and Zn2PO. As thus prepared P₄O is an ofenge-red powder. It very obstinately refains water, the sample made by R. a. G. con-

tained c. 8 p.c. water, but the P and O were in the ratio P₄O. This oxide in moist air evolves PH.; it reacts with boiling alkali solutions forming PH, and alkali phosphite and phosphate; solutions of salts of Au and Ag, and mercurous salts, are reduced with ppn. of the metals; heated in H, P is given off, and P₂O₅ remains.—2. PCl₃ is placed in an open flask, of c. 1 litre capacity, containing a layer about 2 cm. thick of P in small pieces; the PCl_a just covers the P; after c. 2 days the PCl_a is poured off, the pieces of P and the adhering yellow film are loosened from the flask, and allowed to fall slowly into cold water (if water is added in quantity, heat is produced, and the products of the slow oxidation of P are decomposed). After a little, the water is filtered from suspended P. and the clear yellow filtrate is heated to 80°, when a very finely divided yellow solid settles down; this solid is washed with warm water in a filter removed from the filter while moist, and placed in a basin, over H.SO, in vacuo. Le Verrier's P.O was tasteless and odourless, did not change in dry air or O, but in moist air it gave off PH,; it was decomposed somewhat above 360°, giving off P and leaving P,O,; oxidised by Cl to PCl, and P₂O₃; heated with conc. H₂SO₄, gave SO₂; unacted on by HClAq; oxih₂O₄, gave SO₅; unacted on by HNO₄Aq; exploded wifh KClO₅; readily combined with H₂O-to form P₄O.H₂O. The oxide obtained by Thorpe a. Tutton (C. J. 49, 833) was formed by slowly burning P in dry air, transferring the products to a tube filled with CO₂, exhausting by a Sprengel pump, and heating to 290°; as the oxide is described as orange-red, it was probably the form of P.O which reduces salts of Au. Ag.

Preparation and Properties of P.O which does not reduce salts of Ag. Au, and Hg.—POCl, is heated with an excess of P in a sealed tube to 200°-250°; the sides of the tube become covered with a scarlet-coloured solid, which is washed with CS₂ (to remove P) and dried in vacuo (R. a. C., Lc.; the other products are PCl₃, P₂O₃Cl₄ and a little P₂O₃). As thus prepared, P₁O is a scarlet-red solid; S.C. 1-88; it is not constant to the colour scarled in solutions and its constant and it acted on by water or alkali solutions, and it does not reduce salts of Ag, Au, or Hg. This form of P₄O seems to have been obtained by Pelouze (A. 3, 52) by burning P in O; and by Le Verrier (A. 27, 175) by burning P in a thin layer on a porcelain plate, washing with water to remove oxyacids, and boiling with PCl, to remove P.

PHOSPHOROUS OXIDE P.O. (Phosphorus trioxide. Phosphorous anhydride.) Mol. w. 2196; same in solution in C.H. (Thorpe a. Tutton, C. J. 57, 545). Melts at 22.5°; boils at 178.1° (T. a. T.). S.G. $\frac{21^0}{6^0}$ liquid P₄O₆ 1-9431; solid P₄O₆ at $\frac{21^0}{6^0}$ c. 2-135. S.G. at b.p. = 1-6897 (T. a. T.). V.D. 111-9. S.V. 130-2 (T. a. T.). $\mu_{A} = 1.5311$; $\frac{\text{Mol. w.} \times \mu}{\text{S.G.}} = 60.5$ (T. a. T.). Mol. w. $\frac{\mu_H - \mu_A}{8.G.} = 4.17$. M.M. 9.962.

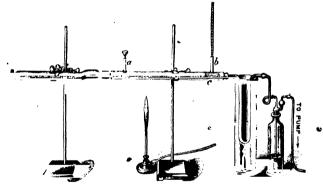
Preparation.—A piece of combustion-tubing about 40 mm. bore is drawn into the shape shown in the figure on following page, and is fitted by a

good cork into a brass tube, which is surrounded by a wider tube of brass; water is introduced at a between the brass tubes, and a thermometer is placed at b. A loose-plug of glass-wool is placed in the inner brass tube at c. The U-shaped condenser is of rather narrow bore, the limbs are about 800 mm. long, a small bottle is attached to the vertical piece at the bottom of the condenser, which is itself connected with the inner brass tube by a good cork; the condenser and small bottle are surrounded by ice and salt. The bottle between the condenser and the pump contains oil of vitriol. Two sticks of P are dried between filter-paper, cut into pieces c. 25 mm. long, and placed in the combustion tube, which is then narrowed at the open end and fitted into the brass tube; the pump is set in action, and the P is ignited by holding a small flame beneath the open end of the combustion-tube. Air is sucked over the P as rapidly as possible; if the combustion is too local, much P.O. is formed; considerable quantities of red P.O are formed near the burning P. When the P has burnt for c. 15 mins. the water in the brass tube is heated to c. 50°, at which temperature it is kept till near

132°. Mol. w. as gas, and also in solution in C.H. (determined by cryoscopic method), corresponds with P_sO_s . Soluble without change in O_sH_s , CS_s , $CHCl_s$, and ether. Heated to c. 200° in sealed tube begins to decompose to P_sO_s and P. Decomposed by light, with separation of red P. T. a. T. (C. J. 59, 1019) several times obtained clear, transparent, perfectly-formed crystals of P4O8 by slow spontaneous sublimation in vacuo, which remained unchanged for many days, although exposed to light. Spec. volume at b.p. = 130.2. (For details of thermal expansion and S.G. at B.p. v. T. a. T., C. J. 57, 545.) Reacts slowly with cold water, forming H_3PO_3Aq; with boiling water reaction is violent, PH, is evolved, and red P, or perhaps P,O, and H,PO,Aq are formed. Oxidises to P2O, by exposure to air or O: if temperature is raised the P.O. ignites and may explode. P.O. has a well marked physiological action; the action of P may be due to P.O., formed by the air oxidising the P (T.a. T., l.c. p. 573).

Reactions.—1. Heat decomposes P.O., form-

ing P2O4 and P (? P4O); the action begins at c. 210° in a sealed tube, and the whole of the P.O.



the end of the experiment, when it is raised to 60°. P.O. begins to collect in the condenser about 80 mins. after starting the combustion; if the glass-wool is packed properly (it should not be too tight) no P₂O₂ passes into the condenser, and if the temperature of the water does not exceed 60° only very small quantities of P pass over. The process is stopped when c. 5ths of the P is burnt, else the P₄O₆ may be oxidised. The condenser is removed, the P₄O₆ is melted by the heat of the hand, and run down into the little bottle, from which it may be transferred to another bottle which has been filled with dry CO.; this bottle should have a very tightlyfitting stopper, and should be kept in the dark in an atmosphere of CO₂ (T. a. T., *l.c.*).

Properties.—A white snow-like solid, with an

alliaceous offour resembling that of P; when melted and cooled slowly crystallises in long thin prisms, probably monoclinic; melts at 22.5° to a clear, colourless, very mobile liquid, which solidifies again at 21°; the liquid may be cooled in a narrow tube several degrees below m.p. without solidifying; boils at 178:1° in CO, or N.

is decomposed at 440° (T. a. T., p. 552). -2. Rapidly acted on by light, becoming yellow and then dark-red (T. a. T., p. 553). The action of light separates red P; the amount obtained after several months' exposure does not exceed 1 p.c. (T. a. T., C. J. 59, 1019). By exposing P.O. to light for some months in a sealed tube filled with dry CO2, then melting, filtering through glass-wool, and repeating this process several times, T. a. T. eventually obtained P4Os which remained perfectly clear and colourless after twelve months' exposure (l.c., p. 1023).-3. Oxidises to P.O. in air or oxygen; when quite free from P, the oxide is not spontaneously inflammable. Under reduced pressure in O the P.O. glows; on raising temperature to c. 70° at ordinary pressure the glow gives place to flame. Combination occurs between vapour of P4O6 and O; ozone is not formed. When P₄O₆ is thrown into O heated to 50°-60° ignition occurs with an intensely brilliant flame (T. a. T., C. J. 57, 569).—4. Glows continuously, and oxidises to P₂O₃, when a stream of ozonised oxygen is passed over it .- 5. Ignites in chlorine, burning with a Can be gasified in Hofmann's V.D. apparatus at greenish flame; when surrounded by ice and

exposed to slow stream of Cl a liquid is formed, which on distillation gives POCl, while PO.Cl (?) remains (T. s. T., C. J. 57, 572).—6. Reacts vio-lently with liquid bromine; using Br vapour at ordinary temperature, T. s. T. (C. J. 59, 1020) obtained PBr, and P₂O₃, and on then heating POBr, and PO₂Br (?) were formed.—7. Iodine reacts slowly; by heating with I and CS₂ under pressure, P₂O₂ and P₂I₄ are produced (T. a. T., *l.c.*, p. 1021). 8. Heated with sulphur, in CO₂ or N, two layers of liquid are formed; at 160° there is violent reaction, and solid P.O.S. is produced (v. Phos-PHORUS, SULPHOXIDE OF, p. 140; T. a. T., l.c., p. 1022) .- 9. Seems to form a Se compound analogous to P,O_aS, by heating with selenion (T. a. T., l.c., p. 1026).—10. Dissolves very slowly in water, forming H_1PO_1Aq (T. a. T., C. J. 57, 567); $P_4O_4 + 6H_2O + Aq = 4H_1PO_1Aq$. The action of hot water is very energetic; red P, or red P,O, is ppd., inflammable hydride of P is evolved, and H₃PO,Aq is formed; if the quantity of P₄O₆ exceeds 2 g. the action of hot water is violently explosive .-- 11. Dry hydrogen chloride is rapidly absorbed; PCl, is formed along with H.PO., H.PO., and yellow P (T. a. T., C. J. 59, 1022). - 12. Conc. sulphuric acid reacts violently, forming H₃PO, and SO₂; if 1 g. or more P4O6 is used, the mass ignites (T. a. T., l.c. p. 1026).—13. P.O. is rapidly oxidised to P.O. by sulphur trioxide, which is reduced to SO.; no compound could be obtained (T. a. T., l.c. p. 1026). According to Adie (C. J. 59, 230), if a little water is present, P₁O₂ and SO₃ form an unstable compound H₂PO₄.3SO₃.—14. Nitrogen tetroxide seems to react like SO₃, forming P₂O₅ and N2O3 or NO (T. a. T., l.c. p. 1028).-15. Phosphorus pentachloride produces PCI, and POCI,; phosphorus trichloride reacts at c. 180° in a sealed tube, forming a mixture of P₂O₃, PCl₃, and red P (T. a. T., l.c. p. 1028).—16. Sulphur chloride reacts violently, producing POCl₃, PSCl₃, SO₂, and S (T. a. T., l.c. p. 1026).—17. Ammonia reacts with some violence, probably producing OH.P.(NH₂)₂(v.Phosphamides, p. 105).—18. Cold dilute caustic soda, or caustic potash solution, slowly dissolves P₄O₄, forming a solution of Na or K phosphite; cold conc. or hot dilute solution. tion of soda or potash produces red P (or P.O?) and alkali phosphate, and evolves inflammable hydride of P.-19. Ignites in contact with absolute alcohol; by allowing the alcohol to drop slowly on to cooled P₄O₂ the acid P(OE1)₂OH is formed (T. a. T., C. J. 57, 559). P₄O₂ seems not to react with H₁ PH₂, CO₂ CO₂, SO₂ N, NO, CN, or C₂H₄ (T. a. T., C. J. 59, 1029).

PHOSPHORUS TETROXIDE P.O. (Phosphoroso-phosphoric oxide. Hypophosphoric oxide). Mol. w. not determined; corresponding sulphide has mol. w. P.S. Hautefeuille a. Perrey (C. R. 99, 33) noticed that a crystalline sublimate is obtained by heating the products of the combus-tion of P; Thorpe a. Tutton (C. J. 49, 833) proved that this sublimate is a definite oxide P₂O₄. Concerning the combustion of P in air v. pp. 128 and 139.

Preparation .- P is burnt slowly in a stream of air dried by H₂SO₄ and P₂O₅; the products are collected in a glass tube, surrounded by an outer tube filled with steam, and are then quickly transferred to a tube filled with dry CO,, the tube is drawn out, exhausted by a Sprengel pump

(care being taken to prevent entrance of moisture), and sealed; at c. 290° the white mass becomes orange-coloured, and then red, and a white crystalline sublimate of P₂O₄ is formed, white erystaine subministe of $r_2 o_4$ is formed, leaving $P_1 O_2$ and $P_4 O$ in the lower part of the tube. T. a. T. (p. 838) think that the $P_1 O_1$ is derived from the $P_2 O_2$, thus $7P_2 O_2 = 5P_2 O_4 + P_4 O_5$; that $P_1 O_4$ is formed by heating $P_2 O_4$ out of contact that $P_1 O_4$ is formed by heating $P_2 O_4$ out of contact that $P_1 O_4$ is formed by heating $P_2 O_4$ out of contact that $P_2 O_4$ is formed by heating $P_3 O_4$ out of contact $P_3 O_4$ is $P_4 O_4$ in $P_4 O_4$ in $P_4 O_4$ in $P_4 O_4$ in $P_4 O_4$ is $P_4 O_4$ in P_4 tact with O is shown by T. a. T. (C. J. 57, 552).

Properties and Reactions.—Colourless crystals, prebably orthorhombic; do not melt at 100°. Volatilises at c. 180°. Very deliquescent, forming H,PO,Aq and H,PO,Aq; from this reaction T. a. T. conclude that P.O. is not the anhydride of H.P.O., as an aqueous solution of this acid does not behave like a mixture of H₂PO₂ and H₂PO₃, and can be boiled without change. Solution of P₂O₄ in water reduces AgNO₃Aq to Ag, and HgCl₂Aq to HgCl; KMnO₄Aq is very slowly decolourised; 'magnesia mixture' gives an immediate ep., and after standing some time the filtrate gives a large pp., with NII, molybdate after heating with HNO.Aq.

PHOSPHORIC OXIDE P.O. (Phosphoric an-PHOSPHORIC OXIDE P.O. [Phosphoric an-hydride. Phosphorus pentoxide]. Formula probably molecular, from analogy of P.S., S.G. 2:387 (Brisson, Peaanteur specifique des Corps [Paris, 1787]). H.F. [P.O.] = 369,900; [P-O.,Aq] = 55,600 (Th. 2, 409). Formation.—1. This oxide is formed by burn-

ing P in a large excess of air; concerning the combustion of P in air v. pp. 128 and 189 .-2. It is also formed by burning P in such gaseous O compounds as NO, NO, ClO2. - 8. By distilling

P20,Cl.

Preparation.—A large glass balloon with a wide opening and two side necks is thoroughly dried; through a cork in the wide opening passes a piece of wide tubing, which reaches to about the centre of the balloon, and from the lower end of this tube a small porcelain basin is suspended by Pt wires; one of the side necks is connected with U-tubes containing pumice soaked in H2SO4, and the other side neck is connected with a wide-mouthed perfectly dry bottle, which is again in connection with a water-pump, a bottle with H2SO, being placed between the pump and the wide-mouthed bottle. A small piece of well-dried P is placed in the little basin, and is ignited by passing a hot wire down the glass tube, the mouth of which is then closed by a good cork; a rapid stream of air is sucked through the apparatus; the P is burnt to P.O., part of which collects on the bottom of the balloon and part passes into the bottle attached to the side neck. When the P is burnt another small piece is dropped down the glass tube into the little basin, and the process is continued. When sufficient P₂O₅ has collected in the bottle this is closed by a well-fitting stopper (Delalande, v. Marchand, J. pr. 16, 373; Mohr, Gm.-K. i. 2, 120. Grabowski (A. 136, 119) has described a vessel of timplate for preparing large quantities

Shenstone says that P₂O₃, prepared by the ordinary process, has generally reducing powers, and is not, therefore, trustworthy as a drying agent. S. recommends to heat for some days at c. 800° in a very slow stream of dry O; then to

heat at 800° in a more liberal, but still limited, supply of dry O until the reddish colour produced by the first heating has disappeared; then to heat at 800° in a more rapid stream of dry O so long as sublimation occurs; and finally to sublime, fractionally, in a current of dry O, from retorts of hard glass into receivers of the same material. The first portions of the sublimate should be rejected. The whole of these processes may be done in glass vessels. The retorts used in the final sublimation may be heated in a combustion furnace (private communication).

Hautefeuille a. Perrey (C. R. 99, 33) say that P.O. can be obtained in three forms : crystalline, amorphous and powdery, and glass-like. They say that when P is burnt in a glass tube in dry air, the crystalline form of P2O, is deposited on the colder part of the tube, the amorphous powdery form on the hotter part, and the vitreous form on that part of the tube which is heated to redness. These authors assert that crystalline P.O. is obtained free from the other forms by distilling the products of the burning of P; that heating the crystals in vapour of S produces the powdery amorphous form; that the vitreous variety is formed by heating either of the others to low redness; and that this vitreous form yields crystalline P.O. when sublimed at a red heat. Considering the facts brought to light by the work of Thorpe a. Tutton on the combustion of P (C. J. 49, 833; 57, 545; v. beginning of this article, p. 139), the existence of various modifications of P₂O₆ must be looked on as very doubtful. T. a. T. (C. J 49, 838) think it very likely that the crystalline form of P2O5 obtained by H. a. P. was P2O4; and it is probable that the differences in the properties of the powdery and vitreous P₂O₂ were due to admixture with P₂O₃. No analytical data are given by H. a. P. Shenstone (priv. comm.) says that P.O. purified by his method is crystalline, but becomes amorphous when suddenly heated.

Properties.—A snow-white, amorphous, inodorous, very deliquescent, solid. Melts and
sublimes below red heat (Lautermann, A. 113,
240); according to Davy (A. Ch. [2] 10, 218)
volatile only at white heat. Absorbs water very
rapidly; hence is used as a very efficacious drying
agent. P.O. is the anhydride of three phosphoric
acids: HPO, H.PO,, and H.P.O., Dry P.O. does
not change the colour of dry litmus paper.
Commercial P.O. often contains traces of P.,
which cause it to redden in light, and also traces
of As.O. derived from the impure P used; it
generally has more or less marked reducing
powers.

Reactions. — 1. Water produces HPO: H.P.O. is formed from HPO. by the long-continued action of moist air; and H.PO. is produced by continued heating of HPO.AQ.—2. P.O. removes H.O from many compounds which contain water or the elements of water; e.g. it produces anhydrides when heated with several acids, H.SO. gives SO., HNO. gives N.O., and hydrocarbons are often formed by heating P.O. with compounds of C. H. and O.—3. Heated with several metals, e.g. Fe, K. Na. Zn. metallic oxide, phosphide, and phosphate are formed.—4. Salis of acids the anhydrides of which are colatile are decomposed by heating with P.O., with formation of phosphates and volatilisation

boric acid.

Combinations. 1. With water (v. supra, Reactions, No. 1).—2. With sulphur trioxide to form P.O. 3SO, decomposed at 30° (Weber, B. 20, 80).—3. With silica and water to form P.O., SiO, 4H.O; formed by heating cone. H.PO, Aq with silica (Hautefeuille a. Margottet, C. R. 104, 156). Similar compounds with oxides of titanium, sirconium, and tin are described by H. a. M. (C. R. 102, 1017).

Phosphorus, oxyacids of. The three phosphoric acids are described in the article Phosphoric acids, p. 124, and the salts of those acids in the article Phosphares, p. 106; the other oxyacids of P and their salts are described under Phosphorus, oxyacids of, and their salts, p. 149

Phosphorus, exybromide of, POBr, (Phosphoryl tribromide). Mol. w. 286-2. Melts at 55° (Baudrimont, A. Ch. [4] 2, 58); at 45°-46° (Ritter, A. 95, 210). Boils at 195° (Ritter, Le.); at 193° (Gladstone, P. M. [3] 35, 345). V.D. 145'5. S.G. 2822 (Ritter, J. 8, 301). H.F. [P.O.Br.] = 108,000 from liquid Br; 120,000 from gaseous Br (Ogier, C. R. 92, 83).

Formation.—1. By the action of moist air or a very little H_oO on PBr₃ (Gladstone, P. M. [3] 35, 345)—2. By the action of oxalic or acetic acid on PBr₄ (Baudrimont, A. Ch. [4] 2, 58; Ritter, A. 95, 210).—3. By passing O into boiling PBr₃; explosions generally occur (Demole, Bl. [2] 34, 201).

Preparation.—To 137.5 parts PCl, are added 18 parts H₂O, and then 160 parts Br are added drop by drop, HBr and HCl are evolved, and POCl, and POBr, remain (part of the PCl, is decomposed to H₂PO, and HCl, and the H₂PO, Br, and remaining PCl, react, (?) thus 2PCl₂ + H₂PO₂ + 3Br₂ = 2POCl₃ + POBr₃ + 3HBr); the liquid is distilled, the portion boiling above 150° being kept separate and surrounded by a freezing mixture till it solidifies (Geuther a. Michaelis, LZ, 6, 242)

Michaelis, J. Z. 6, 242).

Properties and Reactions.—Large colourless plates, which melt and boil in dry air without decomposition; soluble in conc. H,SO, reppd. by H,O; soluble in CHCl., CS, ether, and turpentine. Decomposed rapidly by water to HBrAq and H,PO,Aq; bromine chloride forms POBrCl. or POCl., and Br, according to the quantity used (Geuther, J. Z. 10, 180); hydrogen sulphide probably forms PSBr; chlorine forms POCl. and Br; bromine seems to forme an additive compound which separates into POBr, and Br on heating (Gladstone, Lc.); tin and antimony remove Br (Baudrimont, Lc.).

Phosphorus, exybromechlorides of. Two of these compounds are known, but it is doubtful whether the second is a definite compound of a mixture of POOl₂ and POBr₂.

PHOSPHORUS OXYBROMODIGHLORIDE POBrCl. (Phosphoryl bromodichloride). Mol. w. 1974. Melts at 11°; boils at 1876 (Thorpe, C. J. 37, 848). S.G. & 2·12065 (Thorpe, L.c.). A colourless liquid, which solidifies, when cooled below 0°, to large colourless tablets which melt at 11°: when repeatedly distilled, or more quickly when heated in a closed tube to c. 185°, decomposed to POCl, and POBr, (Chambon, J. Z. 10, 92); decomposed by H₂O to H₂PO₂Aq, HClAq, and HBrAq; with a little alcohol forms POCl₂(OEt) and HBr. Prepared by the reaction of POBr, with BrCl in the ratio POBr, BrCl (Geuther, J. Z. 10, 130); by the action of PBr, on P.O.Cl. (G. a. Michaelis, J. Z. 7, 103). By reacting on P.OEt.Cl, with Br (Menschutkin, A. 139, 343); 80 g. Br are allowed to drop slowly into 74 g. P.OEt.Cl, kept well cooled and constantly shaken; the reaction is very violent; the POBrCl, is separated from the C.H.Br formed by fractionation (Thorpe, C. J. 37, 343). The P.OEt.Cl, is prepared by slowly dropping absolute alcohol into well-cooled PCl, in the ratio C.H.O: PCl, allowing to stand for some time, and fractionating; the boiling-point is 117°-118°.

PHOSPHORUS OXYDIBROMOCHLORIDE POBr,Cl (Phosphoryl dibromochloride). By the reaction of POBr, and BrCl, in the ratio POBr, : 2BrCl, Geuther (J. Z. 10, 130) obtained a liquid boiling between 150° and 160°, and decomposing very easily by heat into POCl, and POBr; analyses agreed with the formula POBr, Cl, but the liquid was possibly a mixture of POCl, and POBr, (3POBr, Cl = POCl, + 2POBr,).

Phosphorus, oxychlorides of. Two oxychlorides of P have been isolated, POCl, and P₂O₂Cl₄. A third substance obtained by Gustavson (B. 4, 853) by heating together P₂O₃ and POCl, and said by him to be PO Cl is declared by Michaelis (G. O. [1881] 2, 396) not to be a definite compound, and this is confirmed by Huntly (C. J. 59, 202).

PHOSPHORYL CHLORIDE POCI. Mol. w. 153-3.
Boils at 107-2° (Thorpe, C. J. 37, 337). Melts at -1.5° (Geuther a. Michaelis, B. 4, 769). S.G. $\frac{6^{\circ}}{4^{\circ}}$ 1.71163 (Thorpe, l.c.). V.D. at $150^{\circ} = 77.2$ (Cahours, A. Ch. [3] 20, 869). For expansion by heat v. Thorpe (l.c.). S.V. 101.4 (T., l.c.). H.F. [P,O,Cl³] = 145,960; [PCl³,O] = 70,660 (Th.

2, 325).

Formation.-1. By heating PCl, in air or O, or with ozone, SO, SO, Cl, and various other oxidisers.—2. By strongly heating PCl, in O, or with SO, SO, B,O, &c., or by decomposing by a little H,O.—3. By distilling NaCl mixed with P,O, (Kolbe a. Lautemann, A. 113, 240).—4. By passing CO and Cl over Ca, 2PO, mixed with C and heated to redness (Riban, C. R. 95, 110; Oglialoro, G. 13, 828).—5. By heating PCl, with P₂O₄.—6. By the reaction of Cl with P₂O₃ (Thorpe a. Tutton, C. J. 57, 572).

Preparation .- An intimate mixture of 1 part P.O. with 2.9 parts POl, is distilled, and the product is again distilled, that boiling at product is again distinct, that coming as 106°-108° being collected separately; the equation P₂O₂ + 8POl₂ = 5POOl₂ is realised.

Properties.—A colourless, highly refractive,

strongly smelling liquid, which fumes in the air; the fundes strongly affect the eyes and respira-tory organs; solidifies at -10°, when touched

with a glass rod, to long, colourless tablets, which melt again at -1.5° (Geuther a. Michaelis, B. 4, 769). POCl, does not conduct electricity even

when heated (Buff, A. 110, 257).

Reactions.—1. Water reacts rapidly, forming Reactions.—1. Water reacts rapidly, forming HClAq and H₂PO₂Aq [POCl², Aq] = 72,190 (Th. 2, 325).—2. Alcohol produces HCl and PO.OEt.Cl. 3. Sulphur trioxide at 160° forms P₂O₂Cl₄ and P₂O₃ (Michaelis, G. O. 2, 393).—4. Sulphuric acid produces SO, OH.Cl, HCl, and HPO, (Michaelis, .c.).-5. Most organic acids react similarly to H.SO., producing acid chlorides; e.g. C.H.O.OH forms C.H.O.Cl; salts of organic acids react similarly, forming acid chloride and metaphosphate.-6. Sulphates form SO Cl. and orthophosphates. -7. Sulphites are partially changed to SO2, mixed with metallic chloride and phosphate (Divers a. Shimidzu, C. J. 47, 208).— 8. Nitrates produce chlorides and P.O. &c.; 8. Nutrates produce chlorides and P₁O_s & O.

(D. a. S. l.c.).—9 POCl₃ separates I from potassism todide (Schiff, A. 102, 181).—10. Chromyl chloride forms Cl. P₂O₃, CrCl₃, and Cr,O₄ (Casselmann, A. 91, 241; 98, 213).—11. Phosphorus pentasulphide at 150° produces PSCl, and P₂O₃. 12. Phosphorus pentoxide reacts at c. 200°, forming P₂O₂Ol₄ and a substance P₂O₁Ol₃, which may prove to be a mixture (Huntly, C. J. 59, 202).— 13. Phosphorus reacts at 200° to form P₄O₂ POl₄. P₂O₃Cl₄, and a little P₂O₅ (Reinitzer a. Gold schmidt, B. 13, 845).—14. POCl₅ is reduced by heating in closed tubes with many finely divided metals, e.g. Ag, Hg, Fe, Cu, As (Pb is without action); the products are generally PCl, and P₂O₃, and oxide, chloride, or phosphate of the metal; sometimes P₂O₃Cl₄ is said to be formed (v. R. a. G., l.c.); Mg, Al, and Zn are said to form red P₄O (R. a. G., l.c.). Zinc-dust with a little POCl, forms Zn phosphide, which evolves inflammable P hydride on addition of a little water (Deniges, Bl. [3] 2, 787).—15. With ammonia forms various phosphumic acids (q. v., p. 105), and also phosphamides (q. v., p. 105).— 16. Boric oxide heated with POCl, in a sealed tube to 150°-170° for 8 to 10 hours forms P₂O₃.B₂O₄ and POCl₂.BCl₃ (Gustavson, B. 4, 975).

Combinations.—1. With ammonia to form a

compound not yet examined .- 2. With several metallic chlorides to form double compounds, e.g. with AlCl₂, MgCl₂, and SnCl₂ (Casselmann, A. 91, 241; 98, 213). Some of these compounds may be vapourised in absence of moisture; they are decomposed by water .- 3. With boric chloride also by heating POCl, with B₂O₈. This substance is decomposed by heat; with water it gives H,PO,Aq, H,BO,Aq, and HClAq (Gustavson,

B. 4, 975).

Constitution of POCl, —Two isomeric forms of POCl, are possible: Cl.POCl and Cl.PO; but the compounds obtained by different methods are identical. Wichelhaus (A. Suppl. 6, 257) thought that POCI, must have the constitution Cl.POCl, because of its formation from Cl.POEt. in which the O atom is in direct union with the P atom (Cl.POEt+Cl. = Cl.POCl+EtCl); but Geuther a. Michaelis (J. Z. 6, 242) pointed out that this formation of POCl, may be interpreted also in favour of the constitution Cl.PO by supposing that Cl first replaces OEt, forming PCl and that the POL and EtOCl then react :

(1) Ol.POEt + Ol. = Cl.P + EtOCl, (2) Cl.P + EtOCl = Cl.PO + EtCl. The experiments of Reinitzer a. Goldschmidt (B. 13, 845) on the action of metals, on POCl, show that in most cases O is withdrawn, leaving PCl.; and that in a few cases the 3 Cl atoms are withdrawn with formation of P₂O₅. These results do not indicate any differences between the functions of the Cl atoms, and hence they tend to favour the formula Cl₂PO. Thorpe (C. J. 37, 387) arrived at the formula Cl₂POCl from consideration of the specific volumes of BOCl, and PCl,. Masson a. Ramsay (C. J. 39, 50), also from considering the specific volumes of P and P compounds, deduced the formula OPCl3. Although but one POCl, has been obtained, the isomeric compounds $(C_gH_s)_gPOC_gH_s$ and $(C_gH_s)_sPO$ have been isolated (La Coste, B. 18, 2118).

PYROPHOSPHORYL CHLORIDE P.O.Cl. phorus trioxytetrachloride). Mol. w. not known. Boils 210°-215°, with partial decomposition. S.G. 1.58 at 7°.

Preparation .- 1. 100 g. PCl, are placed in a cylinder surrounded by ice and salt, and the vapour from 20 g. liquid NO, is passed into the cylinder by a tube which reaches just to the surface of the PCl. The action proceeds at once; the products are P.O., POCl., P.O.Cl., and NOCl. When all the NO, has been distilled into the PCl, the cylinder is placed in warm water to remove NOCI, and its contents are then fractionated; PCl, distils over first, then a considerable quantity of POCl, between 105° and 110°, and then P₂O₂Cl₄ from 200° upwards. is best to prepare a considerable quantity of the impure product before fractionating; 350 g. PCl, yielded 40 g. P.O.Cl. (Geuther a. Michaelis, B. 4, 766).—2. The vapour obtained by heating 30 g. starch with 180 g. HNO, Aq is led into 100 g. PCl,; the product is fractionated, and that boiling under 100° is again treated as before; finally, the whole is fractionated. About 20 g. P₂O₂Cl₄ are obtained from 200 g. PCl₂ (G. a. M., l.c.).

Properties.—A colourless liquid, which fumes in the air; the vapour attacks cork. Has not been solidified by cooling. Boils, with partial decomposition into P.O. and POCl., at 210°-

Reactions.—1. Heat produces partial decomposition into POCl, and P.O.,—2. Decomposed by water to H.PO.Aq and HClAq.—3. Alcohol produces PO.OEt.Cl, PO.OEt.(OH), and HCl. 4. Phosphorus pentachloride produces POCI, 5. Phosphorus pentabromide forms POBr, and POCI, Br (G. a. M., l.c.).

METAPHOSPHORYL CHLORIDE PO.Cl. Gustavson (B. 4, 853) said that a compound of this composition is formed by heating P₂O₈ with POCl_s; but Michaelis (G. O. 2, 396) says that the substance is not a true compound, and this is confirmed by Huntly (C. J. 59, 242).

Phosphorus, oxychlorobromides of, v. Phos-

PHORUS, OXYMOMOCHLORIDES OF, p. 142.
Phosphorus, oxyfluoride of, POF, (Phosphoryl fluoride). Mol. w. 108-92. V.D. 52 phoryl fluoride). Mol. w. 103-92. V.D. 52 (Thorpe, C. J. 55, 759; Moissan, Bl. [3] 4, 260). A gas which fumes in air and is rapidly absorbed by water. Formed by the reaction of P₂O₂ with fluorides (Schulze, J. pr. [2] 21, 438); also by exploding a mixture of 2 yols. PF, and 1 vol. O

by passing electric sparks (Moissan, C. R. 102, 1245); by gently heating an intimate mixture of 2 pts. finely-powdered cryolite with 3 pts. P.O. in a brass tube, and collecting over Hg as soon by NaOHAq (Thorpe, l.c.). Moissan (l.c.) prepares POF, by heating ZnF, with POCl, in a brass tube, fitted with a leaden delivery tube: he allows the gas to pass through a brass tube cooled to - 20°, and then over ZnF, to remove traces of POCI.

PÖF, liquefies at 16° under a pressure of 15 atmos., or at the ordinary pressure by cooling to -50° (M., C. R. 102, 1245). When compressed under 50 atmos. and the pressure then suddenly released, it solidifies to a snow-like mass. When quite dry it is without action on glass or Hg; heated in a glass tube SiF, and an alkaline phosphate are formed.

Phosphorus, oxyiodide of, P.I.O. (Am. 3, 280) obtained a red crystalline compound, to which he gave this composition, as a by-product in preparing C2H.I. M.P. c. 140°; sublimable, with partial decomposition; e. sol. water, alcohol, and ether.

Phosphorus, oxynitride of PON (Phosphoryl nitride. Phosphoryl nitride. Formerly called Phosphomonamide). Mol. w. uncertain. A white powder, which melts at red heat to black glass-like mass. Obtained by heating PO(NH.). or PONHNH,, the former of which is formed by the reaction of POCl₃ with NH₃, and the latter by the reaction of PCl₃ and NH₂ (Schiff, A. 101, 300; of. Phosphamides, p. 105). Gives K₃PO₄ and NH, by action of molten KOH (v. also Gladstone, C. J. [2] 7, 18).

Phosphorus, selenides of. P and Se combine directly to form four compounds: P.Se, P₂Se, P₂Se₃, and P₂Se₅. P2Se, P2Se3, and P₂Se, combine with the selenides of the more positive metals to form compounds R, Se.P, Se, (R,Se), P,Se, and (R,Se), P,Se, The formulæ are not necessarily molecular.

PHOSPHORUS SUBSELENIDE P.Se (Phosphorus hemiselenide). Prepared by melting together Se and ordinary P in the ratio Se: 4P(1:1-57) in an atmosphere free from O, and separating from amorphous P by distillation in absence of O. A dark yellow, oily, fetid-smelling liquid, which solidifies at -12°; e. sol. in CS, insol. alcohol and ether; takes fire in air; decomposed by water containing air, with formation of H, PO, Aq and Se compounds; not acted on by cold alkali solutions, but with boiling alkali solutions gives alkali phosphate and selenite, metallic selenide and P hydride; in solutions of metallic salts becomes covered with a crust of metallic phosphide and selenide (Hahn, J. pr. 93, 430).

DIPHOSPHORUS SELENIDE P.Se. (Phosphorus Prepared by protoselenide or monoselenide). Prepared by melting together, in absence of O, P, and Se in ratio 2P: Se(1:128). A red solid; unchanged in dry air, in moist air gives off H2Se; insoluble alcohol and ether; P is withdrawn by CS2; boiling alkali solutions produce H. Se and a red sub-stance containing Se and P. By heating, in absence of O, with equivalent weights of metallic selenides, compounds R' Se.P Se and R' Se.P Se are formed; R=Ba, Cu, Fe, Mn, K, Ag, Na. The alkali compounds are decomposed by water; the compounds containing heavy metals decompost only at high temperatures, but they generally take fire when rubbed in a mortar; they are slowly decomposed by hot alkali solutions (Hahn, L.). From their empirical composition, R¹PSe, these compounds might be called seleno-meta-kypophosphites.

PROSERIOROUS SELENDE P.Se. (Phosphorus assistational or trisclevide). Prepared by heating together P and Se in ratio 2P:3Se(1:3-82) in absence of O. A dark ruby-red solid; sublimes to yellow vapours when heated out of O; burns when ignited in air. Oxidised slowly in moist air; evolves H₂Se when boiled with water. Insoluble alcohol, ether, and CS₂; easily soluble in potash, less soluble in alkali carbonate solutions. Forms compounds with metallic sclenides (R', Se)_P, Se, and 2R', Se, P, Se, (Hahn, Lc.); R = Ba, Cu, Pb, Mn, K, Ag, Na. From their empirical composition, R', P, Se, these compounds might be called selenopyrophosphites.

Phosphorus SELENDE P. Se. (Phosphorus

PHOSPHOROU SELENINE P₂Se₃ (Phosphorus pentaselenide). Prepared by heating together amorphous P and Se in ratio 2P:5Se (1:6:37) in a stream of CO_x. A dark-red, nearly black, glasslike solid; insoluble in CS₂; crystallises from CCl₄ in black needles. In moist air, or water, decomposes slowly to H₂Se and H₂PO₄Aq; in cone. KOHAq quickly forms K₂Se and K₂PO₄Aq; alcohol forms H₂Se and Et₃PO₂Se₂ and also Et₄HPO₂Se₂. Very unstable compounds probably of the forms (R¹₂Se), P₂Se₃ and 2R¹¹Se, P₂Se₃, are obtained by heating P₂Se₃ with metallic selenides; R - Ba, Cu, Pb, Mn, K, Ag, Na. The empirical composition of these compounds would lead to the name selenopyrophosyhales (Bogen, A. 124, 57; Rathke, A. 152, 200). Rathke (l.c.) supposed that the K salt of a selenophosphoric acid is formed by the reaction of P.Se, with KOHAq.

Phosphorus, selenion acids of, salts of; D. Diphosphorus selenide, Phosphorus selenide, and Phosphorus, sulphides of. P and S combine,

Phosphorus, sulphides of. P and S combine, when heated together, with production of much heat and light; the action is often violently explosive. Four definite compounds seem to exist; the simplest formulæ are P₄S₃, P₂S₂, PS₂, and P₂S.

P₂S.

Two compounds containing less S than P₄S₃, viz. P₂S and P₄S, are often described, and substances said to be compounds of P and S in the ratio P:3S and P:6S have been mentioned by Dupré and Berzelius.

The substance to which the formula P.S was given was obtained by heating P and S in the proper proportions (Berzelius, A. 46, 129, 255), or by digesting P with an alcoholic solution of K.S. (Böttger, J. pr. 12, 357), or according to Wicke (A. 86, 115) by contact of P and S at ordinary temperatures; it was described as a colourless, oily liquid. A solid red form of P.S was said to be formed by heating liquid P.S with Na.CO. (Berzelius, L.). The formula P.S was given to a substance of which two forms were described: a yellow liquid obtained by carefully heating together P and S in the proper ratio, and a dark-red powder obtained by beating the liquid form with dry MnS in JH (Berzelius, L.): Various double compounds of P.S with metallic sulphides, B.S.P.S and R.B.P.S (B = Cu. Fe, Mn, Hg, Ag) were described by Berzelius. The composition of these bodies

would lead to their being called thiometahypophosphites. Isambert (C. R. 96, 1771) has shown that when a solution of P in a large excess of S is distilled in vacuo the whole of the P passes off and leaves S. Schulze (J. pr. [2] 22, 118) found that P separated at 8° from a solution of S in P in the ratio P.S, and that S separated when the elements were present in the ratio P₂S. Schulze also found that a stream of CO₂ removed P from both solutions at 150°; that heating to this temperature generally produced explosions that the so-called liquid P₂S was soluble in CS₂, and that most of the S was removed by shaking this solution with alcohol, ether, or CHCl. Further, Schulze (B. 16, 2066) observed that solutions of S in P, in the ratio P.S and P.S. did not solidify homogeneously. but that P separated from the first, and S from the second, solution. From these facts Isambert and Schulze concluded that the so-called P.S and P.S are merely solutions of S in P. Lemoine (C. R. 96, 1630) maintained that these substances were true compounds. According to Mai (A. 265, 192), when 67 parts P and 96 parts S are melted together, and the product is dis-tilled at 10-11 mm. pressure, a distillate is obtained which slowly solidities, and digestion of this solid with CS₂ under pressure gives a solution from which crystals of P₄S, separate, and the mother-liquor deposits what seems to be a mixture of P.S. and P.S. The melting-points of mixtures of P and S are much below those of either constituent (Pelletier, A. Ch. [2] 4, 1; Faraday, A. Ch. [2] 7, 71; Dupré, A. Ch. [2] 78, 435). The experiments of Faraday (l.c.) and Ramme (B. 12, 940, 1350) show that the crystals obtained by dissolving S in liquid P sulphides to which Berzelius gave the composition PS, and Dupré the composition PS, are merely S with more or less adhering P.

TETRAPHOSPHORUS TRISULPHIDE P.S. (Sesquisulphide of phosphorus. Hypophosphorus sulphide). Mol. w. 219-3. Melts at 166° (Ramme B. 12, 1350). Boils at 380° (Isambert, C. R. 96, 1499). S.G. 2-0 at 11°. V.D. 114-3 (Isambert, Lc.; Ramme, lc.). H.F. [P',S'] = 36,800 (L., lc.). Formation.—1. By heating together P and S

Formation.—1. By heating together P and S in the ratio 4P:3S.—2. By heating P₄S₆ with ordinary P to 320° (Ramme, l.c.).

Preparation.—A mixture of 1 part S with 13 parts amorphous P is placed in a flask with a long wide neck connected with a wide tube dipping beneath the surface of Hg; the mixture is heated towards 260°, when the reaction begins, and proceeds with production of much heat; the product is dissolved in CS, and crystallised (Lomoine, BL. [2] 1, 407). Ramme (B. 12, 1360) heats the rod P and S together in a scaled tube at 260° for eight hours. If ordinary P is used, combination occurs at 130°, with violent explosion. The explosion may be prevented by melting the S and P in the water-bath, and adding twice as much sand from which air has been removed by CO₂ (Isambert, C. R. 96, 1499). Ramme (B. 12, 1351) obtained P₂S, by heating P₂S, with ordinary P in a sealed tube, filled with CO₂, to 320°.

CO, to 320°.

Properties.—A yellow crystalline solid, which melts at 167° to a slightly coloured liquid. Boils 230°-240° at 11 mm. pressure, with 'partial decomposition to red P (Mai, A. 265, 192). 'Crys.

tallises from CS₂, PCl₂, or PSCl₃ in rhombic prisms (Lemoine, BL [2] 1, 407); sublimes under 800°, probably in regular crystals (Isambert, C. R. 96, 1499). Very soluble CS₂, PSCl₃, and PCl₄; dissolved and decomposed by alcohol (Lemoine, l.c.). Burns at c. 100° to P₂O₃ and SO₂; scarcely changed in ordinary air.

scarcely changed in ordinary air.

Reactions.—1. Burns when heated in air to c. 100°, forming P₂O₃ and SO₇—2. Not acted on by cold water; hot water slowly produces HS and H₂PO₂Aq.—3. Dissolves in potash solution, forming K phosphite and sulphide, and evolving H and P hydride (Lemoine, l.c.).—4. Hydrated lead oxide reacts at 200° with separation of PbS (L., l.c.).—5. Soluble in potassium sulphide solution, probably with formation of a double compound (L., l.c.).—6. Chilorine, when moist, slowly produces H₂SO₄ and H₂PO₄ (L., l.c.; I., l.c.).—7. Not acted on by cold sulphuric or hydrochloric acid; nitric acid and aqua regia oxidise P₂S₄ slowly and regularly on warming.

P.S. slowly and regularly on warming.

PHOSPHOROUS SULPHIDE P.S. (Trisulphide of phosphorus. Tetraphosphorus hexasulphide. Thiophosphorous anhydride). Mol. w. 315-72.

Melts at c. 200°, and boils at c. 490° V.D. 147-5, to 173-6 at lower temperatures (Isambert,

C. R. 102, 1386).

Formation.—1. By heating red P and S in the ratio 2P:3S in CO₂. Combination occurs without explosion, but so much heat is produced that a part of the product sublimes rapidly (Kekulé, A. 90, 310; Michaelis, A. 164, 22).—2. By the reaction of PCl₃ with H₂S (Serullas, P. 17, 101). Ramme (B. 12, 940) failed to obtain P₄S₆ by heating a solution of P and S in CS. in a sealed tube.

tain P,S₂, by heating a solution of P and S in OS₂ in a sealed tube.

Preparation.—A mixture is made of 1 part red P with 1.55 parts S; a small portion of this mixture is heated in a long-necked flask in a stream of CO₂ until combination occurs; the flame is removed, and the rest of the mixture is introduced into the flask in small portions at a time; the heat produced by the combination of one quantity suffices to cause combination of the next quantity. The P₄S₄ is sublimed into the neck of the flask; or it may be dissolved in CS₂ and crystallised (Michaelis, A. 164, 22).

Properties.—A greyish-yellow, crystalline, solid (Kekulé, A. 90, 310; Isambert, C. R. 102, 1386). Tasteless, inodorous; does not fume in air; melts readily (c. 200°), and sublimes more easily than S. Soluble in CS... The V.D. shows that the molecular formula is P.S., corresponding with the oxide P.Q.. P.S. acts as a thio-anhydride, forming compounds with the sulphides of several metals (v. Reactions, No. 7). As P.S. is acted on by moist air, it must be kept in sealed tubes.

Reactions.—1. Decomposes rapidly in moist air (? to H₂S and H₂PO₂).—2. Decomposed by water to H₂S and H₂PO₂Aq.—3. Burns when heated in air.—4. Dissolves in potash, soda, or ammonia solution, and is reppd. in yellow flocks by addition of soid.—5. Decomposes carbon compounds containing OH, forming corresponding SH compounds and H₂PO₂.—6. With todine in CS, forms PI₂ (Isambert, C. R. 96, 1771).—7. According to Berzelius, P₂S₃ combines with many metallic sulphides forming compounds 2R¹₂S.P₂S₃ and 2R¹S.P₂S₃ the compounds 2R²S.P₂S₃ and 2R¹S.P₂S₃ the compo-

sition of which would lead to their being calle thiopyrophosphites; R=Cu, Fe, Hg, Ag.—8. B dissolving in caustic scda solution cooled to 0° Lemoine (C. R. 93, 489; 98, 45) obtained th compound P.OS., 2NA, 0.5H₂O and the compound P.OS., 2NA, 0.5H₂O and by using ammonium sulphide he obtained P.OS., 2(NH.), 20.8H₂O and P.OS., 2(NH.), 20.6H₂O. These substances evolved H.S by the action of HClAq; heated to 200°. 240° they gave off H.S. but retained S; they may perhaps be called thio-oxypyrophosphites.

Triphosphorus hexasulphide P_9S_6 (Phosphorus disulphide $[PS_2]$). Phosphorus tetra sulphide $[P_2S_1]$). PMol. w. 284*8. Melts at 296°-298° (Ramme, B. 12, 940); at 248°-249° (Seiler Dissertation, Göttingen, 1876). Boils at 335°-340° at pressure of 10-11 mm. (Mai, A. 265. 192). V.D. Ramme (B. 12, 1350) says that V.D. agrees with formula P_2S_6 , but no numbers are given.

Formation.—1. By heating a solution of P and S in CS₂ in sealed tubes to 210°; according to Ramme (B. 12, 940), P₂S₆ is produced with P and S in the following ratios:—P.S, P:2S, 2P:S, 3P:S, 4P:S, 6P:S (v. also Dervin, Bl. [2] 41, 433).—2. By heating together P and S in the ratio P:2S (Seiler, l.c.).

Preparation.—P and S are dissolved in CS₂ in the ratio P: 2S, the solution is heated in a sealed tube to 210° for 8-10 hours, after cooling the liquid is poured off, and the crystals are recrystallised repeatedly from CS₂ in a sealed tube (Ramme, Lc.).

Properties and Reactions.—Long, clear yellow, needle-shaped crystals. Ramme (l.c.) says that V.D. corresponds with formula P₂S₆ but he gives no data; the corresponding oxide is generally written P₂O₆, but its molecular weight has not yet been determined. Heated with water in a sealed tube to 150° for some hours, P₂S₆ gave H₂S, H₂PO₄Aq, and H₂PO₄Aq and an orange-yellow solid insoluble in CS₂ and not melting at 310° (Ramme, B. 12, 1350).

PHOSPHORIO SULPHIDE- P.S. (Phosphorus pentasulphide or persulphide. Thiophosphoric anhydride). Mol. w. 221-8. Melts at 274°-270° (V. a. C. Meyer, B. 12, 610). Boils at 518°, pressure z 730 mm. (Goldschmidt, B. 15, 603); at 520° (Isambert, C. R. 102, 1386); at 530° (Hittorf, P. 126, 196); at 332°-340°, pressure being 11 mm. (Mai, A. 265, 192). V.D. 110-7, at 530° in N (V. a. C. Meyer, B. 12, 610).

Formation.—1. By heating a solution of ordinary P and S, in the proper ratio, in CS₂ to 210° for 8-10 hours, and crystallising from CS₂ (Ramme, B. 12, 940).—2. By melting together red P and S, in ratio 2P:5S, in CO₂ (Kekulé, A. 90, 310); with ordinary P violent explosion occurs.

Preparation.—A mixture of 40 parts S and 18-5 parts red P is melted together, the mass is powdered, placed in a retort filled with CO₂, and distilled to c. \(\frac{1}{2} \) to \(\frac{1}{2} \) (to remove_0 P, S, and more volatile P sulphides); the residue is again powdered and distilled in CO₂; the distillate is pure P,S, (V. a. C. M., l.c.).

P.S. (V. a. C. M., l.c.).

Properties.—Large, clear, pale-yellow crystals. Vapourises in N or CO, without change, to a yellowish gas. Burns when heated in air.

Soluble in OS₂; P₂S₃ seems to react as a thio-anhydride (v. Reactions, No. 7).

Reactions.-1. Decomposes in moist air or by water, to H₂S and H₂PO₄; burns when heated in air to P₂O₂ and SO₂—2. With phosphorus pentachloride forms PSCl₃ (Weber, J. 1859, 80). 8. With carbon tetrachloride at 200° produces CS₂ and PSCl₃ (Rathke, Z. 1870, 57).—4. With ferric chloride gives FeS₂ and PSCl₃ (Glatzel, B. 23, 37).—5. With sulphonyl chloride, PSCl₃, SO₂, and S are formed (Prinz. J. Z. 13. Supplbd. 1. 90).-6. With many carbon compounds containing O and also with many inorganic oxides, P.S. form S compounds, exchanging S for O (Kekulé, A. 90, 310; Carius, A. 106, 331; 112, 180; v. also Prinz, l.c.).—7. According to Berzelius (A. 46, 129, 255), P.S. combines directly with several metallic sulphides, forming compounds $2R_{12}S_{1}P_{2}S_{3}$ and $2R_{11}S_{11}P_{2}S_{3}$ (R = Cu, Fe, Mn, Hg, Zn): these compounds may be called thiopyrophosphates.

THIO-OXYORTHOPHOSPHATES. Salts of the hypothetical acids II PSO, (monothio-oxyorthophos-phoric acid) and H.PSO, (dithio-oxyorthophosphoric acid) have been obtained by the action of alkali solution on P.S., or on PSCI. Salts of trithio-oxyphosphoric acid (H,PS,O) have not

been isolated.

Monothio-oxyphosphates. The Na salt, Na PSO .. 12II O was obtained by Wurtz by warming PSCI, with fairly conc. NaOHAq (A. Ch. [3] 20, 472), and by Thorpe a. Rodger by the ac-16) 20, 412, and by Interpe a. Rodger by the action of NaOHAq on PSF₃ (C. J. 55, 318). Kubierschi (J. pr. [2] 31, 93) obtained the salt by adding powdered P.S. to NaOHAq, in ratio P.S. 6NaOH, cooling, adding absolute alcohol which ppd. a mixture of Na, PSO, and Na, PSO, (leaving Na polysulphides in solution)-dissolving the pp. in water, warming to 90° till H S ceased to come off, evaporating, and crystallising. Thin ax-sided prisms, melting at 60°. The Mg salt (with 20H,O), and the Mg-NH, salt (with 9H2O) were also obtained.

Dithio-oxyphosphates. The Na salt, Na,PS,O,11H,O was obtained (K., l.c.) by dissolving in water the pp. obtained as above by alcohol, warming to 50°-55°, ppg. by alcohol, and crystallising from water at 40°. Colourless, lustrous, needles, melting at 45°-46°. The NH salt (with 2H₂O), Ba salt (with 8H₂O), and Mg-NH, salt (with 6H₂O) were also obtained in

crystalline form.

For reactions of these thio-oxyorthophosphates v. Kubierschi, l.c. (cf. Michaelis, B. 5, 5). Phosphorus, sulphobromides of. Two compounds, corresponding with the two oxychlorides, have been prepared.

THIOTHOSPHORUL BROMIDE PSBr. (Sulphophosphoryl bromide. Phosphorus sulphobromide). Formula probably molecular, from analogy of

POCI,

Formation .- 1. By reaction of H.S with PBr. (Gladstone, P. M. 35, 345; Baudrimont, A. Ch. [4] 2, 58).—2. By distilling PBr, with S, or Br with P₂S₂.—3. By the action of Br on a solution

of P and S in CS.

Preparation.—Equal parts of P and Seare adissolved in CS, the solution is well cooled, and 8 parts Br are allowed to drop in slowly from a funnel with a stopcock; the CS, is removed by warming in a water-bath, and the liquid is then

distilled quickly over a large flame. Part of the PSBr, solidifies in the neck of the retort, and part passes over and remains liquid in the receiver; the contents of the receiver are shaken with fresh quantities of water until the oily liquid solidifies to a yellow crystalline mass which is PSBr, H,O; this hydrate is dissolved in CS, water is removed by contact with CaCl, is distilled off in a stream of CO, and CS PSBr, remains as a yellow oil, which solidifies on touching it with a glass rod. The solid may be recrystallised from PBr_s (Michaelis, A. 164, 36).

Properties .- Yellow octahedral crystals, with an aromatic but unpleasant odour; vapour attacks the eyes. Melts at 38°, when molten remains for a long time without solidifying unless touched by a solid (Michaelis, B. 4, 777). Easily soluble in ether, CS₂, PBr₃, or PCl₄. Cannot be distilled without decomposition.

Reactions .- 1. Decomposed by heat to S and a yellow liquid, PSBr, PBr, which is resolved by repeated distillation into S and PBr, and by repeated washing with water yields PSBr. H.O peated washing with waters yields PSBr_s,H₂O (Michaelis, A. 164, 36).—2. Decomposed by water, slowly when cold, rather more rapidly when boiling, forming H₂S, S, H₂PO₂Aq and H₂PO₄Aq (v. Michaelis, B. 5, 4).—3. With alcohol forms PS(OEt)₃.—4. Decomposed by ammonia solution, slowly when cold, more rapidly when hot, giving NH₄ phosphite and phosphate, H₂S, S, and NH₄ sulphide (M., Le.).

Beacts with hypotherus poutachleride to 5. Reacts with phosphorus pentachloride to form PSCl₂ and PBr₃ (M., l.c.).

Combinations. — 1. With water to form

PSBr₃.H₄O (v. Preparation). A yellow crystal-line solid; melts at 35°, being resolved into H₄O and PSBr_s; S.G. 2.7937 at 18°; gradually decomposes in air, giving off HBr (Michaelis, A. 164, 36).—2. With phosphorus bromide to form PSBr, PBr,; obtained by heating PSBr, (v.

Reactions, No. 1).

Pyrophosphonyl bromide P2S3Br4 (Phosphorus trisulphotetrabromide). A light-yellow oil, with aromatic and pungent odour; S.G. 2.2621 at 17°; fumes in air, with separation of S. Decomposed by distillation into S, P,S, and Decomposed by distillation into S, P.B., and PSBr., PBr.; decomposed by water, giving S, PSBr., H₂S, P, and a substance probably P.S.₁(OH)₄; alkalis act similarly to, but more violently than, water, but neither S nor PSBr, is formed; with absolute alcohol yields P₂S.₁(OEt)₄Br, P₂S.₂(OEt)₄, P₂S.₃(OEt)₄(SEt)₅; bromine reacts, when heated, forming PBr, and PSBr. (Michaelis A 16A 29). Prepared by PSBr. (Michaelis, A. 164, 22). Prepared by moistening 100 g. finely powdered P.S. with CS. and adding 200 g. Br diluted with an equal volume of CS2, shaking thoroughly, distilling off CS2 in water-bath not above 80°, removing last traces of CS, in stream of CO, dissolving residue in six times its volume of dry ether, and removing ether

by a stream of CO₂ (M., l.c.).

Phosphorus, sulphobromochloride of, PSBrCi. (Thiophosphoryl bromochloride). probably molecular, from analogy of POBrCl. (Michaelis, B. 5, 6). A slightly yellow liquid, with aromatic odour; boils c. 150°, but boilingpoint soon rises and S separates. Decomposed slowly by water, more completely when heated in a sealed tube to 150° for some hours, giving S, H₂S, HClAq, HBrAq, H₂PO₂Aq, and H₂PO₄Aq. Prepared by adding 80 parts Br

drop by drop to 168 parts PCL.SEt [obtained by action of EtSH on PCl,; for details v. Michaelis, etc.]; much heat is produced; the liquid is distilled, the distillate from 150°-180° is shaken with water so long as any action takes place; water is removed by a separating funnel; the liquid is dried by CaCl, and HCl and HBr are removed by warming gently (M., l.c.).

Phosphorus, sulphochlorides of. But one compound, PSCl, is known with certainty. It is doubtful whether the substance obtained by Gladstone (C. J. 8, 5) by the reaction of S with PCl, is a definite compound PS,Cl,, or a double

compound PSCl. SCl.

THIOPHOSPHORYL CHLORIDE PSCI₂ (Phosphorus sulphochloride), Mol. w. 169 05. Boils at 125·12° (Thorpe, C. J. 37, 341). S.G. 40 1·6682 (T., l.c.). V.D. 85 at 160°-300° (Cahours, A. Ch. [3] 20, 869; Chevrier, C. R. 68, 1174). For thermal expansion v. Thorpe (l.c.). S.Y. 116·1.
 Formation.—1. By the reaction of H₂S with

PCI, (Serullas, A. Ch. [2] 42, 25).—2. By heating S with PCl₂ to 130° (Henry, B. 2, 638).—3. By heating P with S_cCl₂ (Wöhler a. Hiller, A. 698, 274).—4. By heating together P_cS_c and PCl₃ (Weber a. Thorpe, Z. 1871, 467).—5. By the re-(Weber a. Inorpe, Z. 1871, 407).—5. By the reaction of PCl, with SO, SO,Cl., or S,Cl.; and by the reaction of PCl, with CS, or with Sb,S, (Michaelis; Cairns, A. 112, 190; 119, 291; Rathks, Z. 1870, 57; Baudrimont, J. pr. 87,

801).

Preparation.—An intimate mixture of P.S.

Preparation.—An intimate mixture of P.S.

1.2 B.S. APCL (= 1:2 82), is and PCla, in the ratio P2Sa: 3PCla(=1:2.82), is heated in a sealed tube to c. 120°; after a short time the liquid which has formed is distilled. Should the product have a yellowish colour, it is shaken with a little water, dried by CaCl, and distilled. The equation P.S. + 3PCl, = 5PSCl. is realised (Thorpe, C. J. 37, 341).

Properties. - A colourless, highly refractive liquid; with an aromatic, somewhat pungent, and very peculiar odour, which becomes very marked on warming. Slowly decomposed by water.

Reactions. -1. Very slowly acted on by water, with formation of H₂PO₁Aq, HClAq, and H₂S. When distilled in steam the greater part of the PSCl, passes over unchanged.—2. Heated with alcohol under pressure, PS(OEt), is formed.—3. Passed through a hot tube, with excess of hydrogen sulphide, P.S. and HCl are formed (Baudrimont, J. pr. 87, 301).—4. Decomposed by chlorine with formation of S.Cl. and PCl. Silver nitrate reacts rapidly, producing Ag.PO., AgCl, SO., NOCl, and NO. (the SO. and NO. then reacting to form S.O.(NO.);; Thorpe B. Dyson, C. J. 41, 297).—6. Alkali solutions form salts of H.PSO. and H.PS.O. (v. Thio-OXYORTHOPHOSPHATES, p. 147) .- 7. The prolonged action of ammonia—continued until 60 p.c. of the PSCI, has reacted with the NH,—produces thiophosphamids PS(NH2):(?); this compound remains as an amorphous, yellow-white solid on washing the product of the action of NH on PSCl₂; B.G. 1.7 at 13°; decomposed at 200°, gives (?)PS(ONH₄), with hot water (Chevrier, C. R. 66, 748; Sohiff, A. 101, 292). Accordring to Gladstone a. Holmes (C. J. 18, 5), thio-phosphamic acid PS(NH₂)(OH), and thio-phosphodiamic acid PS(NH₂)₂OH, are pro-

duced by the action of ammonia on PSCI,; the former by using fairly dilute NH,Aq, and the latter by using NH, gas—which probably forms P(NH₂),ClS—and then washing with water. The work of Chevrier (l.c.) and Schiff (l.c.) makes the isolation of these acids doubtful.

Phosphorus, sulphochlorobromide of; Риовриовия вигриовкомоситовите, р. 147.

Phosphorus, sulphocyanide of, P(SCN), (Phosphorus thiocyanate. Phosphorus rhodan-Mol. w. not determined; formula probably molecular. Prepared by mixing 5 parts Pb(SCN), with an equal weight of dry sand, gradually adding 1 part PCl₃, digesting for some time on a water-bath, and then distilling very carefully from a hard glass tube. A liquid which does not solidify at -- 20°, begins to boil 260°-270°, and decomposes at a higher temperature, giving off CS,; vapour is spontaneously inflammable; S.G. 1.625 at 18'. Soluble in alcohol, ether, CHCl₃, CS₂, and C₆H₆. Slowly decomposed by cold water to H₂PO₃Aq and HSCNAq (Miguel, A. Ch. [5] 11, 349).

Phosphorus, sulphofluoride of, PSF, (Thiophosphoryl fluoride). This compound was prepared and fully described by Thorpe a. Rodgers in 1888 (preliminary notice in C. J. 53, 760; fuller account in C. J. 55, 306). Mol. w. 119.9.

V.D. 59 6 at ordinary temperature.

Formation.—1. By heating a mixture of AsF₃ and PSCl₃, in ratio AsF₃: 4PSCl₃, in a sealed tube at 150°.—2. By heating PbF₂ mixed with P₂S₃ to c. 120°-150°; or by using BiF₃ in place of PbF, and heating to a higher temperature. A mixture of red P, S, and a large excess of PbF, may also be used $(P_aS_a + 3PbF_a = 3PbS + 2PSF_g)$. 3. By heating S with PF_aCl_a to 115° (Poulenc, C.R. 113, 75).

Preparation.-A quantity of P.S. (freshly prepared from well-washed and perfectly dry amorphous P and roll S) is quickly mixted with c. 33 parts of pure freshly fused PbF2, and the mixture is placed in a thin equal layer in a dry tube of lead or 'composition,' one end of which is fitted with a caoutchouc oork carrying a glass delivery tube dipping under dry Hg, and the other end is connected with an apparatus for supplying pure dry N. A rapid stream of N is passed through till the air is driven out, the tube being gently heated to get rid of traces of H.S (produced by moisture on P.S.); the N is stopped, and the tube is heated from behind forwards by a small flame; reaction begins c. 170°; the temperature should be kept as low as possible, it must not exceed 250°. The gas is collected in a dry glass gas-holder containing a few small pieces of quicklime, the gas being allowed to pass into the holder as soon as a sample is wholly absorbed by dilute potash or ammonia. Before collecting the gas, small quantities of dry N should be passed into the gasholder and repeatedly exhausted by the Sprengel pump (this removes air from the pores of the lime), and when 2 or 3 c.c. of the PSCl, have passed into the holder the gas should be sucked out by the Sprengel, and this repeated twice or thrice (the traces of N are thus removed). After standing a few days over the lime, which removes PF. and any traces of SiF, the gas is pure PSF,

Properties,—A transparent, colouriess gas; liquefied at 7.6 atmos. at 3.8°, 9.4 atmos. at 10°,

10.3 atmos. at 18.6°, and 18 atmos. at 20.3°. PSF, is spontaneously inflammable in air or O it is decomposed easily by heat or electric sparks to S, P, and fluorides of P. Somewhat soluble in ether. Not easily dissolved by H₂O, or by solutions of alkalis. No action on Hg, H₂SO, CS₂, or C₆H₆. Neither gaseous nor liquid PSF, acts appreciably on glass at ordinary temperatures.

Reactions. -1. A small stream of PSF, issuing from a Pt jet into air at once takes fire; when mixed with a large volume of air, explosion occurs.-2. Oxidised rapidly and explosively by oxygen; probably with formation of PF, and SO, the PF, and O then producing P₂O, and also POF₃. The ignition-temperature of PSF₃ is very low, and the flame is a very cold (Full details are given by T. a. R., I.c., pp. 312-317.)—3. Slowly decomposed by water, thus: $PSF_3 + 4H_2O + Aq = H_2S + H_3PO_1Aq + 3HI_1Aq.$ 4. Solution of potash or soda slowly reacts, forming Na₂PSO₃ and NaF.—4. With ammonia gas produces a white, deliquescent solid, probably a mixture of NH₁F and P(NH₂)₂SF. For action of water on this substance-perhaps resulting in formation of PS(NII2)2OH-v.T.a.R., l.c., p. 319.—5. Heated in a glass tube, PSF, gives SiF, P, and S.—6. PSF, is decomposed by electric sparks passed from Pt terminals, with separation of S and P, and a gas which is probably PF..

Phosphorus, sulphoselenide of. All attempts to prepare this compound have led to negative results. Michaelis heated PCl, with Se; Bandrimont (A. Ch. [4] 2, 5) tried the reaction of PCl, with SeCl, PCl, with P.Se, Sh.Se, and PbSe, and the action of P on SeCl, and SeCl,

Phosphorus, sulphoxide of, $P_iO_aS_i$. Mol. w. 34752. Melts at 102°, and boils at 295°. V.D. 171:3 at 350°-400°. Formed by heating small quantities P_4O_a with S in an atmosphere of CO_2 or N at c. 160° (Thorpe a. Tutton, G. J. 59, 1022).

Preparation .- A strong glass tube is closed at one end, and filled with dry CO, or N; from 3 to 5 g. freshly-distilled PAO, is placed in the bottom of the tube, and 1.74 g. S, best in small crystals, are added for every 3 g. P.O. used (ratio P.O.: 48). The tube is sealed, and the lower half is immersed in a glycerin-bath, which is gradually heated. At c. 154°-165° the melted S is suddenly projected to the top of the tube, and in a few seconds the action is complete. The product is transferred to a similar tube, which is exhausted by a Sprengel pump, sealed, and warmed at its lower portion; sublimation begins at c. 90°, and proceeds best at 140°-150°, with formation of long feathery needles; part of the P.O.S. remains as a vitreous or crystalline mass.

Properties and Reactions.—A white solid, occurring in feathery aggregations or a vitreous mass, or as colourless, isolated, tetragonal prisms; melts 102°, and boils 295° (cor.). Very deliquescent, smelling in air of H₂S; quickly dissolved by water, forming H₂S and HPO₂Aq, which soon changes to H₂PO₄Aq. Easily sol. in 2 vols. CS₂ from which it crystallises unchanged. Also sol. benzene, but with decomposition.

Phosphorus, sulphur acids of, salts of; v. beginding of article Phosphorus sulphides

(p. 145); Phosphorous sulphide, Reactions 7 and 8 (p. 146); Phosphoric sulphide, Reaction 7 (p. 147); and Thio-oxygethophosphares (p. 147).

Phosphorus, telluride of. Oppenheim (J. 1857, 214) obtained a black amorphous solid, giving off fumes of P₂O₂ in air by heating P with powdered Te.

Phosphorus, thio-acids of, salts of; v. beginning of article Phosphorus suppurpus (p. 145); Phosphorus sulphide, Reaction 7 (p. 140); Phosphorus sulphide, Reaction 7 (p. 147); and Theo-exvormorhosphares (p. 147).

Phosphorus thio-amic acids of, and thio-amide of; v. Thiophosphoryl chlorids, Reaction 7 (p. 148).

Phosphorus, thiobromides of; v. Phosphorus

SULPHOBROMIDES, p. 147.

Phosphorus, thiobromochloride of; v. Phosphorus sulphobromochloride, p. 147.

Phosphorus, thiochlorides of; v. Phosphorus

SULPHACHLORIDES, p. 148.

Phosphorus, thiocyanide of; v. Phosphorus

SULPHOCYANIDE, p. 148. • Phosphorus, thioselenide of; v. Phosphorus Sulphoselenide, ante.

M. M. P. M.
PHOSPHORUS, OXYACIDS OF, AND THEIR
The three phosphoric saids H PO

SALTS. The three phosphoric acids, H₂PO₄, H₄P₂O₇, and HPO₄, are described under Phosphono acids (p. 124); the salts of these acids are described under Phosphates (p. 108); the other oxyacids of P₄ and their salts, are described in this article.

Besides the phosphoric acids, three oxyacids of P, and some salts of a fourth acid, have been isolated; the acids in question are H₂PO₂, H₂PO₃, H₂PO₃ or H₁P₂O₄; and salts of H₂PO₃. No anhydride of H₂PO₄ is known; the hypothetical anhydride would be P₂O (P₂O + 8H₂O - 2H₂PO₃); P₂O₄ is the anhydride of the acid H₂PO₄(P₂O₃ + 3H₂O - 2H₂PO₃), and also the hypothetical anhydride of H₂PO₄(P₂O₄ + 2H₂O - H₂PO₄O₃); P₂O₄ is the hypothetical anhydride of H₂PO₄(P₂O₄ + 2H₂O - H₂PO₄O₃), but this oxide gives H₂PO₃Aq and H₂PO₄Aq with wates (a. Phosphorus Tetroxide, p. 141). The oxyacids of P do not correspond in composition with those of N (v. Table in Nitrocen group of Elements, vol. iii. p. 575).

HYPOPHOSPHOROUS ACID AND SALTS II, PO,; MIL, PO, and MI(H, PO),. Hypophosphites are formed by decomposing phosphide of Ba, Ca, or Sr by water (Dulong, A. Ch. [2] 2, 141); by heating P with potash, milk of lime, or BaOAq (II. Rose, P. 9, 226, 361; 12, 77, 288); by passing PH, into solution of alkalis or alkaline hydrates (Wingkler, P. 11, 443); and by heating P with syrupy H, PO, Aq to 200° (Oppenheim, Bl. [2] 1, 163). The acid is monohasic; it may be regarded as derived from the hypothetical anhydride P₂O. There is no acid, nor are there salts, corresponding with hyponitrous acid II NO, but some salts are known of the form MPS; v. Thiometahypophosphites, at beginning of Phosphorus, sulphides of (p. 146). Sclenometahypophosphites MPSe have also been isolated (v. Diphosphorus sellenide, p. 144).

HYPOPHOSPHORUS ACID H.PO. Melts at 17.4° (Thomsen, B. 7, 994; ? specimen pure). H.F. [H²,P,O²]=139,970 (production of crystallised

said); 187,660 (production of said in liquid state); [H²,P,O²,Aq]=189,800 (Th. 2, 225).

Preparation.—Ba(H,PO₂),H₂O is prepared by warming water with BaO and P (in small state).

pieces) in a basin till inflammable P hydride cesses to come off, filtering, removing excess of BaO by passing in CO₂, filtering again, and crystallising. 285 g. pure Ba(H₂PO₂).H₂O are dissolved in c. 5 litres water, 98 g. H₂SO₄ (c. 1015 g. ordinary conc. acid), diluted with 3 to 4 times its weight of water, are added; after shaking for some time the pp. of BaSO, is allowed to settle, and the clear liquid is syphoned off, and evaporated in a porcelain dish, by boiling, till it is c. 10 of the original volume, when it is placed in a Pt dish; a thermometer is immersed in the liquid, evaporation is continued, the temperature being allowed to rise gradually to 110°; any solid which separates is filtered off while the liquid is hot, and the filtrate is evaporated, without being allowed to boil, at c. 110°. Thom-sen (B. 7, 994) finally heats for 10 mins. to 130° or 138°, filters into r. stoppered bottle, and cools below 0°; Geuther a. Ponndorff (J. Z. 10, Supplbd. 2, 45, 49) say that heating above 110° decomposes H,PO, and that Thomsen's preparation therefore contained HaPOs.

Properties .- Large, white, crystalline tablets; melting at 17.4°; remains liquid considerably above m.p. (Thomsen, l.c.). Decomposed by heat to PH, and H,PO. H,PO.Aq is a very energetic reducing agent. The acid is monobasic, forming

Reactions.—1. Decomposed by heat, giving P hydride and H₂PO₄ (H. Rose, l.c.).—2. H₂PO₂Aq is readily changed to H₃PO₃Aq or H₂PO₄Aq by oxidisers; Cl. Br. HNO₃Aq. KMnO₄Aq. and several metallicoxides produce H₃PO₄Aq (Dulong, Lc.; Rose, Lc.; P. de St. Gilles, A. Ch. [3] 55,374); PbO₂ forms PbHPO₄ (Wurtz, C. R. 18, 702); SO₂ forms H₄PO₄Aq and S (Geuther a. Ponndorff, l.c.). According to Engel (C. R. 110, 786) Pd charged with H oxidises H₄PO₄Aq to H₃PO₃Aq with evolution of H .- 3. HaPO Aq reduces solutions of salts of gold, silver, and mercury, ppg. the metals; of gold, sever, and mercury, ppg. the retais; from copper sulphate solution, Cu,H, is ppd. at 55°-60° (Wurtz, l.c.; Rammelsberg, l.c.).—4. Reduced by nascent hydrogen to PH, (Dusart, C. R. 43, 1126; Blondlot, C. R. 52, 1197).—5. With hydrodic acid forms PH, I (G. a. P., 120). l.c.) .- 6. Heated with conc. sulphuric acid, H.PO., SO., and S are produced (Wurtz, l.c.). 7. Heated with phosphorus pentachloride, POCl, PCl, and HCl are formed; phosphorus trichloride produces P, H,PO, and HCl; with phosphoryl chloride, P, PCl, HPO, and HCl are the products (Geuther, $J_{\bullet}pr$. [2] 8, 359).

HYPOPHOSPHITES M'H,PO, and M"(H,PO,), These salts are formed in several reactions (v. beginning of this article); the greater number are prepared by reacting on the salt of Ba with the sulphates of other metals; the salts of Ba, Ca, and Sr are generally prepared by heating BaOAq, CaOAq, and SrOAq with P. The hypo-phosphites of Cd, Ca, Pb, and Tl crystallise without water; those of Ba, Li, Mn, Na, Sr, and U with one H.O; those of Co, Mg, Ni, and Zn with 6H,O (Rammelsberg, C. J. [2] 11, 12). They are decomposed by heat, evolving P hydride and H, and generally leaving pyro- and meta- phosphate, the Co and Ni salts leave metaphosphate

and phosphide, and the U salt leaves pyro- and meta- phosphate and phosphide (R., l.c.). The hypophosphites are easily oxidised to phosphites and phosphates, hence they react as reducing agents. Heated in solution with alkalis they agents. Heated in solution with Birkhils Lieg give phosphites, and then phosphates, and evolve H (Wurtz; H. Rose, l.c.). The chief memoirs on hypophosphites are by H. Rose (P. 9, 225, 361; 12, 77, 288); Wurtz (A. Ch. [3] 7, 193; 16, 196); and Rammelsberg (C. J. [2] 11, 1, 13).

Ammonium hypophosphite NH, H, PO2. Hexagonal tablets; by decomposing the Ba salt by (NH₄), SO, Aq; easily sol, absolute alcohol (Wurtz.

Rose).

Barium hypophosphite Ba(H2PO2), H2O. Lustrous monoclinic needles (Rammelsberg; Topsöe, W. A. B. 69 [2] 19). By heating BaOAq with P till gas ceases to come off, filtering, removing BaO from the filtrate by CO, filtering, and crystallising. Loses HO at 100°. Soluble in 31 parts cold, and 3 parts boiling, water; insol. alcohol. Heated out of air leaves pyro- and meta- phosphate (Wurtz, Rose, Rammelsberg).

Calcium hypophosphite Ca(H₂PO₂). Prepared like the Ba salt. Berlandt (Ar. Ph. [2] 122, 237) recommends 29 parts P, 47 parts CaO,H, and 24 parts water. Bachmann and Martenson (J. 1864. 191) decompose Ca phosphide by boiling water. Thin, monoclinic tablets (Rammelsberg; Schabus, J. 1854. 325). Very bitter taste; unchanged in air; does not give off H₂O at 300°; heated to redness gives off H, PH₃, and H₂O, and leaves pyro- and meta- phosphate (Rammelsberg; Michaelis, J. 1872. 210). Sol. 6 parts cold water, not much more sol. hot water; insol. strong alcohol (Rose).

Cobalt hypophosphite Co(H.PO2)2.6H2O. Red octahedral crystals, isomorphous with Mg salt (Rose); by decomposing Ba salt by CoSO,Aq, filtering, and evaporating in vacuo (Wurtz). Forms a double salt with Ca(H,PO2)2 (Rose).

Comer himonhosphite Cu(H,PO2)2. Obtained

Copper hypophosphite Cu(H_PO₃). Obtained with difficulty from Ba salt and CuSO, Aq; solution easily decomposes, giving Cu_H₂ (Wurtz).

Lead hypophosphite Pb(H₂PO₃). By adding PbO or PbCO₄ to H₂PO₂Aq (Rose, Wurtz).

Manganese hypophosphite Mn(H,PO,), H,O Small, rose-red crystals; from Ba salt and MnSO Aq (Wurtz, Rammelsberg); or by boiling

Ca salt with Mn oxalate (Rose).

Potassium hypophosphite KH,PO, Prepared by decomposing the Ba or Ca salt by K,CO,Aq, filtering, evaporating to dryness, treating the residue with alcohol, and crystallising the alcoholic solution in vacuo; or by dissolving P in boiling KOHAq, evaporating, and dissolving out from the residue by alcohol; also by decomposing the Basalt by K.SO.Aq (Rose, Wurtz). A white, semi-crystalline mass. Easily sol. water and alcohol; very hygroscopic (Dulong, A. Ch. [2] 2, 141). Burns when heated in air; oxidised violently by evaporation with HNO.Aq. Heated out of air evolves inflammable P hydride, and leaves pyro- and meta- phosphate (Rammelsberg).

Sodium hypophosphite NaH_PO_.H_O. Pre-pared like the K salt. Small, rectangular tablets, easily sol. water and absolute alcohol. Evaporation of the solution is attended with explosions (Marquart, Ar. Ph. [2] 95, 284; Trommsdorff,

ibid. 99, 888).

The salts LiH.PO.H.O. Ni(H.PO.M6H.O.

Sr(H₂PO₂)₂, and Zn(H₂PO₂), are also described; and salts of Al, Be, Cd, Or, and Fe have been obtained, but their compositions are somewhat doubtful.

PHOSPHOROUS ACID AND SALTS H.PO,; M'H.PO, M',HPO, M',HPO, M''HPO,, M''HPO,, M''',(HPO,), P₂O, is the anhydride of H,PO,; the acid is produced by dissolving the oxide in cold water, but the oxide is not obtained by removing H.O from the acid. H.PO, is dibasic; the salt Na,PO, said to be formed by adding a large excess of NaOH to H,PO, (Zimmermann), has been shown by Amat (C. R. 108, 403) not to exist. The acid is formed by oxidising P slowly in moist air; the salts are obtained by reactions between the acid and metallic hydroxides, or by double decomposition from the alkali salts. Neither the acid nor salts of the acid corresponding with nitrous acid, HNO₂, are known, nor have thio-salts of this form been isolated.

PHOSPHOROUS ACID H₃PO₃. Melts at 74° (Geuther a. Hurtzig, A. 111, 159); at 70·1° (Thomsen, J. pr. [2] 8, 359). H.F. [H³,P,O³] = 227,700 (crystallised acid); 224,630 (acid in liquid state); 227,570 (acid in aqueous solution) (Th. 2, 225). Heat of fusion = -3070; one gram-molecule of the liquid acid occupies 49.66 c.c. (Th. 2, 224).

Formation. -1. Along with H, PO, and H, PO, by the long-continued oxidation of P in moist air (v. J. Corne, J. Ph. [5] 6, 123).—2. By dissolving P in dilute HNO₃Aq and allowing to oxidise in air.—3. By the oxidation of H₂PO₂Aq by weak oxidisers.—4. By dissolving P₂O₂ in cold water (Thorpe a. Tutton, C. J. 57, 567).—5. By decomposing PCl, by ILO, or by warming with H.C.O. (Hurtzig a. Gouther, A. 111, 159); or by leading Cl into warm water in presence of an excess of molten P (Droquet, P. 12, 628).

Preparation .- 1. A small quantity of PCl, is shaken with cold water, the reaction is moderated by plunging the beaker into cold water; when the PCl, is all decomposed, a little more is added, and so on (PCl₂ + 3H₂O + Aq = 3HClAq + H₃PO₃Aq). The solution is evaporated, the temperature being raised to 180° near the end of the process; the syrupy liquid thus obtained is placed over H₂SO₄, in vacuo, till it crystallises; addition of a crystal of H₂PO₄ causes rapid crystallisation (Thomson, B. 7, 996). 2. A stream of dry air is passed through PCl, at 60°, and then into two flasks, each containing c. 100 g. water at 0°; after c. 4 hours the first flask is filled with crystals, which are drained under a pump, washed with small quantities of ice cold water, and dried in vacuo (Grosheintz, Bl. [2] 27, 433).—3. A mixture of 1 part PCl, and 2 parts dry H₂C₂O₄ is heated in a flask with a reversed condenser until a clear liquid is obtained; the liquid is evaporated in a stream of CO., and the crystals are washed and dried as in 2 (Hurtzig a. Geuther, A. 111, 159: PCl₂+3H₂C₂O₄ = H₂PO₂+3CO+3CO₂+3HCl).

Properties. A colourless, crystalline mass; obtained in transparent crystals by evaporating H,PO,Aq in vacuo over H,SO, Melts at 74° (H. a. G., l.c.); at 701° (Thomsen, l.c.). Heated above its m.p. decomposes to H.PO, and PH₁. H₂PO, is very deliquescent, and oxidises very slowly in air; it acts as an energetic reducing

agent. H,PO, is dibasic, forming salts M'H,PO, and M, HPO.

Reactions .- 1. Heated above its m.p., H.PO. decomposes to H.PO, and inflammable P hydride (Vigier, Bl. [2] 11, 125; Rose, Davy, Gm. K. 2, 115); according to Hurtzig a. Geuther (A. 111, 159) Palso separates. -2. Slowly oxidised in air to H.PO.; dilute solutions of H.PO. are more rapidly oxidised; according to Salzer (A. 232, 114), H,PO,Aq does not oxidise in air at ordinary temperatures. - 8. Converted into H.PO, by many oxidisers, e.g. HNO, Aq, OlAq, BrAq, KMnO, Aq, hypochlorites; with SO, Aq, H.PO, Aq and H.S are formed along with S (Gm.-K. 2, 116).-4. Reduces many metallic salts in solution; e.g. AgNO₃Aq to Aq, HgClAq to HgCl and then to Hg, CuClAq to Cu,O₃ and then to Cu (Rammelsberg, C. J. [2] 11, 13).—5. Nasto de (Raininesberg, C. 2, 12) 11, 15, 35, 35, 36, 48, 1126). 6. When crystalline H₂PO₄ is heated with bromine to 100° in a sealed tube, H₂PO₄ is former along with HBr and PBr_B, or the products are HPO, and HBr, according to the relative quantity of Br used (Gustavson, J. 1867, 139). According to Ordinaire (C. R. 64, 863), a crystalline compound is obtained -perhaps bromo-phosphorous acid—by heating H,PO, and Br in the ratio H.PO.: 4Br.—7. By heating H.PO. with iodine Gustavson (l.c.) obtained H.PO., HI, PI., and PII, I.—8. Heated with phosphorus trichloride to 170°, P. HCl, and H.PO, or H.P.O, are formed (Geuther, J. pr. [2] 8, 859; Kraut, A. 158, 882; Gautier, C. R. 76, 49). At 70° HCl, H.P.O, and a compound PHO are formed, according to Gautier (l.c.) (v. Phosphorus, compounds of, with HYDROGEN AND OXYGEN, p. 134).—9. With phosphorus pentachloride, POCla HCl, and PCl are produced; and the products of the reaction with phosphoryl chloride are POl, HPO, and HOI (Geuther, J. pr. [2] 8, 359).—10. By neutralisation with alkalis or alkaline carbonates salts of the form M.HPO, are produced.

Qualitative distinction between phosphorous and hypophosphorous acids. H₂PO₂Aq reduces

CuSO, Aq to Cu, while the reduction product with H,PO,Aq is Cu,H,.
PHOSPHITES M'H,PO,, M'2HPO,, M"HPO,,
M"12(HPO,), These salts are generally obtained by neutralising H, PO, Aq by metallic hydroxides or carbonates, or by double decomposition from the alkali salts. They are also formed by the slow oxidation of hypophosphites. Zimmermann's assertion that Na, PO, exists (A. 175, 1) has been disproved by Amat (C. R. 106, 1851), who has shown that the normal Na salt is Na_HPO_s. The alkali phosphites are soluble water; most of the others are insoluble. Phosphites are decomposed by heat, generally giving off H or PH,, and leaving pyrophosphate and phosphide. Solutions of phosphites are scarcely changed in air, but they are readily oxidised to phosphates by energetic oxidisers. The chief memoirs on phosphites are those of H. Rose (P 9, 26, 224; 12, 77, 258), Rammelsberg (P. 181, 263, 359; 132, 481; B. 9, 1577), Kraut (A. 177 274), Wurtz (A. 58, 65).

Ammonium phosphites (NH.)H.PO, and (NH.).HPO, 2H.O. The former is obtained by adding NH, Aq to H, PO, Aq till neutral to methyl orange, concentrating, and drying the crystals over H₂SO₄; melts 128°; above 150° gives off

NH, and PH,, and leaves H,PO,; absorbs NH, at 80°-100°, forming (NH,),HPO, (Amat, C. R. 105, 80°). The salt (NH,),HPO,2H,O was obtained by Rose by adding slight excess NH,Aq then at 150° (A., La.). The acid salt to the acid and crystallising; in vacuo at ordinary temperature, or at 100° in air, loses NH, and gives NH, H,PO, (Amat, l.c.).

and gives NH₂H₂PO₅ (Amat, l.c.).

Barium phosphites. The normal salt
BaHPO₅ is obtained by adding BaCl₂Aq to
(NH₃).HPO₅Aq (Berzelius, Gm. K. 2, 270), also
by boiling BaHPO₅Aq with KOHAq. A crystalline powder; strongly heated gives Ba₂P₂O₅, H,
and Ba phosphide (v. Hamfinelsberg, B. 9,
1577); very slightly sol. water; on boiling
with water gives a basic and an acid salt
(Dulong, Gm.-K. 2. 270). The acid salts
(Dulong, All₂PO₅, 2H₂O are said to be formed by
the action of H₂PO₅Aq on the normal salt the action of H_aPO_aAq on the normal salt (Rammelsberg, Rose, Wurtz).

Calcium phosphites. CaHPO₃,xH₆O; from CaCl₂Aq and (NH₃,HFO₂Aq (Wurtz, Rose, Rammelsberg). The acid sait CaH₂(HPO₃)₂,H₆O is obtained by dissolving marble in H₂PO₃Aq,

and evaporating in vacuo (Wurtz).

Cobalt phosphite CoHPO, 2H.O. powder, obtained by CoCl,Aq+(NH,),HPO,Aq, or by dissolving freshly ppd. CoCO, in H,PO,Aq; goes blue at 250° (Rose, Rammelsberg).

Copper phosphite CuHPO3.2H2O. By double decomposition from (NH₄), HPO₃ (Rose); also by acting on Cu acetate by H₃PO₃Aq (Wurtz). Un-

acting on Cu acetate by H₂PO₂Aq (Wurtz). Unchanged by boiling water (Rammelsberg), but reduced to Cu by boiling with H₂PO₂Aq (Rose). Lead phosphiles. The normal salt PbHPO₃ is obtained by ppg. Pb acetate by (NH₄)₂HPO₂Aq (Rose). A white powder; heated gives off H and PH₃, leaving Pb₂PO₃ and Pb phosphide. Insol water (Amat, C. E. 110, 901). By adding NaH₂PO₃Aq to excess of Pb2NO₃Aq, the compound PbHPO₃Pb(NO₃), is obtained (Amat, l.c.). The acid salt PbH₂(HPO₃)₂ is formed by dissolving the normal salt in very cone. H₂PO₂Aq, and drying the crystals at 100°; with water gives PbHPO₃ and H₃PO₃Aq (Amat, with water gives PbHPO₃ and H₃PO₃Aq (Amat) with water gives PbHPO, and H,PO,Aq (Amat,

Le.).

Magnesium phosphite MgHPO,xH.O. By
DDR. boiling MgSO,Aq by Na.HPO,Aq

MgSO,Aq by Na.HPO,Aq

Agailla salt (Rammelsberg). Forms a double salt Mgs(NH₄)₂(HPO₃), 16H₂O (Rammelsberg, Rose), Manganese phosphite MnHPO₂, H₂O. A red-

dish, powder; very slightly sol. water, more sol. solutions of Mn salts; loses H₂O at 200°. From NH, salt and a Mn salt; or by dissolving MnCO, in H,PO,Aq, and adding Na,CO, till ppn. begins, but not enough to remove acid reaction (Rose, Rammelsberg).

Potassius phosphites. The normal salt K.HPO, is formed from H.PO, Aq and KOHAq A.H.P. 18 formed from H. P. V. Aq and K. OH. Aq r. K. O. Aq; semi-crystalline, syrup-like mass; very hygroscopic; insol. alcohol (Wurtz, Rose). The acid salt K. H.P. O. 2H. P. O. was obtained by Wurtz (A. 58, 63). Amat (C. R. 106, 1351) obtained the acid salt K. H. P. O. by adding KOHAq ore K. C. O. Aq to H. P. O. Aq till neutral to

methyl orange, concentrating, and cooling.

Sodium phosphites. The normal salt
Na,HPO,-5H,O is obtained by dissolving H,PO, in an excess of NaOHAq, and evaporating in vocuo (Amat, C. R. 108, 403). Zimmermann (4. 175, 1) supposed that Na,PO, is formed

heat of solution at $18.5^{\circ} = -4600$ (Amat, C. R 110, 191). Debydrated by drying in vacuo, and then at 150° (A., l.c.). The acid salt 2NaH,PO,5H,O is produced by making H₃PO₄Aq neutral to methyl orange by NaOHAq The property of the property 106, 1351).

Zinc phosphite 2ZnHPO, 5H,0; from ZnSO,Aq and ammoniacal solution of PCl, (Rose); also from PCl,Aq and ZnO (Rammela-

The following phosphites have also been described:—Di₂(HPO₃)₃ (Frerichs a. Smith, A. 191, 331); Fe₂(HPO₃)₃, 9H₂O (Rose, Rammelsberg); La₂(HPO₃), (F. a. S., L.c.); SnHPO₃ (Rose). Phosphites of Al, Be, Bi, Cd, Cr, ferman rous Fe, Hg, Ni, and Sr have also been prepared, but their compositions are somewhat doubtful (v. especially Rose, l.c.)

(9. cspecially rose, i.e.).

HYPOPHOSPHORIC ACID AND SALTS

H₁P₂O₀, M'H₂P₂O₀, M'₂H₂P₂O₀,

M'₄P₂O₀, M'H₂P₂O₀, M''₂P₂O₀. When sticks of

P are partly covered with water and left for some time in a large vessel, an acid liquid is obtained; this liquid was formerly called Pelletier's phosphatic acid (P., Crell. Ann. 1796 [2] 447). Dulong (A. Ch. [2] 2, 141) found 478 p.c. P and 52-2 p.c. O in this substance, and supposed it to be P₂O₉. In 1856 Pagel (J. pr. 69, 24) showed that the acid liquid contained phosphoric and phosphorous acids; and in 1877 Salzer (A. 187, 322) proved the presence of small quantiities of a new acid to which he gave the composition nH_2PO_1 and the name hypophosphoric acid. The acid has been found to be tetrabasic, hence the formula is written H₄P₂O₆. The hypophosphates are generally formed directly from the acid, or by double decomposition from the alkali salts. The hypophosphates are more stable than the hypophosphites and phosphites; normal salts pass into phosphates by taking up O; they are decomposed by heating strongly giving of PH3 or H, and leaving phosphate and phosphide.

Hypophosphoric acid H,P.O. Melts at c. 55° (Joly, C. R. 102, 110). Heat of solution = 3,850 (J., l.c.).

Formation.—1. Along with H₂PO₃ and H₃PO₄, by the slow oxidation of P in moist air (Salzer, A. 187, 322; 194, 28; 211, 1; 232, 114. 271).-2. The Ag salt is formed by oxidising P by dilute HNO, Aq in presence of AgNO, (Philipp. B. 18, 749); also by reacting on H₃PO₃Aq with AgNO₃Aq (Sänger, A. 232, 1); and the Cu salt by reacting on P with Cu(NO3)2Aq (Corne, J. Ph. [5] 6, 123).

Preparation .- Sticks of P are placed in glass tubes narrowed at the lower end; these are arranged inside a funnel, which is placed in the mouth of a bottle containing a little water; the bottle is set in a basin, and the whole is covered with a large bell-jar open at the top. The apparatus is placed in a cool place (best in In a apparatus is piaced in a cool piace (local in a cellar) for some weeks or months; according to Joly (C. R. 101, 1958), from $\frac{1}{2}$ to $\frac{1}{2}$ of the P is oxidised to $H_1P_2O_8$ if the process is conducted in winter, and not more than $\frac{1}{10}$ in sammer.

The sold liquid is mixed with a cold cone. solution of Na scetate, the ppd. Na,H,P,O,.6H,O is collected, washed with a very little cold water, then dissolved in water (sol. in c. 45 parts cold water), and ppd. by Pb acetate; the Pb,P,O, is collected, washed with cold water, suspended in water, and decomposed by H,S; the filtrate is evaporated at a low temperature-not exceeding -or in vacuo over H.SO, until crystals of H,P2O4 are deposited. Joly (C. R. 101, 1058, 1148) heats to boiling the acid liquid obtained by oxidising P, as described above, adds Na CO, till nearly neutral to methyl orange, and crystallises by concentration; he washes the crystals of Na₂H₂P₂O₈.6H₂O with cold water, and recrystallises from hot water, dissolves in hot water, adds an equivalent of BaCl, in hot water, washes the ppd. BaH₂P₂O₆, decomposes it by an equivalent of H₂SO₁ diluted with its own weight of water, filters after two or three days, and evaporates in vacuo over H.SO. Drawe (B. 21, 3401) carries out the oxidation of P in presence of Na acetate solution.

Properties .- Small colourless crystals, which melt at c. 55° (Joly, C. R. 102, 110); very hygroscopic; solution is unchanged in air at ordinary temperatures. Heated to c. 70° suddenly decomposes to H₃PO₃ and HPO₃ (J., l.c.); at c. 120° gives H₄P₂O₇ and P hydride (J., C. R. 102, 760).

Reactions and Combination .- 1. Heat decomposes H₄P₂O₆ (v. supra).—2. Not oxidised by such oxidisers as H₂O₂Aq, ClAq, CrO₃Aq, HgCl₂Aq, &c .- 3. Not reduced by such reducers as SO, Aq. H2S, or Zn and H2SO, Aq. -4. Potassium per manganate is slowly reduced in the cold, quickly on heating, by H₁P₂O₂Aq to which H₂SO₄Aq has been added.—5. Heated with nitric acid, HaPO, Aq is formed .- 6. Heated with dilute sulphuric acid, H,PO,Aq and H,PO,Ag are produced.—7. Silver nitrate solution gives a white pp., which does not blacken in light and is soluble in warm HNO Aq (1:1). 8. By evaporating H.P.O. Aq till the liquid had the composition P.O. ill.O, and then placing over H.SO. in wacuo, Joly (C. R. 101, 1058; 102, 110) obtained crystals of the hydrate H,P,O,2H,O, melting at 62°-62.5°.

salts have been examined chiefly by Salzer (A. 187, 322; 194, 28; 211,1; 232, 114, 271), and crystallographically by Haushofer a. Fresenius (Z. K. 1, 257, 620; 3, 605; 6, 113; 9, 254). The hypophosphates are much more stable towards oxidisers than the hypophosphites or phosphites. They reduce KMnO, Aq very slowly in the cold after addition of H.SO Ag, and give white pp. with AgNO, Aq unchanged in light.

Ammonium hypophosphates. The normal salt (NH₁), P.O., xH₂O is obtained by adding excess of NH₃Aq to the acid; on drying, loses NH₃ and effloresces. The acid salts NH, and efforesces. The acid salts (NH,)₂H₂P₂O₄ and (NH₄)₃HP₄O₅ are formed, the former by boiling a solution of the normal salt, the latter by adding the proper quantity of H.P.O. to the former salt.

Barium hypophosphates. The normal salt Ba,P,O is obtained from BaCl,Aq and Na,P,O,Aq; the acid salt BnH,P,O,2H,O is formed from NaH,P,O,Aq and BaCl,Aq (v. Joly, C. R. 101, 1058).

Cadmium hypophosphate Cd.P.O. 2H.O; and the double salt CdNa.P.O. 6H.O (Drawe, B. 21, 3401).

hypophosphates Ca2P.O. Calcium CaH.P.O. 6H.O.

Cobalt hypophosphate Co.P.O.8H.O; and the double salt 2CoNa.P.O.3H.O (Drawe, l.c.). Copper hypophosphate Cu,P2O.6H2O (Drawe,

Lead hypophosphate Pb_P_O. Magnesium hipophosphates Mg_P_O.12H_O and MgH_P_O.4H_O; and the double salt

Mg(NI₁),P₂O₆OI₂O.

Nickel hypophosphate Ni,P₂O₆12H₂O; and the double salt NiNa, P.O., 12H,O (Drawe,

Potassium hypophosphates K₄P₂O₆.8H₂O, K₂HP₂O₆.3H₂O, K₂H₂P₃O₆, and KH₃P₂O₆.

Silver hypophosphate Ag.P.O. (v. Philipp, B. 14, 749).

Sodium hypophosphates. The acid salt Na₂H₂P₂O₃.6H₂O is obtained by slowly oxidising P in moist air, and adding Na acctate solution as described under Preparation of hypophosphoric acid (p. 154); sol. 45 parts cold, or 5 parts boiling, water; insol. alcohol; on strongly heating gives off H and P hydride and leaves NaPO₃. The normal salt Na,P₂O₆:10H₂O is obtained by adding an equivalent of Na_CO₃ to Na_H_P_O₄Aq; sol. c. 30 parts cold water, much more sol. hot water; solution reacts alkaline, and gives a mixture of salts on evaporation. The acid salt Na, HP, O, 9H, O is formed by mixing the Na, and Na, salts in the ratio Na, H.P.O. : Na, P.O. The acid salt NaH.P.O. : 2H.O is formed by adding the proper quantity of H₁P₂O₆Aq to Na₂H₂P₂O₆. For reaction of the Na salts with different indicators v. Joly, C. R. 101, 1058.

Another acid salt Na, H, (P,O,). 20H,O is said to be formed by adding rather more than one molecular weight NaOH to 4Na₂H₂P₂O₆.6Π₂O.

Zinc hypophosphate Zn.P.O. 2II.O (Drawe,

PYROPHOSPHITES. In 1887 Amat (C. R. 106, 1400) showed that when 2NaH2PO35H2O is heated to 160° it loses 6H O and gives the salt Na₂H₂P₂O₃. A few other salts of the form M.H.P.O. have been obtained, but the acid has not been isolated. When the Ba salt is decomposed by an equivalent of H.SO.Aq, the solution shows the reactions of pyrophosphites, but the pyrophosphite gradually changes to phosphite (Amat, C. R. 108, 1056). The pyrophosphites in solution slowly change to phosphites, the more rapidly the more cone. the solution and the higher the temperature; the presence of an acid, e.g. H.SO, greatly quickens the rate of change (A., l.c.). Addition of NaOHAq to a boiling solution of the Na salt produces Na₂HPO₂ (A., C. R. 106, 1400). Pyrophosphites in very dilute solutions give no pp. with Ph(NO₃)2Aq until boiled; phosphites give an immediate white pp.; this reaction serves as a qualitative test for the two classes of salts (A., C. R. 110, 901).

Lead pyrophosphite PbH.P.O. is obtained by heating PbH (HPO), in a lry vacuum to c. 140

It is insol. water, but is gradually changed by water to H₂PO₂Aq and PbHPO₂ (A., C. R. 110, 901).

Sodium pyrophosphits Na,H,P,O, is formed by heating 2NaH,PO,.5H,O, which has been partially dehydrated in vacuo, to c. 160°. V. sol. water; solution changes to NaH,PO,Aq, but by careful evaporation in vacuo over H,SO, crystals of Na,H,P,O, can be again obtained (A., C. R. 108, 1056). Presence of acid hastens the change to NaH,PO,Aq; this change is also effected by adding NaOHAq to boiling Na,H,P,O,Aq. Heat of solution of Na,H,P,O,3 = 300 (A., C. R. 110, 191).

For thiopyrophosphites M,P,S, and thio-oxypyrophosphites M,P,O,S, and M,P,O,S v. Phosphosous sulphide, Reactions 7 and 8, p. 146; and for selenopyrophosphites M,P,Se, v. Phosphosous selenide, p. 145). M. M. P. M.

PHOSPHORYL COMPOUNDS. Compounds of the radicle PO are generally called hosphoryl compounds; and compounds of the radicle PS are often called this phosphoryl compounds. These compounds are described in this Dictionary as phosphorus caychloride, oxylfuoride, sulphochloride, &c. The phosphoryl compounds are PO(NH₂), POCl, POBr, POBrCl, and POBr,Cl, POF, FO.NH.NH., PON. The thiophosphoryl compounds are PS(NH₂), PSCl, PSBr, PSBrCl, PSF, The compounds P,O,Cl, and P,S,Br₂, are sometimes called pyrophosphoryl chloride and pyrothiophosphoryl bromide, respectively.

(a)-PHOSPHOTOLUIC ACID M. M. P. M.

C_sH_sMe(PO_sH_s).CO_sH [3:4:1]. Toluphosphinic acid. [262⁵]. Formed by oxidising m-xyleno phosphonic acid with hot alkaline KMnO_s (Weller, B. 20, 1723; 21, 1492). Prisms, v. sol. hot water, v. e. sol. alcohol. Yields HPO_s and m-toluic acid when heated.—PCl, yields oily C_sH_sMe(POCl_s).COCl.—PbHA''' aq: needles (from dilute HOAc).—Ag_sA'''.

(β)-Phosphotoluic acid

C₄H,Me(PO,H₂).CO₂H [5:3:1]. [220°]. Formed by oxidising s-m-xylene phosphonic acid (Weller). Yields HPO, and m-toluic acid on heating.—Ag₂A": amorphous pp.

Chloride C.H.Me(POCl.).COCl. (249° at

147 mm.). Oil.

Phosphotoluic acid

C_zH_zMe(PO_zH_z).CO_zH(4:x:1]. [278°]. Formed by oxidising p-xylene phosphonic acid. Needles, decid. when the property of the property o

Chloride C_eH₃Me(POCl₂).COCl. [62°]. Crystalline mass.

PHOTO-CHEMISTRY v. Influence of light on chemical change, under Chemical Change, vol. i. p. 748; also next article (Photographic Chemistry); also Optical methods, a section of Physical methods, in this volume, p. 221.

PHOTOGRAPHIC OHEMISTRY. The photographic processes at present in use depend primarily upon the photo-chemical decomposition of certain metallic compounds in the presence of suitable oxidisable substances known as sensitisers. Broadly speaking, the photodecomposable compound may be regarded from a chemical point of view as an oxidising agent, of which the oxidising power is only brought

into action under the stimulus of light, the associated compound or sensitiser being at the same time oxidised by the oxygen or haloger thus liberated. Very many metallic compounds are thus susceptible to the influence of light although only a few of these have up to the present time found practical application. The nature of the chemical change undergone in such cases may be well illustrated by the action of light upon ferric salts. An aqueous solution of ferric chloride, for example, is not acted upon by light because the associated substance (water) is not capable of reacting with the liberated chlorine with sufficient rapidity; in other words, water is incapable of acting as a sensitiser towards ferric chloride. But if some oxidisable organic compound is present, light then reduces the ferric to the ferrous salt. Thus an alcoholic solution of ferric chloride exposed for a few minutes to sunlight gives a blue colouration with potassium ferricyanide, indicating the presence of a ferrous salt, rockelly formed according to the equation probably formed according to the equation Fe, Cl_s + C, H_oO = Fe, Cl_s + C, H_oO + 2HCl. In a similar way paper coated with a solution of ferric chloride can be used to obtain prints, because the paper (or the size contained in it) plays the part of a sensitiser, and the exposed portions of the surface thus become covered with a ferrous instead of a ferric compound, and on brushing over with a solution of ferricyanide the print is developed in blue. In practice ferric oxalate is found to be the most sensitive ferric compound. the organic acid being the sensitiser : Fe2(C2O4)3

= Fc₂(C₂O₄)₂ + 2CO₂.

Although the chemical action of light upon metallic compounds generally is of the nature of reduction, and is accompanied by the simultane, ous oxidation of the compound which plays the part of a sensitiser, there are many instances in which light promotes the action of atmospheric oxygen or other oxidising agent. Thus potassium iodide may be kept in a dry atmosphere in the dark for any length of time without undergoing change, but in the presence of light and moisture photo-chemical oxidation takes place,

and the salt becomes alkaline:

 $4KI + 2H_2O + O_2 = 4KOH + 2I_{2*}$ Action of light upon silver salts. Of all known metallic compounds the salts of silver are the most sensitive to the action of light, and these salts accordingly form the basis of all existing photographic processes. The most familiar instance of the photo-decomposition of a silver salt is the well-known change in colour experienced by silver chloride on exposure to light, a phenomenon which has been familiar since the sixteenth century. The other silver haloids, viz. the bromide and iodide, are also decomposed by light, the latter only in the presence of some sensitiser capable of rapidly absorbing iodine. The absolute sensitiveness of the silver haloids cannot be estimated by the degree of darkening on exposure, because the product of photo-decomposition is of a darker colour in the case of the chleride than in the case of the bromide, and the product is darker in the case of the bromide than in that of the iodide. The sensitiveness is actually determined by two conditions, viz. the nature of the sensitiser and the state of molecular aggregation of the silver haloid. In most of the negative processes

ow in use, the bromide or iodide, or a mixture t the two, forms the sensitive surface.

The nature of the chemical change undergone n exposure to light has not yet been completely lucidated for all the silver haloids. It is known hat the chloride loses chlorine on exposure, and hat the darkened product contains less chlorine han the unaltered haloid. It is as yet uncerain whether the halogen which is given off is lways evolved in the free state or not; it has been hown, however, that silver chloride on exposure o light gives off a gas which rapidly turns potasium iodide and starch paper bine (Meldola, hemistry of Photography, p. 66). It is stated y many writers that the darkened product is a whehloride formed according to the equation:
AgCl = 2Ag₂Cl + Cl₂. There is, however, no satisactory evidence of the existence of such a subalt, and it seems more probable that the dark roduct consists of an oxychloride, in combinaion, or admixture, with unaltered chloride. Acording to some analyses by Hodgkinson, the xychloride has the formula Ag OCl2. In support if this conclusion it is found that the chloride loes not darken in absolutely dry air, unless apour of mercury is present (Abney), thus naking it appear that moisture is essential for he decomposition. The latest investigation of he action of light on AgCl by Baker (C. J. 61, '28) confirms the view that the darkened product ontains an oxychloride; Baker gives the formula lg₂ClO. A second, white, oxychloride also robably exists (Richardson, C. J. 59, 536). Silver chloride is thus analogous to cuprous or hallous chloride, which also darken under the nfluence of light, with the formation of what are believed to be oxychlorides. Whatever may se the chemical composition of the darkened product, it is probable that the bromide and iodide rive rise to the formation of analogous com-ounds, and that the invisible picture in the older processes is formed of these products on The unbackground of unaltered haloid. leveloped image on modern dry plates, coated with gelatin emulsion, may, however, have a diferent composition, owing to the presence of the organic sensitiser.

Photosalts of silver. These are coloured forms of the silver haloids prepared by the action of certain reducing agents upon silver compounds, and the subsequent conversion of the partially reduced products into the haloids by treatment with the necessary acids. These compounds are of a red or purple colour, and have been shown to contain less halogen than the unaltered haloids. It is probable that they consist of physical combinations of the oxyhaloid or hydrated oxyhaloid with the unaltered haloid; their discoverer (Carey Lea) has shown that they closely resemble, if they are not actually identical with, the products of the photo-chemisal reduction of the sliver haloids. If this be admitted, it follows that the product which forms the photographic image can be prepared

by purely chemical methods (Am. S. 1887). Photographic processes. In all photographic processes the first operation is the exposure of a surface coated with a uniform film of the silver haloid to the image formed by a lens in a camera. The image thus depicted on the film

slight difference in colour between the product of photo-reduction and the unaltered haloid, and in the next place because the short period of exposure does not produce a sufficient quantity of the product of reduction to render the latter visible. The invisible image thus consists of a layer of reduction-product of infinitesimal thinness, and the picture is afterwards made visible by the deposition of metallic silver on this reduction-product by the application of certain solutions known as 'developers,' the chemical

action of which will be described subsequently.

Daguerreotype. This process is historically interesting as having been the first method of photography with a silver salt successfully applied to the production of a picture from the image formed in a camera. It takes its name from Daguerre, who announced the discovery in 1839. The process is no longer used; it has been superseded by more rapid methods. order to prepare a Daguerreotype plate, a plate of copper is silvered, and the polished surface is exposed to the vapour of iodine and bromine alternately. The sensitive film is therefore a mixture of silver iodide and bromide. Silver iodide can act to some extent as its own sensitiser, but the substratum of metallic silver is chiefly effective in this capacity as it is capable of rapidly absorbing the halogen liberated by the action of light upon the sensitive surface. The invisible image is developed by exposure to the vapour of mercury, which condenses on the product of reduction but not on the unaltered haloid.

Collodion processes. In these processes the sensitive film consists of a silver haloid formed by double decomposition in collodion as a vehicle. Collodion is a solution of the tri- and tetranitrate of cellulose (collodion pyroxyline) in alco-hol and ether (v. vol. i. p. 716), and on coating a glass plate with this solution the solvents evaporate and leave a uniform layer of the pyroxyline attached to the plate. Some soluble iodide, NH₄I or CdI₂, sometimes mixed with a small quantity of a bromide, is first dissolved in the collodion, the plate is coated with this salted collodion, and when dry is sensitised by immersion in a silver nitrate solution. The sensitive surface in this process is therefore a silver haloid wetted with a film of silver nitrate solution, the latter playing the part of a sensitiser by absorbing the liberated halogen: 31, + 6AgNO, + 3H,O = 5AgI + AgIO, + 6HNO, By washing out the soluble salts after the plate has been removed from the silver solution the sensitiveness is practically destroyed, because the pyroxyline by itself has no halogen-absorbing power. On drying such a washed plate, and then coating it with a solution of tannin or some organic sensitiser, the sensitiveness is partially restored. Plates thus treated can be used in the dry state, and dry-plate photography by this method was made practically successful in 1861 by Colonel Russell.

Emulsion processes. All the photographic methods at present in vogue are comprised in this group. The silver haloid is precipitated in a finely divided state in some vehicle, usually gelatin, and the plates coated with this emul-sion are allowed to dry and are then ready for use. A brief description of a method for preis invisible, in the first place because of the very paring a gelatin emulsion will suffice to make

clear the general mode of procedure. The soluble bromide (potassium or ammonium), sometimes mixed with a little iodide, is dissolved in water, together with a certain quantity of the gelatin, and to this solution the calculated quantity of silver nitrate (previously dissolved in water) is added little by little with constant agitation. The quantities are so adjusted as to leave no excess of silver nitrate. The silver haloid is by this means precipitated in an extremely fine state of division in the viscid gelatin solution, with which it forms an emulsion. A stronger solution of gelatin is then mixed intimately with the first dilute emulsion, and the whole is heated on a water-bath for about an hour to become 'ripened.' cold, the semi-solid emulsion is washed by immersion in a fine state of division in cold water, so as to remove all soluble salts (nitrates formed by double decomposition, excess of soluble haloids, &c.). The washed emusion is then mixed with the necessary quantity of strong gelatin solution to reduce it to the required consistency, and the plates are coated and allowed to dry. Many variations in the details of mixing have been introduced, but these involve no change in principle. Ripening can also be effected at ordinary temperatures by the action of ammonia.

Ripening of emulsions. The process of ripening above referred to is necessary in order to increase the sensitiveness of the silver haloid. since the latter when first precipitated is comparatively insensitive. The increase of sensitiveness is no doubt due, partially if not wholly, to a physical change in the state of molecular aggregation of the silver haloid, as it is accompanied by a growth in the size of the particles and by a change in the absorption spectrum, the unripened emulsion transmitting more of the red rays, and, therefore, absorbing less of this part of the spectrum, than the ripened emulsion. The extreme sensitiveness of the emulsions at-present in use is thus due in great measure to the circumstance that the haloid is rendered sensitive to a much wider range of spectral colours than is the case with ordinary silver bromide precipitated in a non-emulsifying medium. The increased sensitiveness of a ripened emulsion may also be ascribed, in part, to the formation of an actual compound of the silver haloid with the gelatin or some constituent thereof (Meldola, Cantor Lectures on Photographic Chemistry, 1891. 20.

21).

Development of the photographic image. Acid development. In the wet collodion process the image is developed by the application of a solution of ferrous sulphate mixed with acetic acid and alcohol (to insure uniformity of flow). The film being already wet with silver nitrate solution, the action of the developer is simply to reduce this salt according to the reaction: 6AgNO₃ + 6FeSO₄ = 2Fe_c(SO₄)₂ + Fe_c(NO₃)₆ + 6Ag. Metallic silver is thus contained as a potential deposit in the mixed solutions, but its precipitation is retarded by the acetic acid, which plays the part of what is technically called a 'restrainer.' The finely-divided metal is deposited only on the product of photo-decomposition (the invisible picture), the density of the deposit being proportional to the amount of decompo-

sition on each portion of the sensitive surface. The image thus continues to gain in density as long as there is silver to feed it, so that the picture is built up by accretion and is raised in relief on the surface of the film. If the film is treated with dilute nitric acid after development, the picture is dissolved off, leaving the film in the same condition as before exposure, thus proving that the image is purely superficial. The ferrors sulphate developer, which acts in the manner described, is a type of the class of acid developers.

Alkaline levelopment. Gelatin emulsions contain no excess of silver nitrate, so that the foregoing process of development is inapplicable. The gelatin itself, being a bromine absorbent, is in this case the sensitiser. Development is effected in modern processes by means of an alkaline or neutral solution of some reducing agent, usually an easily oxidisable organic compound, such as ammonium pyrogallate, first introduced hy Colonel Russell in 1862. In this method the developer acts directly as a reducing agent upon the product of photo-reduction, replacing the latter by its equivalent of metallic silver. image at the same time gains in density by the further reduction of those portions of the unaltered silver haloid which are in immediate contact with the nascent silver being generated by the developer; the action is probably electrolytic, since the image goes on increasing in density as long as the developer can exert a reducing action. A very small amount of the silver deposit may also be due to the reduction of the minute quantity of silver actually dissolved out of the film by the ammonia or other solvent in the developer. In alkaline development the main portion of the silver image is therefore built up by growth from the silver haloid in the film, and after development the image can be dissolved out by dilute nitric acid, leaving its impression sunk in the gelatin, instead of leaving a plane surface, as in the case of a collodion picture similarly treated.1 The developers belonging to this class are all strong reducing agents capable of directly reducing the silver haloids, so that the action has to be moderated by means of restrainers, potassium bromide being generally employed for this purpose. The restraining action of this salt is probably due to its tendency to form a double potassio-silver bromide, which is more stable than the silver bromide itself. In addition to ammonium pyrogallate several other developers acting in a similar manner have come into use, Of these may be mentioned potassio-ferrous

to the equation: $3Br_z + 6FeC_zO_1 + 3K_1O_zO_4$ = $3Fe_z(C_zO_3)_z + 6KBr$. The bromine in this case is derived primarily from the reduction-product. Other developers coming under this category are an alkaline solution of hydroquinone (quinol), hydroxylamine, phenylhydrazine, and an alkaline salt of amido- β -naphthol-monosulphonic acid (Meldola, C. J. 39, 47), introduced by Andresen (Etkonogen). Among the most recently introduced developers are certain amido-phenols,

oxalate (Carey Lea, 1877), which acts according

¹ An able investigation of the connection between the density of the deposit of reduced silver and the period of exposure, &c., is published by Harter a. Driffield &C. f. v, 455; 10, 100; v. also other papers in same volume; also Armstrong, Conjerence No. of Journ. of the Camera Club, 1892, and discussion in same journal, July 1892).

amide-phenolic and carboxylic acids, and their alkyl derivatives, known as 'amidol,' 'metol,' &c. Those which contain the basic and hydroxyl substituents in the para-position seem to be the most effective (Hauff, Engl. Patents [1891] 15, 431; 20, 690).

In the processes of alkaline development the gelatin itself also acts the part of a restrainer by preventing too intimate a contact between the reducing solution and the silver haloid. Any viscous substance exerts this protecting influence (sugar, glycerin, &c.), and such compounds are sometimes called physical restrainers, to distinguish them from chemical restrainers, such as the acid in the ferrous sulphate developer or the potassium bromide in alkaline developers. A developer of very great reducing power is for this reason available in dry plate photography, and upon this fact largely depends the extreme sensitiveness of modern processes.

Development by vapour. The Daguerreotype picture was developed by exposure to mercury vapour, this metal having the property of condensing on the product of photo-reduction (the invisible image) but not on the unaltered silver haloid. It is not known whether the combination of the mercury with the reduction-product is of a chemical or physical nature. method of development is at present the sole

representative of its class.

Fixing the picture. The image developed by the foregoing methods is always on a back ground of unchanged silver haloid, which must obviously be removed before the picture can be exposed to white light. In the early days of photography strong solutions of potassium, solium, or ammonium chloride were used as fixing agents, these salts having the property of forming soluble double salts with the silver haloids. The action of these salts was, however, very imperfect, and a certain amount of undissolved silver haloid was always left in the film, which led on exposure to the gradual darkening and obliteration of the whole picture. Potassium cyanide has since been employed, this salt forming with the silver haloid an extremely soluble double cyanide: AgBr+2KCN =AgK(CN)2+KBr. The fixing agent now generally preferred is sodium thiosulphate (Sir J. Herschel, 1839); this salt, if used in excess, forming the extremely soluble sodio-silver thiosulphate Ag₂Na₄(S₂O₃)₃, 2aq: 2AgBr + 3Na₂S₂O₃ = Ag₂Na₄(S₂O₄)₂ + 2NaBr. If the fixing solution is dilute, the insoluble NaAgS₂O₃ is formed, which remains in the film and spoils the picture: AgBr + Na₂S₁O₃ = AgNaS₂O₃ + NaBr. After immersion in the fixing bath, the soluble salts are removed by thorough washing in a stream

Intensification, and reduction, of density. In cases where the image is wanting in density through under-exposure, bad light, insufficient development, &c., a process of intensification is resorted to. The process as applied to modern dry plates consists in substituting for the silver, of which the image is composed, some denser of which the image is composed, some denosit. Thus, by immersing a negative in as solution of mercuric chloride, the image is bleached by conversion into a mixture of mercurous and silver chlorides: 2Ag+2HgCl₂=2AgCl+Hg,Cl₂. By treating this mixture

with a solution of potassic-ferrous exalate the image is restored in silver and mer-cury, and thus in a condition of increased density: $2AgCl + Hg_{\circ}Cl_{2} + 4I^{\circ}eC_{\circ}O_{4} + 2K_{\circ}C_{\bullet}O_{4}$ = $2Ag + 2Hg + 2Fe_{\circ}(C_{\circ}O_{4})_{3} + 4KCl$. Many other density: intensifiers are known, some acting by simple substitution, such as auric or platinic chloride: 4Ag + PtCl, $6Ag + 2AuCl_{s} = 2Au + 6AgCl_{s}$ or = Pt + 4AgCl; others giving rise to a mixture of products together denser than the original deprosit, e.g. lead or uranium ferricyanide: $4Ag + 2Pb_xFe_y(CN)_{xy}^{-2}Ag_xFe_y(CN)_{xy}^{-2}Ag_xFe_y(CN)_{xy}$. In cases where too dense an image has been obtained, and it is desired to thin it down, a reducing solution is applied; the chemical principle may be described as a conversion of the metallic silver into some compound which can be simultaneously removed by a solvent such as sodium thiosulphate. Thus a mixture of potassium ferricyanide with thiosulphate is often used for gelatino-bromide plates: $4Ag + 2K_cFe_c(CN)_{12} = Ag_iFe_i(CN)_a + 3K_cFe_i(CN)_a$. The silver ferro-cyanide is dissolved off by the thiosulphate, as fast as formed: Ag, Fe(CN), + 6Na, S,O, = $2\Lambda g_2 Na_1(S_2O_3)_3 + Na_1 Fe(CN)_6$. When the necessary reduction of density has been attained, the action of the solution is stopped by washing the film with water.

Reversal of the photographic image and allied phenomena. Any influence which affects a sensitive film in a way similar to the action of light gives rise to a developable image. Thus mechanical pressure-marks produced by rubbing a film with a glass rod can be developed by ferrous oxalate &c., so as to show a corresponding set of dark streaks. It is probable that the friction in this case induces a minute amount of chemical change between the sensitive haloid and its associated sensitiser (gelatin, &c.), this small quantity of reduction-product being afterwards exaggerated by the cumulative action of the developer. Whether the compound resulting from this mechanical action is identical with that produced by the action of light is at pre-ent uncertain, but the associated sensitiser appears to be as essential to the success of the phenomenon in this case as in the ordinary formation of the invisible picture by the action of light. The sensitiser, as has already been explained, is an essential part of any photographic system, and this is best shown by the so-called 'reversal' of the photographic image by over exposure or other means. It has been found that a very strong light allowed to act on a sensitive film for too long a period gives a weaker image on development than is produced with a shorter exposure, and that under some circumstances the image is even 'reversed,' i.c. the high lights come out lighter, on development, than the shadows. The explanation of this phenomenon is probably to be found in the circumstance that while the silver haloid is losing halogen under the influence of light, the sensitiser is simultaneously becoming halogenised, so that when the charge of halogen in the latter exceeds a certain amount the chemical chaffge sets in in a reversed direction, i.e. the halogenised sensitiser begins to re-halogenise the product of photo-decomposition and thus to destroy the invisible image. That this explanation is, in the main, correct in principle, is shown by the fact that the most sensitive processes are just those which

are most prone to give rise to reversal, because it is in such films that the sensitiser becomes most rapidly halogenised. A preliminary exposure to diffused light also promotes reversal, because this imparts a certain initial charge of halogen to the sensitiser. Then, again, oxidising agents favour reversal, because these lessen the halogen-absorbing power of the sensitiser: on the other hand, reducing agents prevent reversal, because they retard or prevent the halogenation of the sensitiser. Thus plates exposed in ozone or in solutions of K₂Cr₂O, and K₂Mn₂O₈ are easily reversed, while nitrites, sulphites, &c., prevent reversal (Abney). Atmospheric oxygen in many cases probably plays a part in the process by assisting in the liberation of halogen from the sensitiser. Thus, by way of illustration, if a plate be given a preliminary exposure to diffused light, and be then coated with a solution of potassium iodide, a completely reversed image can be obtained on exposure in the camera and development. The chemical reaction is in this case: $4KI + 2H_2O + O_2 = 2I_2 + 4KOH$. The iodine is here absorbed by the reduction-product, and thus reverses the picture; the surface of the film is in fact the sensitiser in this case, and the potassium iodide is the photo-sensitive compound.

Waterhouse has recently found that a small quantity of a thio-carbamide added to the developer produces a 'reversed' image (Photo. News, 1890. 727, 743, 804; v. also Journ. of Camera Club, July 1892; also Rawlins, S. C. I. 10, 18).

Printing processes. It is obvious that the photographic image, after normal development, represents the object with its lights and shadows reversed, i.e. the picture is a negative one. A positive print is obtained by exposing suitable sensitive surfaces under such a negative.

Silver prints. A very general method of obtaining silver prints depends upon the use of a sensitive surface (usually paper) consisting of a mixture of silver chloride and an organic compound of silver with albumen, this surface being obtained by first coating the substratum with a solution of albumen containing ammonium chloride, and then (when dry) floating on a solu-tion of silver nitrate. The printing is carried on to the required depth of colour, and the visible print consists of the reduction-products of silver chloride, and of the organic silver compound. which is also susceptible of photo-reduction. To correct the reddish colour of these mixed reduction-products the print is 'toned' by immersion in a solution of auric chloride, kept neutral by the addition of sodium carbonate, acetate, or phosphate, chalk, borax, &c. The function of these salts is to neutralise the hydrogen chloride liberated by the reduction of the auric chloride by the reducing compounds which constitute the picture. The gold is thus precipitated in a state of fine division only on the products of photodecomposition (the picture), and imparts the desired tone. The accumulation of acid in the toning bath retards the precipitation of gold, and

¹ Potassium bromido similarly acts as a reversing agont though to a less extent. It is for this reason that every trace of this sath has to be washed out of a gelatino-bromido emulsion after the process of ripening, since the presence of the soluble bromide materially diminishes the sensitireness of the smulsion. the deposit is not of a good tone; hence the necessity for the presence of one of the salts referred to. The unaltered silver chloride &c. is removed by fixing with thiosulphate, and washing. In some recent processes the albumenised silver paper is replaced by paper coated with gelatino-bromide or chloride emulsion, a short exposure being given, and the invisible (positive) picture being developed in the usual manner.

Printing with iron and uranium salts. Ferric and uranic salts in the presence of organic sensitisers become reduced on exposure to light, and the ferrous or uranous compounds thus formed can be developed by treatment with potassium ferricyanide or other salts which give coloured products with the ferrous or uranous, but not with the unreduced, salts. Thus paper coated with ferric oxalate gives a faint image of the ferrous salt, which comes out as a deepblue print on development with ferricyanide: 6FeC₂O₄+2K₄Fo₂Cy₁₂=2Fo₃(Fe₂Oy₁₂)+6K₂Cy₀Many printing processes depending upon the foregoing principles have come into use, and will be found described in works on practical photography.

Platinotype. Prints in finely-divided platinum can be obtained by exposing a surface coated with a mixture of ferric oxalate and potassium chloroplatinite under a negative. The ferrous salt thus produced does not react with the chloroplatinite till the picture is developed by immersion in a solution of potassium oxalate, which dissolves the ferrous oxalate, with the formation of a double salt, which simultaneously reduces the chloroplatinite:

3K.PtCl. + 6FeC.O.

3K,PtCl₁+6FeC₂O₄
= 3Pt+2Fe₂(C₂O₃+Fe₂Cl₄+6KCl. The soluble salts are then removed by washing with dilute hydrochloric acid, and finally with water.

Pigment printing. A mixture of gelatin with potassium dichroniate undergoes a chemical change on exposure to light, in the course of which the dichromate is reduced and the gelatin at the same time becomes insoluble in water. The chemical composition of this insoluble gelatin is unknown, but it appears to contain an oxide of chromium as an essential constituent (Eder). Many printing processes are based upon this property of gelatin, such, for example, as the so-called carbon and pigment prints, in which the finely divided carbon or pigment is intimately mixed with the gelatin solution and the mixture sensitised by the addition of dichromate. After exposure under a negative the picture is developed by warm water, which dissolves away those portions of the tissue unacted upon by light. Many of the photo-mechanical printing processes de-

pend also on this property of gelatin.

Photo-etching processes. When a layer of asphalt or bitumen is spread over a surface and exposed under a design, those portions of the film which are acted on by light become insoluble in hydrocarbon oils, so that the design can be developed by such solvents, and the surface, if of metal, can be converted into a printing block by etching with acid. The change experienced by the bitumen is probably the result of photo-chemical oxidation. The processes based on this property are much in vogue at the present time under various modifications. This action of

light upon bitumen furnished the earliest successful permanent reproduction of the camera sisture (Joseph Nicephore Niepoe, 1824).

Bibliography.-It has not been considered advisable in the present article to give the authority for every statement, as most of the results achieved by photographers are to be found in publications rarely consulted by chemists. The following general works contain practically all that is known of photographic chemistry at the present time : - Robert Hunt, Researches on Light, 2nd edit., 1854; E. Becquerel, La Lumière, Paris, 1867; J. W. Draper, Scient fic Memoirs, a collection of reprints, 1878; J. M. Eder, Ueber die Reactionen der Chromsäure u. der Chromate auf Gelatine, Gummi, Zucker, &c. Wien, 1878; J. M. Eder, Ausführliches Handbuch der Photographie, Halle, 1884 9; H. W. Vogel, La Photographie des Objets Colores avec leurs Valeurs Reelles, Paris, 1887; Pizzighelli and Hübl, La Platinotypie, Paris, 1887; W. de W. Abney, Treatise on Photography, 5th edit., 1888; by the same author, Instructions in Photography, and Photography with Emulsions; Chapman Jones, Introduction to the Science and Practice of Photography, 1888; R. Meldola, The Chemistry of Photography, 1889; H. W. Vogel, Handbuch
der Photographie, Berlin, 1890. 1.

PHOTOSANTONIN v. SANTONIN.

PHRENOSIN C4H,NO. A substance oc-

curring, according to Thudichum (J. pr. [2] 25,

19), in the brain.

PHTHALACENE C₂₁H₁₆. [173°]. Formed by reduction of phthalacone carboxylic ether with HI and P at 170° (Gabriel, B. 17, 1390). Crystals (from HOAc). Yields O₂₁H₁₈Br [184°], which is oxidised by K,Cr₂O, and HOAc to C₂₁H₁₈BrO [c. 200°]. Fuming HNO₂ and HOAc vield di-nitro-phthalacenc, which separates from hot nitro-benzene in yellow needles. K₂Cr₂O, and HOAc oxidise phthalacene to 'phthalacene oxide' C₂H₁O [211°-214°], which yields an oxim C₂H₁(NOH) [205°]. PHTHALACENIC ACID C₂H₁, CO₂H. [247°].

Formed by heating phthalacene-oxide with soda-lime (Gabriel, B. 17, 1399). Crysta's.—A'Ag. PHTHALACONE CARBOXYLIC ACID

C₁₁H₁₁O₂(CO₂H). [281°]. Formed by dissolving its ether in conc. H₂SO₂ and pouring into water (Gabriel, B. 17, 1389). Minute yellow needles, sol. hot alcohol. The acid yields a dioxim $C_{s_1}H_{11}(NOH)_2CO_2H$ [273°] and the salts KA'aq and NaA'aq. Zinc-dust and NaOHAq yield a tetrahydride C₂₂H_{1c}O₄, melting above 280°, which

gives AgA', crystallising in needles.

Ethyl ether EtA'. [211°]. A product of the action of phthalic anhydride and NaOAc on acetoacetic ether at 140°. Yellow needles, sol. hot HCAc. Yields a di-nitro- derivative [above 280°] and a dioxim C₂₁H₁₁(NOH) CO₂Et [264°]. 2807 and a dioxim Caldinition 1.00 p. 100 p.

CHO.C.H.CO.H.[1:2]. [97°]. Formed, together with C.H.Co. (221°), by heating a bromophthalide with water (Racine, B, 19, 778; A. 239, 78; C. R. 106, 947). Formed also by boiling a brown of the control o ing penta-w-chloro-o-xylene with water (Colson a. Gautier, Bl. [2] 45, 509). V. sol. water, alcohol, and ether. Reduces ammoniscal AgNO₄.

Phenyl-hydrazine yields C₁,H₁₈N,O [103°]. Alcoholic NH₅ forms C_{...}H₁₈N,O₆ [187°], while an alcoholic solution of aniline gives C_{1,H1}NO₂ [174°]. Ac,O at 200° forms CHO.C.H.,CO.Ac [60°-63°]. Ures forms NH₂,CO.N:CH.C.H.,CO.H. [240°].—CaA', 2sq.—AgA': slendor needles.

Ethers MeA'. [44°].—EtA'. [66°].

Anhydrids C₁₆H₁₀O₃. [221°]. Got by heating the acid with bromo-phthalide.

Oxim CH(NOH).C.H.,CO.H. [120°].

Oxim CH(NOH).C,H,.CO,H. Formed by adding hydroxylamine hydrochloride to a cold aqueous solution of the acid. In an alcoholic solution the product is C.H. CO.O [120°], which is converted by heat first into CN.C.H. CO.H and then into phthalimide (Allendorff, B. 24, 2346, 3264).

Isomeride v. p-Aldehydo-Benzoic acid.
Diphthalaldehydic acid v. Di-Phthalyl-Lag-TONIC ACID

PHTHABAMIC ACID v. PHTHALIC ACID. PUTHALAMIDE v. PHTHALIG ACID.

ISOPHTHALAMIDINE C.H., N. i.e.
C.H., (C(NH).NH.), [1:3]. Formed from
C.H., (C(NH).OEt), and alcoholic NH, (Luckenbach, B. 17, 1432). Small needles, insol. benzene and ether, v. sol. alcohol and water. Its aqueous solution soon decomposes, giving off NH, - B"H,Cl2: needles, v. sol. water.—B"H,PtCl4.—

B''H_SO, -B''2HNO, -B''HNO,: needles (Grabowski, A. 205, 168).—CH_(NAg,NH_),

ISOPHTHALAMIDOXIM C,H₁₀N₁O, i.e.
C,H₁(C(NOH),NH_), [193°]. Formed from C.H.Cy. [1:3] and hydroxylamine (Goldberg, B. 22, 2976). Prisms (from alcohol) containing aq?, v. sol. hot water.

Phthalanil v. Phenylimide of PHTHALIC ACID. PHTHALBENZO-TÖLUIDE v. Phthalyl-

AMIDO-TOLYL PHENYL KETONE. PHTHAL-o-CYANO-BENZYL-IMIDE

O-CYANO-BENZYL-PHTHALIMIDE. PHTHALEÏNS. Colouring-matters obtained by condensation of phthalic anhydride with phenois (e.g. Phenoi. Phithalein and Fluon-escein). They may be reduced to colourless 'phthalins,' which are re-oxidised by air to phthaleins.

PHTHALIC ACID C,H,O, i.e. [1:2] C.H. (CO.H)... Mol. w. 166. [184°] (Lossen, A. 144, 76); [203°] (Ador, A. 164, 230; Baeyer, A. 269, 184). S. 54 at 14°; 18 at 99° (Graebe, H. 230, 331; S. (alcohol) 10 at 15° (Bourgoin, Bl. [2] 29, 247); S. (ether) 684 at 15°. H.C. 771,600. H.F. 187,400 (Stohmann, J. pr. [2] 48, 540); 153,000 (von Rechenberg). S.H. (175° to 119°) 256 (Hess, A. Ch. [2] 35, 410). S.H. (from

Formation .- 1. By the action of nitric scid on naphthalene, naphthalene dichloride, alizarin, purpurin, munjistin, naphthoquinone, o-toluic acid (Laurent, A. Ch. [2] 61, 113; Marignac, A. 42, 215; Schunck, A. 66, 197; Wolff a. Strecker, A. 75, 12, 25; Stenhouse, A. 130, 334; Liebermann a. Dittler, B. 6, 94°; Piccard, B. 12, 579; Beilstein a. Kurbatoff, A. 202, 215).—2. By the action of various oxidising agents on naphthalene (Lossen, A. 144, 71; Hermann, Z. [2] 4, 551; Depouilly, C. R. 56, 82; Häussermann, D. P. J. 223, 310).—3. A product of the action of MnO, and H₄SO, on benzene (Carius, Z. [2] 4, 705; A. 148, 60).—4. By oxidising o-toluic acid with KMnO₄ (Weith, B. 7, 1057).—5. By

oxidising isoquinoline with alkaline KMnO₄ [Hoogewerff a. Van Dorp, R. T. C. 4, 285].—6. By heating salicylic acid with H₂SO₂ and K₄FeO₇ (Guyard, Bl. [2] 29, 247).—7. By heating resorcin or salicylic acid with formic acid and H₂SO₄ (G.).—8. By the action of a hot solution of accompany paragraphs are suppression as a superposition of a solution tion of cuprous potassium cyanide upon o-diazo benzoic chloride (from anthranilic acid), and subsequent saponification of the product (Sandmeyer, B. 18, 1499).

Properties .- Trimetric plates. Yields an anhydride when heated. Insolachlorotorm.

Reactions .- 1. Distillation with lime yields benzoic acid and benzene. - 2. Sodium-amalgam reduces it to a dihydride .- 3. Chromic acid mixture oxidises it to CO₂ (Fittig, A. 156, 242).— 4. The soid aniline salt A"H(NH₂Ph) of orthophthalic acid loses H2O when its aqueous solution is boiled, phenyl-phthalimide crystallising out. The para- and meta- phthalic acids do not react in this way; the reaction therefore serves as a means of separating ordinary phthalia acid from its isomers (Michael a. Palmer, B. 19, 1376; Am. 9, 202).

Salts.-(NH.)HA": prisms, v. sol. water. BaA": v. 8l. sol. water (Carius, A. 148, 04).—
 Ba₄A"₂O: monoclinic prisms.—CuA"aq.—PbA".
 —Ag₂A": crystalline pp.—A niline salt: needles [146°] (Clarke, B. 12, 1066).
 Di-methyl ether Mc₂A" (280° i.V.) at 734 mm. (Graebe, B. 16, 860). H.F. 164,600 (Stohman) (Graebe, B. 16, 860).

mann, J. pr. [2] 40, 353).

Mono-ethyl ether EtHA". Formed by heating phthalic anhydride with absolute alcohol at 100° (Michael, Am. 1, 413). Liquid, m. sol. water. Decomposed by heat into phthalic

anhydride and alcohol.—Ba(EtA"),.—AgEtA". Di-ethyl ether Et,A". (295° cor.). Got by passing HCl into an alcoholic solution of phthalic acid (Graebe a. Born, J. 1866, 411). Formed also from phthalyl chloride and alcohol. Liquid. Not attacked by hydroxylamine (Jeau-renaud, B. 22, 1273). When warmed with When warmed with NaOEt and EtOAc it yields the compound C_eH₄<CO>CH.CO₂Et [75°..78°] (Wislicenus, A. 246, 349). PCl, followed by sodium malonic ether forms the acid C21H16O10 [c. 180°] (Zelinsky, B. 20, 1010).

Phenyl ether Ph.A". [70°]. Formed by heating phthalyl chloride with phenol (Schreder, B. 7, 704; von Gerichten, B. 13, 419). Colourless crystals.

Anhydride C.H.O. i.e. C.H. COOO. Mol. w. 148. V.D. 5·26 (calc. 5·13) (Troost, C. R. 89, 851). [128]. (284·5' i.V.). H.C.p. 784,000. H.F. 106,000 (Stohmann, J. pr. [2] 40, 139). Formed by heating phthalic acid alone or with AcCl (Laurent; Anschütz, B. 10, 326). Formed also by the action of lead nitrate on phthalyl v. sol. alcohol and ether, sl. sol. cold water.

Reactions.—1. When heated with phenols it yields phthaleins, with elimination of water (Baeyer, B. 7, 968).—2. Heated with NaOAc and HOAc it yields phthalyl-acetic acid C10HaOa, while phenyl-acetic acid gives benzylidene-

phthalide. Phenyl-acetonitrile gives rise to C.H. COO, [165°], and isobutyric acid and ZnOl, at 250° give a ketone C₁₁H₁₀O₂ [96°]. 3. Boiling with NaOAo and phenoxyacetic acid yields C₂H₄:C₂O₂:CH.OPh [143°] while p-totyloxy-acetic acid and sodium acetate give rise to C,H,:C,O2:CH.OC,H,Me [174°] (Gabriel, B. 14, 922) .- 4. Acetoacetic ether gives C, H, Bz, and phthalacone carboxylic ether .- 5. On heating with succinic acid and sodium succinate it yields CO₂ and C₁₈H₁₀O₄ [above 300°].—6. Di methyl-quinolme and zine chloride at 200° give C.H.;C.O.;C.,H.,N [238°] (Beyer, J. pr. [2] 33, 407).—7. Ethenyl-amido-phenyl-mercaptan and ZnCl₂ at 200° give C₈H₄C_S C.CHC_{CO}C₈H₄ crystallising in yellow needles [above 320°] (Jacobson, B. 21, 2630).—8. Cyanethine forms, on heating, C_bH₁₃N_{...}N:C₂O₂:C_cH₁ [128°] (E. von Meyer, J. pr. [2] 30, 262).—9. Coal-tar picoline and zinc chloride at 200° form pyrophthalone C_bH₁O₂:Cli.C,H₁N [above 260°] (Jacobsen a. Reimer, B. 16, 2604) crystallising from alcohol in yellow plates.—10. Benzente and AlOl, yield a hearzoth-honyoic soid and other aromatic by o-benzoyl-benzoic acid, and other aromatic hydrocarbons act in like manner (Friedel a. Crafts, C. R. 92, 833) .- 11. Benzyl chloride and zincdust at 75° yield C_{so}H_{sc} (?) [73°] (Wislicenus, A. 248, 68).—12. On heating with amines and amides, phthalic anhydride yields derivatives of the imide and amide of phthalic acid; thus acetamide yields phthalimide and HOAc, while ethylamine yields ethyl-phthalimide. Secondary amines form derivatives of the amic acid and of the amide (Piutti, A. 227, 181; G. 16, 1, 251) .-13. Amido-acids are converted by phthalic an-hydride into their phthalyl derivatives (Reese, A. 242, 1).-14. On fusion with sinc-dust phthalio anhydride gives diphthalyl. Zinc-dust and HOAc yield a mixture of phthalide, diphthalyl

dihydride C_eH, CO.00.CO C_eH₄, [229°] and CH, [199°], which is reсо,н.с.н,.сп..сп/

CO₂H₂CH₂CH₂CC₂H₃CC₂H₁CC₂H₂(Wislicenus, B. 17, 2178).—15. Tri-anido-phenol (picranic acid) forms (C₂H₂C;N₂C;H₂C) Habove 300°] converted by potash into the compound (CO₂H₂C;H₂CONH)₂C;H₂OH [above 300°], from which nitric acid produces the quinone (C,H,O,:N),C,H,O, [277°] reduced by SO, to (C,H,O,:N),C,H,(OH), [above \$10°] (Piutti, G. 16, 254).

10, 209).

Chloride C₆H₁ CCl₂ O. Phthalyl chloride. [0°] (Wisehin, A. 143, 259). (275°) at 726 mm. S.G. ²⁰ 1.4089. $\mu_{\rm s} = 1.569$ (Brithl, A. 235, 14). Formed by heating phthalic acid with PCl, for 2 hours at 190 (H. Müller, Z. 1863, 257; Graebe, A. 238, 320). Oil, absorbs moisture from the air, forming phthalic anhydride. Slowly onverted into phthalic acid by water or Na₂CO₂Aq. Reduced by zinc and HClAq to phthalide. Sodium-amalgam and HOAc form C₂H₄(CH₂OH)₂. PCl₃ forms two isomeric chlorides C₃H₄ CCl₂ O and C₄H₄ CCl₃, one melting the control of ing at 88° and boiling at 275°, the other melting

at 47° and boiling at 262°; both are converted by aniline into C_eH₄ C(NPh) NPh [153°] (von Gerichten, B. 13, 417; Claus, B. 19, 1188). Excess of PCl, yields chloro-benzoic acid, CCl,, and other products (Claus). Aqueous NH, forms C₈H₁O₂(NH₂)₂ [90°] not identical with phthalamide, but converted by HClAq into C,H,O,(NH) [145°] which is changed by fusion into the isomeric phthalimide [228°] (Auger, A. Ch. [6] 22, 303; cf. Kuhara, Am. 3, 26). Dry NH, acting on the benzene solution behaves in like manner. Hydroxylamine yields C₂H₄:C₂O₂:NOII [230°] (v. vol. ii. p. 738). o-Amido-phenyl mercaptan hydrochloride forms $C_{20}H_{12}N_{23}$ [112°] (Hofmann, B. 13, 1233). $Z_{11}M_{12}$ (Forms $C_{10}H_{12}N_{23}$ [112°] (Bosantzeff, Bl. [3] 1, 166). Zniči, followed by water gives, in like manner, C12H14O2 [54°] (250°).

Semi-nitrile v. o-CYANO-BENZOIC ACID.

Amic acid C, II (CO.NH.) CO, II. Phthalamic acid. [c. 140°] (Auger); [149°] (Aschan, B. 19, 1401). Formed by heating phthalic anhydride with alcoholic NH, or phthalimide with baryta-water. Prepared by evaporating phthalic anhydride with NH, Aq, and decomposing the resulting ammonium salt by HCl (Auger, Bl. [2] 49. 349). Prisms, sl. sol. water, v. sol. alcohol. Converted by heat into phthalimide, and by hot water into hydrogen ammonium phthalate. cess of HClAq forms phthalic acid.—NH,A'.—KA'.—BaA'.,—BaA'., aq.—AgA': needles, v. sl. sol. water (Landsberg, A. 215, 197).

Isoamyl-amic acid 180amyt-amic acia C₄H₁(CO₂H),CO.NHC₂H₁₁. Isoamyl-phthalamic acid. [115°]. Formed by warming isoamyl-phthalimide with KOHAq (Neumann, B. 23, 998). Crystalline pp.—AgA'.

Phonyl-amic acid C.H.(CO.H).CO.NHPh. Phenyl-phthalamic acid. Phthalanilic acid. [192°]. Got by boiling phenyl-phthalimide with NH,Aq and some alcohol (Laurent a. Gerhardt, A. Ch. [3] 24, 188). Plates, sl. sol. cold water, v. sol. alcohol.

Phenyl-ethyl-amic acid C₁₆H₁₅NO₃ i.e. C₄H₄(CO₂H).CONPhEt. Phenyl-ethyl-phthal. Phenyl-cthyl-phthal. amic acid. Got by dissolving phthalic anhydride in ethyl-aniline (Piutti, G. 13, 545; A. 227, 185). Heavy oil, v. sl. sol. water.

Di-phenyl-amic acid C₂H₄(CO₂H).CONPh₂. Di-phenyl-phthalamic acid. [148°]. Made from diphenylamine and phthalic anhydride (P.). Hard prisms, sl. sol. ether, v. sol. alcohol. AgA'.

o-Tolyl-amic acid
C.H.(CO.H).CONHC.H.Me. Got by boiling
o-toly-phthalimide with NH.Aq (Kuhara, An.

9,51). Needles.—Ag₂C₁,H₁₁NO₃: pp.
m. Methyl-benzyl-amic acid
C₆H₄(CO₂H).CO.NHCH₂C₆H₄Me. [13 [131°]. from m-xylyl-phthalimide and caustic soda (Brömme, B. 21, 2700). Needles, sol. alcohol.— AgA': white pp.

ψ-Cumyl-amic acid C₂H₄(CO₂H).CO.NHC₂H₄Me₂. Phthal-ψ-cumidic acid. [179°]. Needles, v. sol. alcohol, sl. sol. ether (Fröhlich, B. 17, 1808).

Naphthyl-amic acids
C.H.(CO.H).CO.NHC.H., The (a)-acid [185°]
is got from (a)-paphthyl-phthalimide. The (β)-

acid crystallises from alcohol in tables (Piutti. G. 15, 480).

Phenyl-oxy-ethyl-amic acid C₄H₄(CO,H).CO.NH.C₂H₄.OPh. [125°] Formed by warming phenyl-oxyethyl-phthalimide with KOHAq (Schmidt, B. 22, 3255).

p-Tolyl-oxy-ethyl-amio acid C.H. (CO.H).CO.NH.CH,.CH,.O.C,H,Me. [137°]. Formed from the corresponding imide which is

got by heating potassium phthalimide with C₆H,Mc,QC,H,Br (Schreiber, B. 24, 191).

Phenyl-andido-phenyl-amic acid
C₅H₁(CO.II).CO.NH.C₆H,NIIPh. [120°-130°].

Powder (Gabriel, B. 22, 2223).

Benzoylethyl-amic acid C.H.(CO.H).CO.NH.CH. CH.Bz. Propiophenone. phthalamic acid. [140°]. Made from the imide (Schmidt, B. 22, 3251). Needles.—AgA': pp. Di-sulphido-di-ethyl-amic acid

(C.H.(CO.H).CO.NH.CH.,CH.),S., [130°]. Formed from stllphocyano-ethyl-phthalimide

rotined from supprocyano-ethyl-pathalimide and (10 p.c.) KOHAq (Coblega, B. 24, 2131). Scales. HClAq at 180° forms S₂(C₂H₁NH₂)... Uramic acid C₃H₁(CO₂H).CONH.CO.NH... Phthaluric acid. S. 3°5 at 99°. Formed by leating phthalic anhydride with urea at 115° control of the control (Piutti, A. 214, 19; G. 12, 173). Silvery scales, sol. alcohol. May be converted by POCl, into C₆H₄ CO.NH CO, which yields AgC₆H₅N₂O₆.

Salts.-NaA' 2aq.-BaA'2.-AgA': needles. Thio-uramic acid

C₆H₄(CO₂H).CO.NII.CSNH₂. [172°]. Got by heating phthalic anhydride with thio-ures (P.).

Silvery needles (from alcohol).—BaA'₄7a₄7a₄.

s-Amide C₁H₁(CO.NH₂)₂. Phihalamide.
[220°] (Bülow, A. 236, 188 Formed from phthalimide and cold NH₃Aq (Aschan, B. 19, 1399). Minute crystals, insol. cold water, alcohol, and ether. Boiling water converts it into phthalimide. Alkaline KOBr at 80° forms C₂H₄CO.NH (Hoogewerf a. Van Dorp, R. T. C.

10, 9).

 $C_4H_4 < CO \longrightarrow 0$. u-Amide[c. 90]. Formed from phthalyl chloride and NH,Aq (Auger, A. Ch. [6] 22, 304). Long transparent prisms, v. sol. water, sol. hot alcohol. AgNO. ppts. C,H,O,NAg in white lustrous scales. NH. being eliminated.

Phenyl-ethyl-amide C₂H₄CO(NPhEt)₂>0. [141°]. Formed by heating the ethyl-aniline salt of phenyl-ethyl-phthalamic acid above 200° (Piutti, G. 13, 547; A. 227, 187). Prisms, insol. water, sol. alcohol and ether. Not attacked by KOHAq, but split up by potash-fusion into phthalic acid and ethyl-aniline.

Di-phenyl-amide C.H.; C.O., (NPh.), Di-phenylamine-phthalein. [238]. Formed from phthalyl chloride and diphenylamine (Lellmann, B. 15, 830). Formed also by boiling, phthalic anhydride with diphenylamine (P.). Needles (from alcohol). H₂SO, containing HNO, forms an intense violet solution.

m-Phenylene-diamids C.H.O.:N.H.;C.H., [179]. Formed, together with (C.H.O.:N.J.C.H., [252°]), by fusing m-phenylene-diamine with phthalic anhydride (Bieder mann, B. 10, 1160). Nodules.

p-Phenylens-diamids $C_0H_1:C_2O_2:N_2H_2:C_0H_4$. [182°]. Converted by warming with dilute HClAq into a base $C_3:H_2:N_0O_4$ and $(C_0H_1:C_2O_2:N)_2C_0H_4$ [295°] (Biedermann, B. 10, 1163).

u-Imide $C_{\bullet}H_{\bullet} < C(NH) > 0$. u-Phthal-

imide. [c. 145°]. Formed by the action of HClAq on the *u*-amide (Auger). Slender needles, exactly resembling the s-imide, into which it changes when heated. Differs from the s-imide by decomposing moist BaCO, in the cold, hence it may possibly be o-cyano-benzoic

s.Imids C.H. CONH. Phthalimide.

[228°]. Formed by heating C_sH₄(CO₂H)(CO₂NH₄) or C₄H₄(CO₂H).CONH₂ (Laurent, A. 41, 110; A. Ch. [2] 61, 121; [3] 23, 119; Lansberg, A. 215, 181). Got also by heating the u-gnide, and by the action of CuCy₂ and KCy on o-diazo-benzoic acid (Sandmeyer, B. 18, 1499). Sixsided prisms (from ether). May be sublimed. Reduced by tin and HCl to phthalidine C, H, O(NH) (Graebe, B. 17, 2598). When distilled with steam (Graebe, B. 17, 2098). When distrible with steam over heated zine-dust it yields $C_{15}H_{11}N$ [100°] (Gabriel, B. 13, 1684). Boiling Ac₂O forms $C_{8}H_{1}$: $C_{2}O_{2}$:NAc [132°-135°] (Aschan, B. 19, 1398). Amyl alcohol and Na reduce phthalimide to o-methyl-benzyl-amine (Bamberger, B. 21, 1888). Yields benzonitrile when distilled with lime (Reese, A. 242, 5). Alkaline KOBr at 80° forms o-amido-benzoic acid (Hoogewerff a. Van Dorp, R. T. C. 10, 8) C, II, O, NK. Formed from phthalimide and alcoholic potash (Cohn, A. 205, 301; Gabriel, B. 20, 2225). Plates, converted into potassium phthalamate by boiling water. Converted by alkyl iodides into alkylwater. Converted by alkyl iodides into alkylphthalimides. [1:2]C,H₄(CH,Br)₂ gives rise to C₂H₄(CH,N:C₃H,O₂)₂[253], while the m-isomeride melts at 237°. Reacts with epichlorhydrin, forming C,H,O,N.C,H,O [201*] (Goedeckemeyer, B. 21, 2689) with (a) - diehlorhydrin, forming (O,H,O,N.CH₂),CHO.OII (201*), and with \(\gamma\)-bromobutyronitrile, forming C,H,O,N.CH.,CH.,CH.,CN. [81*5*] (Gabriel, B. 22, 224, 3337; 23, 1771).

C,H,O,NAa. — (C,H,O,N),Mg; white pp.— (C,H,O,N),Cu aq. — (C,H,O,N),Cu daq. — (C,H,O,N),C

Imidoxim $C_sH_sN_2O_2$ i.e. $C_oH_4 < {CO \choose CO} > O$.

[250°]. Formed by heating o-cyano-benzoic ether with an alcoholic solution of hydroxylamine at 90° for a long time (Müller, B. 19, 1498). Needles (from dilute alcohol), insol. bonzene. Boiling with HClAq and FeCl, converts it into phthalimide.

Methyl · imide C,H,O,:NMe. [132°]. (286°). Formed from potassium-phthalimide and MeI at 150° (Gracho, B. 17, 1174; A. 247, 302). Needles, reduced by tin and HCl to C.H.,NO [120°] (300°), which yields a gold salt [196°].

Ethyl imide C.H.:C.O.NEt. Ethyl-phthalimide. [79°]. (282°) at 720 mm. Formed by distilling a solution of phthalic anhydride in aqueous ethylamine; and formed also from potassium phthalimide and EtI (Michael, B. 10, 1645; Graebe, A. 247, 302; Wallach a. Kamenski, B. 14, 171). Needles. Br at 140° forms C₁₀H₆Br₃NO₂ [c. 189°]. Bromo - ethyl - imide

C,H,O,:N.CH,,CH,Br. [83°]. Formed from C_aH₁O_c:N.CH_.CH_aBr. [83°]. Formed from potassium phthalimide and C_aH_aBr_c (Gabriel, B. 20, 2225; 21, 566; 22, 1137). Needles. Converted by aniline into phenyl-amido-ethyl-phthalimide [10°], and by p-toluidine into both (C_aH₁O_c:N.C_aH₁),NC_aH_aMe [200°] and C_aH₁O_c:N.C_aH_a,NHC_aH_aMe [96°]. \(\psi - \text{Cumidine} \) form (C_aH₁O_c:N.C_aH_a,NHC_aH_aMe, [146°], while (a)- and (β)-naphthylamines form compounds C,H₁O₂:N.C.H₁.WHC₁₀H₁ [158°] and [141°] respectively (Newman, B. 24, 2196). Potassium sulphocyanide forms C,H,O,:N.C,H,SCy [108°] (Coblenz, B. 24, 2131).

Sulphydro-ethyl-imide C_aH₁O₂:N.C.H.SH. [77°]. Formed from the bromo-ethyl-imide and KSH at 100°. Converted bromo-ethyl-imide and RSH at 100°. Converted by NaOEt and glycollic chlorhydrin into syrupy C_nH₁O₂:N.C₂H₁,S.C₂H₁OH, whence POCl₃ forms C₂H₁O₂:N.C₃H₂,S.C₄H₄DI [70°], while POBr₄ forms C₃H₄O₂:N.C₄H₃S,C₄H₄Br [90°]. Reacts with C₃H₄O₂:N.C₄H₄Dr and NaOEt, forming (C₄H₄O₂:N.C₄H₄Dr [129°], which is oxidised by braining water, to the corresponding subsocial bromine water to the corresponding sulphoxide [191°], and by chromic acid to the sulphone [256]. Iodine in alcoholic solution forms (C₈H₁O₂:N.C₂H₁)₂S₂ [139°], whence B"H₂Cl₂ [203°] (Gabriel, B. 24, 1122, 3098).

n - Propyl - imide C₈H₁O₂:NPr. (283°). Crystals (Gabriel, B. 24, 3105).

Isopropyl · imide [85°]. (273°).

B · Bromo · propyl · imide

C_sH₁O₂:N.CH₂:CHBr.CH₃. [105°]. Formed from the allylimide and HBr (Seitz, B. 24, 2627). Converted by KSH into C,H,O,:N.CH,CHMe,SH [88°], which is oxidised in alcoholic solution by I to (C₈H₄O₂:N.CH₂.Cl1Me)₂S [161°]. Potassium sulphocyanide forms C,H,O,:N.CH,CHMe.SCy

γ · Bromo · propyl · imide C₈H₁O₂:N.CH₂CH₂CH₂Br. [73°]. Got from trimethylene bromide and potassium phthalimide methylene bromide and potassimi primarimae (Gabriel, B. 21, 2671; 23, 90). Needles (from ligroin). Converted by sodium ethyl-malonic ether into C₈H₁O₂:N.C₃H_a·CEt(CO₂Et)₂ [62°], and by sodium benzyl-malonic ether into C₈H₁O₂:N.C₄H_a·C(CH₁Ph)(CO₂Et)₂ [c. 110°] (Aschan, B. 23, 3692). Potassium sulphocyanide forms C₈H₄O₂:NC₃H₆SC₃ [98°].

Ethylene - di - imide $(C_8H_4O_2.N)_2C_9H_4.$ [232°]. Formed by heating potassium phthalimide with ethylene bromide at 200° (G.).

Butyl · imide C,H4O2:NC4H9. Formed by distilling cupric phthalyl-amido-hexoate (Reese, A. 242, 16). Tables (from dilute alcohol).

Isobutyl - imide C.H.O.: N.CH.Pr. [939]. Formed from isobutyl bromide and potassium phthalimide (Neumann, B. 23, 999). Plates.

Isoamyl · imide C,H,O,:N.C,H,11. (308°). Solidifies when strongly cooled (N.).

Allyl-imide C₄H₁O₄:NC₃H₂, Allyl-phthal-imide. [71^o]. (295^o). Tables. Yields a dichloride C₄H₁O₂:NC₄H₂Cl₄ [93^o], and a dibromide [114^o]. When nitrous acid is passed into its solution in cold benzene, and the product heated to 145°, there is formed C.H.O.NC.H.NO, crystallising in plates [178°] (Neumann, B. 28, 1000).

Acetonyl - imide C,H,O,:N.CH,Ac. [117°] Made by heating potassium phthalimide with enhoro-acetone at 120° (Goedeckemeyer, B. 21, 2684). Plates and needles. Gives rise to an oxim [172°] and also to a phenyl-hydrazide CH,C(N,HPh).CH,N:C,H,O, [152°].

Desyl - imide C,H,O,:N.CHP)Bz. [158°].

Desyl-inide C,H,O,N,CHPhBz. [158°]. Formed from phenyl bromo-benzyl ketone and potassium phthalimide (Neumann, B. 23, 994). Yellowish crystals, v. sl. sol. alcohol.

Phenyl-imide C₆H₁<CO>NPh. Phthalanil. [205°]. Formed by distilling phthalic acid (1 mol.) with aniline (1 mol.), and by heating phthalimide with aniline (Laurent; Doebner, 4. 210, 267; Pintti, B. 16, 1322); Michael a. Palmer, Am. 9, 202). Needles (from alcohol), insol. water. Converted by heating with BzCl and ZnCl₂, into C, H₂O₂N.C, H₃Bz [183°] (Deebner, A. 210, 267). The p-chloro, p-bromo, p-iqdo, and m-nitro-phenyl-imides of phthalic acid melt at 195°, 201°, 228°, and 243° respectively (Gabriel, B. 11, 2260).

Ben'zyl-imide C.H.O.:NCH.Ph. [116°]. Formed from potassium-phthalimide and benzyl chloride (Gabriel, B. 20, 2227). Needles (from alcohol). The o- and m-nitro-benzylimides melt at 219° and 155° respectively.

o-Cy ino-benzyl-imide C.H., C.O.; NCH., C., H., CN. [182°]. Prisms (from HOAc) (G.). The p-isomeride [184°] is converted into CO.H.C., H., CO.NH.CH., C., H., CO.H. [255°] by NaOHAq (Günther, B. 23, 1059).

Tolyl'-imides C_aH_cCO_aNC_aH₄Me. The o-, m-, and p-compounds melt at 182², 153², and 204² respectively (Michael, B. 10, 579; Piutti, A. 227, 205; Fröhlich, B. 17, 2679; Kuhara, Am. 9, 52).

m-Methyl-benzyl-imide C.H.:C.Q.:N.CH.C.H.Me. [118]

Formed by heating potassium phthalicaide with C.H.Me.CH.Br at 200° (Brömme, B. 21, 2700). White needles, v. sol. alcohol. The compound (C.H.;C.O.;N.CH.), C.H., [237°] is formed by using [1:3] C.H., (CH.Br),

ψ-Cumyl-imide C₁, H₁, NO₂ i.e. C₈H₄:C.O.:NC₈H₄Me₂. [148³]. (above 360°). Formed by heating phthalic anhydride with e-cumidine (Fröhlich, B. 17, 1802). Trimetric crystals. Converted by ammonia into the compound C₈H₄(CONH₂).CONHC₈H₂Me₈ [218°], crystallising in needles, while methylamine and allyl-anine yield the corresponding compounds C₈H₄(CONHMe).CONHC₈H₂Me₃ [215°] and

s.Tri.methyl-phenyl-imide C₅H₄:C₂O₂:NC₄H₂Me₃. Phthalmesidil. [171]. Got by boiling mesidine with phthalic anhydride (Eisenberg, B. 15, 1017). Silky needles (from alcohol), insol. water. Yields, on nitration, the compounds C₂H₁O₂:NC₂HMe₃(NO₂) [210²] and C₃H₁O₂:NC₆Me₃(NO₂)₂ [242²].

C.H. (CONHC, H.). CONHC, H. Me. [179°].

Isocymyl-imide C.H.O.;NC₁₀H₁,. [145°]. Formed by heating the anhydride with m-isocymidine (Kelbe a. Warth, A. 221, 169). Yields C.H.O.;NC.H.₁₂NO. [167°] on nitration.

Naphthyl-imides C.H.;O.O.;NO.H., The

Naphthyl-imides C₂H, C₂O₂:NO₃H, The (a)- compound [166°] (P.); [182°] (M.) and its (β)- isomeride [216°] are got by heating the corresponding naphthylamines with phthalic an-

hydride (Piutti, G. 15, 479; Maschke, C. C. 1886, 824).

Tri-nitro-phenyl-imide C₂H₄O₂N.C₄H₄(NO₂)₂. [259°]. From potassium phthalimide and pieryl chloride (Schmidt, B. 22,

3257). Stair-like groups of crystals.

o - 0.xy - phen yl - imide
C.H.; C.O.; NC, H., OH. Oxpphthalantl. [220°].
Formed by heating phthalic anhydride with
o-amido-phenol (Ladenburg, B. 9, 1528). Converted by sodium carbonate solution into
CO.H.C., H., CO.N.H.C.H., OH [223°].

p · Oxy · phenyl · imide. [288]. Got in like manner from p-amido-phenol (Piutti, G. 16, 252). Yields C,H.;CO.;N.C,H.;OAc [239] and CO.H.C,H.;CO.;NI.C,H.;OH [289]. HNO, forms C,H.;C.O.;NC,H(NO),OH [210], which yields an acetyl derivative [177].

m-Nitro-phenacyl-imide

C.H.O.:N.CH.CO.C.H.NO. [204]. Formed from the brome of the control of the control

Phenyl hydrazide C.H.;C.O.;N.HPh. [1782]. Formed from phthalyl chloride and phenyl-hydrazine in ethercal solution (Piakel, A. 232, 233). Yellow needles, insol. water, sol. hot alcohol and chloroform.

Hydrides of phthalic acid. When reduced by sodium-amalgam in a solution kept acid by HOAc phthalic acid yields trans (1, 2)-dihydride. Neutral sodium phthalate reduced by sodiumamalgam without addition of acid yields the stable (4,5)-dihydride (Baeyer, A. 269, 154; cf. Graebe a. Born, A. 142, 330). Phthalic acid, suspended in water, is reduced by sodium-ancalgam to a lactonic acid which yields a crystalline lactone [255°]; phthalide, and the (1,2)-dihydride are also formed. Both the (1,2)-dihydrides reduce aqueous AgNO₄ (sic) on warning, forming at once a black pp. Boiling aqueous cupric accetate gives off CO. and forms a white pp. which on addition of HOAc deposits Cu₂O. The which on addition of HOAc deposits Cu.O. The liquid contains benzoic acid (Baeyer, A. 269, 151). None of the other dihydrides of phthalic acid are attacked by cupric acetate. ammoniacal AgNO3 gives with: the (1,2)-dihydride a black pp.; the (4,5)- and (1,6)- dihydrides a brown pp.; the (3,6)-dihydride a white pp. not turning frown. The (1,2)-(1,6)- and (4,6)dihydrides give benzoic acid and CO₂ when feebly oxidised. The (3,6)-dihydride gives phthalic acid (Baeyer, A, 269, 179). The hoxahydrides are most stable, the tetra-hydrides next, and the dihydrides least stable (Baeyer, A. 269, 169). The cis anhydrides are more stable than the trans anhydrides. The trans acids are more stable than the cis acids. The anhydrides of the dihydrides are well crystallised, and yield the corresponding acids when boiled with water. The anhydrides are got by means of AcCl or Ac.O. The (1,2) dihydride will not stand AcCl. The (4,5)-dihydride needs long boiling with AcCl. Boiling Az₂O often changes the trans to the cis var ety. The anhydrides of the cis melt at lower temperatures than their trans isomerides (Baeyer, A. 269,

In the following hydrides the two carboxyls are in the positions 1 and 2. The small numbers following Δ indicate the position of \mathbb{Q}

atoms supposed doubly united to the adjacent | C atoms.

Trans. A^{8,5} or (1,2). di-hydrids. CH:CH.CO.H. [210°]. S. 16 at 10°; 6 at CH:CH.CH.CO.H. [210°]. S. 16 at 10°; 6 at 10°. Formed by reducing phthalic acid (20 g.) dissolved in NaOAc (32°8 g.) and water 200 c.c. at 0° by adding successive quantities of 3 p.c. sodium-amalgam (40 g.) and 50 p.c. acetic acid (6 c.c.), and finally adding H.SO. (Baeyer, A. 269, 189). Prisms (from hot water). Not reduced by sodium-amalgam in the cold. Lead acetate gives a flocculent pp., sol. HOAc.

Reactions.—1. Boiling NaOHAq changes it

entirely to the (4,5)-isomeride. Nine hours boiling with water does the same. - 2. KMnO. hot ammoniacal AgNO, and aqueous AgNO, at 100° are at once reduced .- 3. Aqueous cupric acetate forms a green pp., which gives off CO₂. On adding HOAc the liquid becomes clear and contains benzoic acid, Cu₂O being ppd.—4. Oxidised by boiling CuSO, to benzoic acid (Baever, A. 269, 191) .- 5. The acid takes up Br (4 at.) and the product is reduced by zinc-dust and HOAc to the original dihydride.-6. Combines with HCl, hence cannot be etherified by alcohol and HCl. -7. Combines with HBr (2 mols.) in aqueous solution at 100°. The product could not be crystallised, is reduced by sodium-amalgam to a hexahydride, while zinc and HOAc do not form an unsaturated acid.

Cis (1,2)-dihydride. [175°]. S. 18 at 10°. Does not accompany the trans form in the product of reduction of phthalic acid (Baeyer, A. 269, 192). The trans acid boiled with Ac₂O (but not AcCl) for 7 minutes is changed to the anhydride of the cis isomeride. The lead salt of the cis acid is insol. HOAc, while that of the trans acid is soluble therein. Large colourless many-faced prisms. Readily converted into anhydride by warming with Ac₂O. The anhydride [100°] crystallises from ether in colourless needles, and is re-converted into the acid by boiling water. The cis acid is converted into the (4,5)-dihydride by boiling NaOHAq, by 9 hours' boiling with water, and even (unlike the trans isomeride) by standing for 2 days with 15 p.c. NaOHAq. Reacts with silver and copper salts like the trans acid.

Δ^{2,6} or (4,5) - Dihydride. CH_CH:C.CO,H [215°]. S. ·8 at 25°; ·2 at 10°. Got by reducing phthalic acid (60 g.) with sodium-amalgam (1200 g.) (Baeyer, A. 269, 195; c. Astié, A. 258, 187). Lustrous triclinic crystals.

Reactions.—1. Not affected by evaporating with boiling NaOHAq, but by long warming with very cone. aqueous or alcoholic KOH it is partially changed to the A^{2,4} or (1,6)- dihydride.—2. Reduced by sodium-amalgam in a current of CO₂ at 100° to A' or (1,4,5,6)- and cis and trans A' or (1,2,3,6)-tetrahydrides.—3. KMnO₄ oxidises it to oxalic and phthalic acids (no succinic acid).—4. Alkaline K,FeOy, on boiling forms benzoic acid. Cold dilute H,SO₄ and MnO₂ also form benzoic acid.—5. PCl₃ gives phthalic anhydride.—6. Br in the dark forms C,H₂Br₂O₄ [185°].—7. With HBr (2 mols.) it combines forming crystalline di-bromo-phthalic acid bexahydride (Baeyer, A. 269, 198), which is re-

duced by sodium amalgam to phthalic acid trans-hexallydride. AcCl converts the acid into an anhydride [157°]. The silver salt boiled with water is reconverted into the (4,5)-dihydride. Alcoholic potash converts dibromophthalic acid hexallydride into the $\Delta^{2,4}$ or (1,6)-dihydride.

Methyl ether MeA'. (250°).

Anhydride [84°]. Got by boiling the (4,5) acid with AcCl (Baeyer, A. 269, 196). The product is evaporated over soda-lime and H₂SO₄ in vacuo, when the anhydride separates in large tables or prisms, sl. sol. ether, v. sol. chloroform. Hot water readily dissolves the anhydride, converting it into the parent acid. Na₂CO₂Aq forms an orange-red solution, which bleaches litmus as long as any anhydride is undissolved, the blue colour afterwards returning when all is dissolved. On adding H₂SO₄ to the solution a resin is ppd. Heating on the water-bath resinifies the anhydride, forming some phthalic anhydride,

Δ²⁴ or (1,6)-dihydride. CH CH_xCH.CO_xH [180°]. Formed by boiling the di-hydro-dibromide of the (4,5)- dihydride of phthalic acid CH_xCHBr.CH.CO_xH with a solution of KOH (1 pt.) in MeOH (2 pts.) for 1½ hours (Baeyer, A. 269, 199). Formed also in small quantity by heating the (4,5)- acid with conc. aqueous or alcoholic KOH or NaOH. Rosettes of prisms (from water). More soluble in water than the (4,5)-dihydride. Hot cupric acctate forms a white pp. which dissolves on cooling.

Reactions.—1. KMnO₄ and Na₂CO₂Aq form oxalic acid in the cold, and some phthalic acid. 2. Ammoniacal AgNO₃ forms a white pp. turning brown on warming.—3. Cold dilute H₂SO₄ and MnO₂ form benzoic acid and CO₂—4. Boiling alkaline K₄FeCy₈ also forms benzoic acid.—5. Converted by Ac₂O in the cold into the anhydride which crystallises from chloroform in cubes [104°] and is reconverted into the acid by warm water. The anhydride dissolves in Na₂CO₃Aq and bleaches litmus meanwhile. The anhydride is converted by heat into the anhydride of the (3,6)- dihydride.—6. Sodiumanalgam reduces it in the cold (difference from isomerides) to the cis-(1,2,3,6)- tetrahydride.—7. Combines with HBr (2 mols.) when heated at 100° with a solution of HBr in HOAc (Baeyer, A. 269, 200). The product [190°] crystallises from ether in plates, and is reduced by sodiumanalgam to the trans hexahydride.

Reactions.—1. When heated at 100° for a long time it is partially converted into anhydride. Evaporation of its aqueous solution also partially converts it into anhydride. The anhydride [185°] is also got by heating the acid with Ac.O. It crystallises in plates.

Readily sublimes in feathery plates. Does not bleach litmus .- 2. Sodium-amalgam does not reduce it even when gently warmed (Baeyer, A. 269, 205).—3. Dilute H.SO, and MnO. oxidise it to phthalic acid. Boiling alkaline K.FeCy, also forms phthalic acid.—4. KMnO, is at once depolarized.—5. Relians (10 no.) No.OMA (2000). colourised.-5. Boiling (10 p.c.) NaOHAq forms (4,5) and (1,6) isomerides.

A' or (3,4,5,6) - Tetrahydride CH₂CH₂CCO₂H [120°]. Formed by dissolving its anhydride in boiling water (Baeyer a. Astie, A. 258, 203; 269, 176). Got also by distilling the tetrahydride of pyromellitic acid (Baeyer, A. 166, 346). Monoclinic leaflets (containing aq). When heated at 100° for some time it melts, forming the anhydride. KMnO, oxidises it to adipic acid. Boiling conc. KOHAq changes it to the A' acid. Oxidised by Br and alkalis to di-oxy-phthalic acid hexahydride (tartrophthalic acid).-BaA" aq: crystalline pp.

Methyl ether Me,A". Combines with Br, forming two dibromides [84] and [124].

Anhydride C,H,O₃. [749]. Formed by heat-

ing the A2 acid or its anhydride at 215° for some time. Plates (from ether), v. sol. ether.

Δ² or (1,4,5,6). Tetrahydride CH₂CH₂CH₂CO₂H. (215°). S. 88 at 10° H.C.p. 881,600. H.F. 215,400 (Stohmann, J. pr. [2] 43, 540). Got by reducing a boiling solution of sodium phthalate with sodium-amalgam (Baeyer, A. 258, 175). Formed also, together with the trans A' isomeride, by reducing the (4,5)-dihydride in the same way. Prisms (from water). Bromine vapour yields a dibromide [225°]. MeOH and HCl form an oily methyl ether, which KMnO, yields a crystalline dibromide [74°]. oxidises it to oxalic and succinic acids

Anhydride CaH,O,. [79°]. Formed from the acid and AcCl. Prisms. Changed by heat into the anhydride of the A' acid.

Trans-A' or (1,2,3,6) - Tetrahydride сн.сн.сн.со.н сн.сн.сн.со.н [218°]. S. .145 at 6°. Formed, together with the (1,4,5,6)-tetrahydride, by reducing the (4,5)-dihydride in boiling solution by sodium-amalgam (Baeyer, A. 258, 210; 269, 161). Leaflets (from water). De-colourises KMnO, at once. Yields a methyl ether Me, A" [40°], which forms a dibromide [117°]. Anhydride C.H.O. [140]. Got from the acid and Accl. Needles (from ether). Changed by heat into the cis- isomeride.

Cis-A' or (1,2,3,6) · Tetrahydride
[174°]. S. 9 at 6°. Formed by adding sodiumamalgam at 0° to a solution of the Na salt of the (1,6)-dihydride in a current of CO₂ (Baeyer, A. 269, 202). Formed also by boiling the trans Δ^4 tetrahydride with Ac.O for 15 minutes. Large prisms. Boiling Ac.O forms the anhydride, which crystallises from ether in tables [59°].

Trans (or fumatoid) hexahydride C.H. (CO.H). [221°]. S. 23 at 20°. Formed by reducing the hydrobromides of the di- and tetra- hydrides with sodium-amalgam or with seine-dust and HOAc (Baeyer, A. 166, 350; 258, 214; 269, 161; cf. Mizerski, B. 4, 558). By reducing the (3,4,5,6)-tetrahydride in a hot solution a mixture of trans- and cis- hexahydrides is obtained. Leaflets (from water). May be

distilled unchanged if quickly heated, but yields the cis- anhydride when slowly heated. Not oxidised by cold squeous KMnO. Yields a dimethyl ether [83°], m. sol. ligroin.—PbA" aq:

Anhydride. [140°]. Formed from the acid and AcCl. Long needles (from ether). Changes when heated into the cis-isomeride.

Cis- (or maleoid) hexahydride. [c. 1920]. Got from its anhydride, which is formed by heating the anhydride of the trans- isomeride at 220° for eight hours. Short four-sided prisms, more soluble than the trans- isomeride. Not attacked by cold aqueous KMnO, Conc. HClAq at 180° changes it to the trans variety. The Ba and Zn salts are less sol. hot than cold water.

Anhydride. [32°].

Isophthalic acid [1:3] C_oH₁(CO₂H)₂. [c. 300°]. S. 013 at 25°; '22 at 100°. H.C.v. 769,100. H.C.p. 768,800. 11.F. 190,200 (Stoh-

mann, J. pr. [2] 40, 138).

Formation.—1. By exidising m-xylene with K.Cr.O, and H.SO, (Fittig a. Velguth, Z. [2] 8, 526; A. 148, 11; 153, 268).—2. By fusing sedium formate with potassium m-sulpho-benzoate (V. Meyer, A. 156, 265; 159, 1).-3. The ether is formed by the action of ClCO, Et and sodiumamalgam on m-di-bromo-benzene (Wurster, A. 176, 149) .- 4. By fusing potassium formate with potassium benzoate (Richter, B. 6, 876), mbromo benzoate (Ador a. Meyer, A. 159, 16), or di-sulpho-benzoate (Barth a. Senhofer, A. 159, 228). -5. By oxidation of m-toluic acid (Weith a. Landolt, B. 8, 715) .-- 6. By saponification of its nitrile .- 7. By heating the hydrides of prehnitic and pyromellitic acids with H,SO, (Baeyer, A. 166, 334; Suppl. 7, 4).-8. By strongly heating NaOBz (Conrad, B. 6, 1395) .- 9. By oxidation of colophony with dilute nitric soid (Schreder, A. 172, 93).-10. By the action of a hot aqueous solution of cuprous potassium cyanide upon m-diazo-benzoic chloride, and saponification of the resulting nitrile (Sandmeyer, B. 18, 1498).

Preparation.-m-Xylene is converted, by heating with bromine at 125°, into C_aH₄(CH₄Br)₄, which is boiled with alcoholic potash, and the resulting C.H. (CH.OEt), oxidised with chromic acid mixture (Kipping, B. 21, 46).

Properties.—Long slender needles (from water), m. sol. alcohol. May be sublimed.

Salts.—K₂A".—BaA" 6aq. Triclinic crystals (by spontaneous evaporation) (Lossen, A. 266, V. sol. water. BaA" 4aq? Needles (by cooling hot saturated solutions). - CaA" 2 aq:

needles.—Ag,h": amorphous pp.

Methyl cther Me,A". [65°]. Needles
(from dilute alcohol). H.F. 173,300 (Stohmann,

J. pr. [2] 40, 353).

J. pr. [2] 40, 533).

Diethylether Et, A". [0°]. (285°).

Diephenylether Ph, A". [120°]. Got by boiling the chloride with phenol. Long needles.

Chloride C, H. (COCl). [41°]. (276°).

Formed by heating the acid with PCl, at 200°

(Schreder, B. 7 708; Münchmeyer, B. 19, 1849).

Amide C.H.(CO.NH₂). [265°] (B. Beyer, J. pr. [2] 22, 351); [above 270°] (Luckenbach, B. 17, 1431). Got from the chloride and NH₂. Plates, al. sol. water and alcohol.

Nitrils C.H.Cy. [158°]. Formed by distilling potassium cyanide with potassium bens-

ene m-disulphonate (Barth a. Senhofer, A. 174, 236; Meyer a. Michler, B. 8, 672; Nölting, B.8, 1112; Luckenbach, B. 17, 1428), or with potassium m-chloro- or bromo- benzene sulphonate (Meyer a. Stüber, A. 165, 165; Limpricht, A. 180, 92). Formed also by heating the oxim of isophthalic aldehyde C.H.(CH:NOH), with excess of AcCl at 100° for a long time (Münchmeyer, B. 20, 508), by the dry distillation of calcium m-cyano-benzoate (Brömme, B. 20, 521). and by boiling an alcoholic solution of C, H, (CS.NH,), with an aqueous solution of lead acetate (Luckenbach). Small needles (from alcohol), insol. water, m. sol. ether. Converted by alcohol and dry HCl into phthalimido-ethyl ether C. H. (C(NH).OEt), [66°]. MeOH and HCl yield C. H. (C(NH).OMe), [c. 62°]; while mercaptan and HCl form C. H. (C(NH).SEt), which, like the two preceding bodies, forms a crystalline hydrochloride (Luckenbach).

Semi-nitrile v. m-CYANO-BENZOIC ACID. Tetrahydride of Isophthalic acid

C₆H_g(CO₂H)₂. [199°]. Formed by reduction of isophthalic acid by boiling its alkaline solution with sodium-annalgam (Baeyer, B. 19, 1806). Needles, v. sol. hot water.—Ag.A": white pp. Methyl ether Me.A". Oil.

Isomeride v. TEREPHTHALIC ACID.

References .- AMIDO-, BROMO-, BROMO-NITRO-, CHLORO-, IODO-, NITRO-, OXY-, and OXY-AMIDO-PHTHALIC ACIDS.

Homo-phthalic acid v. CARBOXY-PHENYL-ACETIC ACID.

Diphthalic acid v. DIPHTHALYLIC ACID.

PHTHALIC ALCOHOL v. DI-OXY-XYLENE.

PHTHALIC ALDEHYDE C₈H₆O₂ ie. **C.H.**(CHO), [1:2]. Mol. w. 134. [52²]. Formed by boiling C_aH₁(CHCl₂, (1 mol.) with NaOHΛq (4 mols.) (Colson a. Gautier, Bl. [2] 45, 509; A. Ch. [6] 11, 29). Formed also by oxidising C.H. (CH2.OH) (Hijelt, B. 19, 411). Solid, v. sl. sol, water. Coloured blue by NH Aq. Slowly oxidised by air.

Oxim C_dH₄(CH:NOH)₂. [2 needles (Münchmeyer, B. 20, 509). [215°]. Small

Isophthalic aldehyde C.H. (CHO). [1:3]. [90°]. Formed by boiling C₆H₄(CHCl₂)₂[1:3] with water (Colson a. Gautier, Bl. [2] 45, 509; V. Meyer, B. 20, 2005). Needles. Reduces silver solution with difficulty. Gives a violet-red tint with rosaniline reduced by SO₂. Oxidised by KMnO₄ to isophthalic acid.

Oxim C₆H₁(CH:NOII)₂. [212°] (Münchmeyer); [180°] (Meyer). Plates (from hot alcohol). Converted by AcCl at 100° into C₆H₄Cy₂. Yields the ethers C₂H₄(CH:NOMe)₂ [77°] and C.H. (CH:NOEt), [165°].

Reference. -OXY-ISOPHTHALIC ALDERYDE.

Isomerides. TEREPHTHALIC ALDEHYDE and PHTHALIDE

PHTHALIC ALDEHYDE ACID v. ALDEHYDO-BENZOIC ACID and PHTHALALDEHYDIC ACID.

PHTHALIDE C₈H₉O₂ i.e. C₆H₄< CH₂>O. Lactone of w-Oxy-o-toluic acid. [73°]. (290°

Formation. -1. By reducing phthalyl chlor-ide with zine and HClAq (Kolbe a. Wischin, C. J. 19, 339), or with Mg and HOAc (Baeyer, Z. [2] 5,399; 10,123,1445; 11,637). -2. Occurs among the products of reduction of phthalic an-

hydride by zinc-dust and HOAc (Wislicenus, B. 17, 2178). - 3. By passing bromine-vapour over o-toluic acid at 140° (Hjelt, B. 19, 412).

Preparation .-- Phthalimide (1 pt.) is reduced to phthalidene by means of tin (13 pts.) and HCl. The tin is ppd. by zinc, and sodium nitrate added to the filtrate. The yellow pp. of the nitrosamine of phthalidine is filtered off, washed, and heated with dilute NaOH. The phthalide is ppd. by HCl and distilled. Yield on the phthalic anhydride -70 p.c. of the theoretical

(Graebe, B. 17, 2599).

Properties. Needles (from hot water), sl. sol. cold water, v. sol. alcohol and ether. Does not combine with NaHSO, (Hessert, B. 11, 238), or reduce ammoniacal AgNO. Does not react with

hydroxylamine.

Reactions.-1. Oxidised by alkaline KMnO to phthalic acid. -- 2. Alkalis and alkaline carbonates form w-oxy-o-toluic acid, v. vol. iii. 781. - 3. Sodium-amalgam forms hydrophthalide C.H.O., a viscid mass, v. sol. alcohol and other, and also 'phthalylpinacone' CusHisO. [197°] .- 4. Ammonia on heating forms phthalimidine .- 5. Aniline at 210' forms phenylphthalimidine .- 6. Phthalic anhydride on heating forms diphthalyl.—7. KCy at 185° forms $C_aH_1(CH_a,CN),CO_2H_1$ [116°], which forms CaA'_2 2aq, and yields carboxy-phenyl-acctic acid ORA 2.201, and remarks on saponification (Wislicenus, B. 18, 172; 233, 112). KCy at 200° yields C₁₈H₁₁N₁O₃ (?) [240°-245°].—8. Boiling IIIAq forms o-toluic acid. 9. Br at 140° forms exo-bromo-phthalide. at 160° yields phthalyl chloride (Racine, A. 239, 79) .- 10. NaOEt acting on an ethereal solution of oxalic ether and phthalide forms an ether C12H10O5 [122°] crystallising from alcohol in needles, and forming with phenyl-hydrazine the compound $C_{18}H_{18}N.O.$ [1595] (Wislicenus, B. 20, 2062; A. 246, 342).

Phenyl-hydrazine compound C₁,H₁,N₂O₂i.e.CH₂(OH).C₄H₃,CO.N₂H₂Ph. [174°]. Readily formed by warming phthalide with phenyl-hydrazine for a few hours (Meyer a. Münchmeyer, B. 19, 1707, 2132; Wislicenus, B. 20, 401). Sol. hot water and alcohol, sl. sol. ether. Silvery needles. Partially resolved into the parent substances by fusion. Very unstable towards acids and alkalis. H.SO forms a colourless solution, turned raddish-violet by FeCl,

References. -- AMIDO-, BROMO-, CHLORO-, NITRO-, and OXY-PHTHALIDE.

PHTHALIDE CARBOXYLIC ACID v. Oxy-CARBOXYL-PHENYL-ACETIC ACID

PHTHALIDE SULPHONIC ACID

 $SO_3H.C_bH_4 < \stackrel{CH}{CO} > O$. Formed by warming phthalide with fuming H.SO, (20 p.c. SO, extra) (Hoenig, B. 18, 3453), Needles, v. sol. alcohol, insol. ether. - BaA'2 - CuA'2 2aq: light-blue prisms.

PHTHALIDINE is PHTHALIMIDINE. PHTHALIMIDINE Call, NO i.e.

 $C_{e}H_{i} < \frac{CH_{2}}{CO} > NH$. [150°]. (337°) at 730 mm. Formed by reducing phthalimide with tin and HCl, and by heating phthalide in a current of NH₂ (Gracbe, B. 17, 2598; 18, 1408; A. 247, 290; Barbier, C. R. 107, 918). Needles or prisms, sl. sol. cold water, v. e. sol. alcohol and other. Not volatile with steam. Oxidised by

KMnO₄ to phthalimide. Bromine forms C_{1e}H₂N₂O₂Br₃ [150°]. Distillation over zincdust forms phenyl-isoquinoline. Yields a nitroderivative $C_6H_4 < \frac{CH(NO_4)}{CO} > NH$ [210°], converted by oxidation

a di-nitro- derivative [195].

B'HCl. [150°]. verted by oxidation into phthalide. Yields also

Thin white needles, v. sol. water. $-B'_{*}H_{*}PtCl_{*} - B'_{*}HAuCl_{*}$. [176°]. $-B'C_{*}H_{*}(NO_{*})_{*}OH$. [140°]. $-C_{*}H_{*}AgNO_{*}$. Acetyl derivative C. H. AcNO. [151].

Needles (from dilute HOAc).

Yellow needles (from water or alcohol). Converted by NaOHAO inte verted by NaOHAq into ω-oxy-o-toluic acid, and by NaSH into thio-phthalide C.H.OS [60].

Reference.—DI-CHLORO-PHTHALIMIDINE. pseudo-Phthalimidine C, H, NO probably $C_{\bullet}H_{\bullet} < \stackrel{CH_{\circ}}{<} NH$. This compound is formed, as hydrochloride, by heating w-chloro o-toluylamide C_aH₁(CH₂Cl).CO.NH₂ to 150 160. The picrate B'C_aH₂(NO₂)₃OH forms a crystalline yellow pp.; the salt B'₂H₂Cl_PtCl, 2aq forms flat orange yellow needles (Gabriel, B. 20, 2231).

ISO-PHTHALIMIDO-ETHYL ETHER $[66^{\circ}].$ C,H,(C(NH).OEt), [1:3]. The hydrochloride is got by passing dry HCl into a mix-ture of isophthalic nitrile (1 mol.) and absolute alcohol (2 mols.) dissolved in benzene (Luckenbach, B. 17, 1431). The free base crystallises in small needles, v. sol. alcohol and other. It decomposes on heating into alcohol and isophthalic nitrile.—B"H.Cl., [270°]. Crystalline. PHTHALIMIDYL-BENZYL v. BENZYLIDENE-

PHTHALIMIDYL PROPIONIC ACID

PHTHALIMIDINE.

 $\mathbf{C}_{11}\mathbf{H}_{9}\mathbf{NO}_{3}$ i.s. $\mathbf{C}_{6}\mathbf{H}_{4} < \mathbf{CO.NH}_{2}\mathbf{CO.NH}_{2}$

[2257]. Formed by dissolving the dilactone of thenyl ethyl ketone dicarboxylic acid in NH,Aq (Roser, B. 18, 3119). Long yellowish needles, v.

sol. hot alcohol.—BaA'₂.—CaA'₂ laq.—AgA'.

Lactone C₁₁H₈NO₃. [c. 205°]. Formed by evaporating the dilactone mentioned above with conc. NH₂Aq on the water-bath. Small tables, v. sol. alcohol, sl. sol. cold water. Reconverted by boiling HClAq into the dilactone. Dissolves easily in cold aqueous alkalis, forming salts of a dibasic acid C, H, NO.

PHTHALONITRILE v. Nitrile of PHTHALIC ACID.

PHTHALOPHENONE v. DI-PHENYL-PHTHAL-WE.

o-Phthalophenone C,H,Bz, [1:2]. [146°]. Got by oxidising o-di-benzyl benzene (Zincke, L. 9,

31). Tables (from alcohol).

Sophthalophenone C.H.Bz. [1:3]. Phenylene
di-phenyl diketone. [100]. Formed by the
action of benzene and AlCl, on isophthalyl
chloride (Ador, B. 33, 320). Plates (from alcohol). Yields two dinitro- derivatives [200°] and [100°]?

[100°]?

Mono-oxim C.H., C(NOH), C.H., Bz. [201°]
(Nölting, B. 19, 146). Nodules, v. sol. alcohol.

Di-oxim (C.H., C(NOH)), C.H., [70°-55°]
(Münchmeyer, B. 19, 1849). Small crystals.

p-Phthalophenone C.H., Bz., [1:4]. Tere
**C.H., Bz., [1:4]. Tere
**C.H., Bz., [1:4]. [160]

phthalophenone. (a)-Di-benzoyl-benzene. [160]. Formed by oxidising p-di-benzyl-benzene with CrO₂ and HQAc (Zincke, B. 9, 31; Wehnen, B.

9, 309). Got also from terephthalyl chloride, benzene, and AlCl₁(N.). Plates (from benzene). PCl₃ yields C₂₀H₁₁Cl₄ [92°]. Sodium amalgam forms di-oxy-di-benzyl-benzene [171°].

Mono oxim. [213°]. Nodules. Dioxim. [235°]. Crystal.. PHTHALOXYL-AMIDO-ACETIC ACID

C₁₀H_aNO, i.e. CO₂H.C₆H₄.CO.NH.CH₂CO₂H. Giveocoll-phthaloptic acid. [106°]. Formed by the action of alkalis on phthalyl-amido-acetic acid (Reese, A. 242, 6; Gabriel a. Kroseberg, B. 22, 426). Six-sided plates (containing as).— 22, 420). SIX-Butta praces containing May.
A. A. K.A.: hygroscopic necdles. - BnA...
Ag.A.: plates, sl. sol. hot water.
PHTHALOXYL-AMIDO BENZOIC ACID

CO.H.C.H., CO.NH.C.H., CO.H. [277°]. Formed by exidation of the p-tolylimide of phthalicacid with KMnO, (Michael, B. 10, 576).

PHTHALOXYL AMIDO HEXOIC ACID CO.H.C. H. CO.NH.C. H. Mc.CO.H. Occurs in two varieties, the active [1327] and inactive [103], which are got by boiling the corresponding phthalyl-amido-hexoic acids with NaOHAq (Reese, A. 242, 20). Both acids are decomposed by boiling water into leucine and phthalic acid.

PHTHALURIC ACID v. Uramic acid of Ригиалле асто

DIPHTHALYL C, II,O, i.c.

C, H, CO, O, CO C, H, [335°].

Formation. 1. By heating phthalyl chloride with reduced silver at 150° (Ador, A. 164, 229). 2. By fusing phthalic anhydride with zinedust; and, together with other products, by reducing phthalic anhydride with zine dust and HOAc (Wislicenus, B. 17, 2178). 3. By heating phthalide with NaOAc and phthalic anhydride or thio-phthalic anhydride (Graebe a. Guye, B. 17, 2851; A. 228, 126; 233, 241). - 4. By boiling phthalaldehydic ether with alcoholic KCN (Goldschmidt a. Egger, M. 12, 60).

Properties .-- Needles, insol. water, v. sl. sol. alcohol and ether. May be sublimed in a current of CO... Combines with Br forming C₁₆H₈Br₂O₄ [c. 225]. PCl₃ at 160° forms the chloride C₁₆H₈Cl₂O₄ [245°]. Bromine and water at 100° form bromo-diphthalyl, which crystallises from benzene. Alkalis form diphthalyllactonic acid.

H_y tride C_{1.}H₁₀O₄ i.e.
C₀H₁(C_{0.0}, O.Co) C₀H₁ [229°] (W.); [250°] (Hasselbach, A. 243, 249), a product of the action of zinc dust and HOAc on phthalic anhydride (Wislicenus). Needles (from alcohol), v. sol. HOAc. Potash forms di-oxy-di-phenyl-ethane

dicarboxylic acid. References .- TEFRA-CHLORO-, NITRO-, and Oxy- Diphthalyl.

PHTHALYL-ACETIC ACID C, H,O, i.e.

-Ç:CH.CO.H. [c. 246°] (G.); [above $C^{a}H^{4} < CO^{\circ}Q^{\circ}$ 260°] (Roser, B. 17, 2620). Formed by boiling phthalic anhydride (10 pts.) with Ac O (20 pts.) and NaOAc (2 pts.) (Michael a. Gabriel, B. 10, 391, 1551, 2199). Formed also by dissolving acetophenone ow-dicarboxylic acid in H.SO. (Gabriel, B. 17, 2521). Needles (from nitrobenzene), insol. water, v. sl. sol. hot alcohol.

Reactions .- 1. Aqueous Na()H (1 mol.) forms a solution of its Na salt, but ercess of alkali con-

verts it into acetophenone ow-dicarboxylic acid. 2. Distillation in vacuo splits it up into CO₂.

and methylene-phthalide.—3. Bromine in HOAc
gives CBr₄.CO.C₆H₄.CO₂H [160°]. Dry Br gives
C₂H₄.O₂:CBr.CO₂H [c. 235°].—4. Chlorine acting on the HOAc solution forms CCl, CO.C, H, CO, H [144°].-5. H.SO, at 100° forms tri-benzoylenebenzene (v. vol. i. p. 485).—6. Ammonia gives rise to phthalimidyl-acetic acid C₁₀H,NO₃ i.e. -C:CH.CO₂H (?) which crystallises C'H' CO'NH from water in needles [c. 200°] and yields CaA', 2a, BaA', 4aq, and AgA' (Roser, B. 17, 2623; Gabriel, B. 18, 2451).—7. NMeH, Aq at 0° forms NHMe.CO.C, H, CO.CH, CO.H [145°], which is converted by concentrated H.SO, into C.H. CO.NMe [c. 212°], crystallising from alcohol in silky needles, split up by heat into CO2 and C8H. CO NMQ2, a crystalline mass which is converted by bromine-water into C₁₀H₁₀BrNO₂ [126°] (Gabriel, B. 18, 2453). 8. Cold H.SO. into C.H. CO.H. CO.H. [180] cold H2SO, into C4H4 CONEt -C:CH₂ (Merand by heat into liquid C_sH₄ CO·NEt

tens, B. 19, 2368).—9. Propylanine forms, in the cold, C_{1.1}H_{2.N}O₂ [103°], crystallising in prisms (M.).—10. Aniline at 100° forms C_{1.2}H_{1.2}NO₂ [192°], crystallising from benzene in cubes, converted by cold H.SO, into C_{1.3}H_{1.1}NO [265°] and by heating at 204°–230° into the isomeric C₂H₄ CO·NPh [100°] (Mortens, D. 19, 2371).—11. Secondary and tertiary amines have

2871).—11. Secondary and tertiary amines have no action.—12. Sodium-analgam forms the lactone of oxy-carboxy-phenyl-propionic acid (2. v.).

Salt.—AgC 10H,O.: amorphous pp. PHTHALYL-DIACETIC ACID

C.H. CO.O C(CH₂CO₂H)₂. [158°]. Formed by saponifying phthalyl-di-malonic ether with KOHAq (Wislicenus, A. 242, 80). Prisms.—BaA'2aq: prisms, v. sol. water.—Ag₂A''.

PHTHALYL-ACETOACETIC ETHER C₁₁H₁₂O₃

i.s. C₄H₄CO.0 C:CAc.CO₂Et. [121°]. Formed from sodium acotoacetic ether and phthalyl chlorido (Fischer a. Koch, B. 16, 651; Bülow, A. 236, 185). Prisms (from alcohol). Decomposed by H₂SO₄ at 65° into HOAc and phthalyl-acetic acid. Alcoholic KOH forms deliquescent crystalline K₂O₄H₄O₇. Phenyl-hydrazine acetate forms C₂₀H₄N₄O₄ [238°], which is reduced by zinc-dust and HOAc to carboxy-benzyl-acetoacetic ether [92°].

PHTHALYL ALCOHOL v. DI-w-OXY-O-

PHTHALYL-AMIDO-ACETIC ACID

C₁₀H,NO₄ i.e. C,H.;C₂O₂;N.CH₂CO₂H. Phthalyl glycocoll. [192³]. Formed by heating phthalia anhydride (2 pts.) with glycocoll (1 pt.) (Drechsel, J. pr. [2] 27, 418; Resse, A. 242, 1). Crystals (from water), decomposed by boiling HClAq into phthalic acid and glycocoll. Cold NaOHAq forms phthaloxy-amido-acetic acid (q. v.).—NaA'aq.—NH₂A'. [206³].—CaA',2aq.—CuA',3aq.—AgA'.

-Pt(N₂H₂A')₂. Colourless prisms; got by evaporating a solution of the acid with oxide of plato-diammonium.

Ethyl tther Eth'. [105°] (R.); [113°] (G.). (above 800°). Formed from Ag₂A" and Etl (R.), and also by heating potassium plthalimide with CH₂Cl.CO₂Et (Goedeckemcyer, B. 21, 2688; Gabriel, B. 22, 426). Needles, v. sol. benzene.

PHTHALYL. p. AMIDO. BENZENE SUL-PHONIC ACID C_sH.;C₂O₂:N.C_sH.;SO H. The Na salt, got by heating plthalic anhydride with sodium p-amido benzene sulphonic acid at 250°, crystallises from water in silky needles (Pellizzari, A. 248, 153; G. 18, 314). It is converted by boiling ammonia into phthalimide and sodium p-amido-benzene sulphonate. The Ba and NH₄ salts are also crystalline.

PHTHALYI. o. AMIDO BENZOIC ACID C₀H₁:C₂O₂:NC₆H₄.CO₂H₁ [217°]. Formed by heating anthranilic acid with phthalic anhydrid (Gabriel, B. 11, 2261). Prisms, sol. HOAc. Phthalyl-m-amido-benzoic acid. [276°] (G.);

Phthalyl-m-amido-benzoic acid. [276°] (G.); [282°] (P.). Formed from phthalic anhydride and m-amido-benzoic acid, and also by saponifying its ether [152°], which is formed by heating phthalic ether with m-amido-benzoic acid (Pellizzari, B. 18, 216; A. 232, 147). Needles. The amide is described in vol. i. p. 158.

Anilide. [209°]. Prisms (Piutti, B. 16,

PHTHALYL-AMIDO-ETHANE SULPHONIC ACID C₃H₄O₂:N.C.₂H₃SO₃H. Salt. — KA' ½aq. Formed by heating potassium amido-ethane sulphonate with phthalic anhydride (Pellizzari, G. 18, 324). Monoclinic crystals; aibic = 7:908:1:2·594; β = 60° 42′. Decomposed by alcoholic NH, into phthalinide and taurine.

PHTHALYL - AMIDO - HEXOIC

C₁,II₁,NO₄ i.e. O₈H₄O₂:N.CH(C₄H₉).CO₂H. [116°].

[a]_n = -21 97° in a 5 p.c. alcoholic solution at 22°. Formed by fusing leucine with phthalic anhydride (Recse, A. 242, 9). Needles, v. sl. sol. hot water. Laworotatory. Converted by distillation into an inactive variety [142°], which yields PtN,H₆A'₃A³₃aq. Conc. HClAq at 150° forms leucine and phthalic acid. NaOHAq forms phthaloxy-amido-hexoic acid (q, v.).—NaA'.—NII,A'. *[160°-165°].—PtN,H₆A'₃3aq.

PHTHALYL-AMIDO-NAPHTHALENE SUL-

PHTHALVI.-AMIDO. NAPHTHALENE SUL-PHONIC ACID C₄H₁:C₂O₂:N.C₁₀H₆:SO₃H. The salt KA'3aq is got by heating sodium (a)naphthylamine sulphonate with phthalic anhydride (Pellizzari a. Matteuci, G. 18, 321). It crystallises in needles, sol. water.

PHTHALYL-γ-AMIDO-n-PROPYL-MALONIG ETHER C,H.(C,O,:N.CH,-CH,-CH,-CH,(CO,Et),-(18°). Formed by the action of sodium malonic ether on the γ-bromo-propyl-imide of phthalic acid (Gabriel, B. 23, 1767). Monoclinic plates (from ligroin); α:b:c=3·260 il:1·644; β=81°4′. Converted into δ-amido-valeric acid by heating with HClAq at 190°.

Phthalyl-amido-di-propyl-malonic ether

Phthalyl - amido - di - propyl - malonie ether C_sH₁O_z:N.OH_zCH_zCH_zCPr(CO_zEt)_z. [57°]. Formed in like manner from propyl-malonio ether (Aschan, B. 23, 3698). Prisms, insol.

water, v. sol. alcohol and ether.
DI - PHTHALYL - DI - AMIDO - QUINONE
C.H., N.O., s.c. C.H., O.(N.C.O.; C.H.), Fi.2:46].
[2777]. Prepared by heating tri-amido-pheno

hydrochloride with phthalic anhydride, dissolving the resulting C.H.(OH)(N.C.O.;C.H.), [above 800°] in potash, and treating the product C.H.(OH)(NH.CO.C.H., CO.H.), [above 300°] with intric acid (S.G. 148) (Piutti, G. 16, 254). Yellow needles (from HNO₃). Forms a compound [174°] with phenyl-hydrazine. IL,S passed into its solution in dilute HOAc forms crystalline C.H.,(OH),(N:C.O.;C.H.),, not melted at 310°. PHTHALYL-AMIDO-SUCCINIC ACID

C₁₇H₂NO₄ i.e. C₂H₄O₂:N.CH(CO₂H).CH₂CO₂H. [225°]. Formed by heating aspartic acid with phthalic anhydride for 1 hour at 180° (Piutti, G. 14, 473; 16, 2). Tufts of prisms (from water). Decomposed into phthalic and aspartic acids by heating with HClAq. Boiling aniline forms aspartic acid and the phenylimides of phthalic and phthalyl-amido-succinic acids. Diphenylamine forms three di-phenyl-amic acids C₄H_{O2}:N.C₂H₃(CONPh₂)(CO.H) [180°], [204°], and [194°]; the first and third crystallises with aq, and all three yield a salt AgA' and are decomposed by potash-fusion into aspartic acid, phthalic acid, and diphenylamine.

Salt .- CuA', 4aq : blue prisms.

C.H.O.N:CH CH.CO. Phonylimide [264°]. Formed from the acid and aniline.

Small needles (from HOAc), nearly insol. alcohol.

Tetra-phenyl-diamids
C_hH,O₂:N.C₂H₃:C₂O₂(NPh₂)_x. Two isomerides,
[273°] and [286°], are got by heating the acid with diphenylamine for 5 hours at 1903. Both are split up by HClAq at 200° into phthalic acid, diphenylamine, and aspartic acid.

PHTHALYL CHLORIDE v. Chloride of

PHTHALIC ACID.

PHTHALYL-ETHANE v. Anhudride of PHENYLOETHYL KETONE O-CARBOXYLIC ACID.

Di-phthalyl-ethane C18H10O, i.e.

-С:СП.СН:С— 0.0 О.СО С.Н. C'H' < CO'O Ethine-di-

phthalyl. [above 350°].

Formation.—1. Together with other products by the condensation of phthalic anhydride with succinic acid (Gabriel, B. 10, 1559; 19, 837).-2. By the action of conc. H.SO, upon di-phenyl ethylene diketone di-o carboxylic acid C,H,(CO,H),CO,CH,CH,CO,CH,(CO,H), or its ether .-- 3. By further elimination of H.O from the (a) or (B) anhydrides $C_{18}H_{12}O_{3}$ of the latter acid (Roser, B. 17, 2770; 18, 3115).

Properties. — Yellow needles (from nitro-benzene), insol. water and alcohol. By boiling with alkalis it is converted into di-phenyl ethylene diketone di-o-carboxylic acid. Nitrous acid forms C18H10N2O8 a crystalline body decomposing

at 160°, and converted by boiling HOAc into C₁₁H₂NO₆ [c. 240°].

Isomeride C₁₈H₁₈O₄. Formed as a by-product in preparing the preceding body by heating phthalic anhydride with succinic acid and NaOAc. Red needles with green lustre, not melted at 280°. Insql. water and alcohol, v. sol, hot aniline and nitrobenzene. Weak acid, forming unstable violet salts.

PHTHALYL-ETHYL-HYDROXYLAMINE v. vol. ii. p. 740. PHT#ALYL-HYDROXYLAMINE e. vol. ii.

p. 788.

C_{1e}H_{1e}O_s i.e. Diphthalia DI-PHTHALYLIC ACID CO.H.C.H., CO.Co.C.H., CO.H. (?) Diphthalic acid. [272°]. Formed by oxidation of diphthalyl (Ador, A. 164, 236), of (β)-dinaphthyl-diquinone $C_{20}H_{10}O_4$ (Korn, B. 17, 3021), and of di-phenylethane dicarboxylic acid (Dobreff, A. 239, 68). Formed also by the action of alcoholic potash on diphthalyl dibromide (Graebe, A. 228, 132; 242, 221). Minute tables, almost insol. water, alcohol, and ether. Converted by boiling conc. KOHAq into phthalic acid. Dilute NaOHAq at 110° forms di-phenyl-carbinol tricarboxylic acid. Reduced by HI to (CO.H.C.H.), C.H. Alcoholic hydroxylamine hydrochloride forms, on heating, C₁₈H₁₈NO₅ [152°] and C₁₈H₈N₂O₄ [286°]. Salts: BaA" 2uq: plates.—Ag₂A".

Methyl ether Me, A". [192°]. Formed from Ag, A" and MeI. Lemon-yellow plates. By passing HCl into a hot solution of the acid in McOH there is formed a colourless isomeric body [278°], partially converted into the methyl ether by heating with McOII at 200°, and split up by HClAq at 150" into diphthalylic acid and MeCi.

Ethyl ether Et.A". [155°]. Got from Ag.A" and Etl. Lemon-yellow needles. The colourless is omeride [174°] is formed by ethylation with alcohol and HCl.

Anhydride C₁₆H₈O₅. [165°]. Formed by heating the acid with Ac.O at 200°. Crystals (from HOAc), v. sol, chloroform.

DIPHTHALYLIMIDE C, II, NO, i.e.

 $C_{u}H_{i} < \overline{C(NH),O,O,CO} > C_{u}H_{i}$? [above 360°].

Got by warming di-phthalyl-lactonic acid with NII,Aq and by heating phthalimidine with NaOAc and phthalic anhydride or phthalimide at 220° (Graebe, A. 228, 137; 233, 246). Needles (from HOAc) forming a yellow solution in NaOHAq.

DIPHTHALYL-LACTONIC ACID C, H12O, i.e. -- Ç:C(OII).C₄H₄.CO₂H C'H'< Diphthal-

aldehydic acid. Formed by warming diphthalyl, in an atmosphere of H, with alcoholic potash (Graebe a. Schmülzigang, A. 228, 126; cf. Ador, A. 164, 229). Crystals (from alcohol). When heated for some time at 220° it splits up into water and diphthalyl, which then melts above 300°. When quickly heated it decomposes at 235°-240° with partial fusion. Conc. H₂SO₄ converts it into diphthalyl. Its alkaline solution is yellow, but becomes colourless through absorption of atmospheric oxygen, yielding diphthalic acid.

PHTHALYL-MALONIC ETHER C, H, Ot, i.s. C₀H₄CO.0 S. (ether) 7.1 C:C(CO₂Et)₂. [75°]. S. (ether) 7.1 at 9°; 58.8 at 35°. One of the products of the action of phthalyl chloride on sodium malonic ether (Wislicenus, A. 242, 23). Triclinic prisms (from ether), v. sol. alcohol.

Reactions. -1. Decomposed by long boiling with water into phthalic acid and malonic ether. 2. Hot potasa forms malonic and phthalic acids. A solution of caustic potash at 0° forms

C.H. CO.O. C(OH).CK(CO,Et), whence acids liberate oily 'phthalyloxymalonic' ether, which

malonic ether .- 3. NaOEt forms the compound ! C(OEt).CNa(CO2Et), crystallising in prisms, v. e. sol. water, yielding the cupric salt Cu(C₁,H₁₀O₂)₂2aq and, on adding an acid, oily C₁,H₂₀O₂. The dry salt, NaC₁,H₁₀O₂ is converted by EtI at 100° into oily C₁,H₁₀EtO,, upon which alcoholic potash reacts forming the salt ---C(OK) CEt(CO2K)2 ppd. as very de-

liquescent plates on adding alcohol to its aqueous solution, yielding amorphous, Ag, C, H,O,, and splitting up on acidification into ethyl-malonic acid and phthalic acid.—4. Zinc-dust and HOAc yield o-carboxy-benzyl-malonic ether (v. vol. i. p. 705).-5. Alcoholic NH, forms the diamides of malonic and phthalic acids .- 6. Sodium-malonic ether forms yellow C22H21Na2O101 decomposed by boiling water into phthalyl-dimalonic ether, malonic ether, and phthalic acid.

 $C_{\sigma}H \swarrow^{CO.O} \ ^{\bullet}$ Seminitrile

-- C:CCy.CQ.Et [c. 175°]. Formed from phthalyl chloride and sodium cyano-acetic ether in dry Et O (Muller, C. R. 112, 1140). White substance, sol. benzene.

Phthalyl-di-malonic ether $C_{22}H_{26}O_{10}$, i.e. -C(CH(CO₂Et)₂)₂· [49°]. Formed from

sodium-malonic ether and phthalyl chloride (Wislicenus, A. 242, 23, 80). Prisms (from

containing C22H24K2O10, which separates as orange

needles (containing 2aq) when Et,O is added to

alcohol), insol. water. Reactions .- 1. Potash forms a yellow solution

a solution of the other in alcoholic potash. Boiling aqueous potash forms phthalyl-diacetic acid C12H10Oa [158°] .- 2. Alcoholic NaOH forms. in like manner, lemon-yellow C22H21Na2O10 2aq, decomposed by hot water into malonic and phthalyl-dimalonic ethers and sodium phthalate. EtI at 100° converts the Na derivative into C₂₂H₂₄Et₂O₁₀, which yields ethyl-malonic ether on boiling with water.—3. The di-sodium derivative C₂₂H₂₁Na₂O₁₀ is converted by treatment with Ac₂O, phthalic anhydride, or phthalyl chloride into 'phthaloxy-dimalonic ether' C22H24O, or C₂H₄ CO.C(CO₂Et)₂ (?), S. (alcohol) 57 at 14°, which crystallises from ether in needles melting at 117° when slowly heated and at 106° when quickly heated. 'Phthaloxy-dimalonic ether' is also one of the products of the action of phthalyl chloride on sodium malonic ether (Wislicenus, A. 242, 28, 61). It forms a yellow solution with aqueous K₂CO, and KOH. Alcoholic potash forms C22H25KO10, which is the monopotassium derivative of phthalyl-dimalonic ether. Zinc-dust and HOAc reduce 'phaloxy-dimalonic

ether' to oily C<sub>2.H₂₈O₃.

PHTHALYL-PROPIONIC ACID C₁₁H₈O₄ i.e.</sub> C.H. CO.O. [245°-248°]. Formed by boiling phthalic anhydride (5 pts.) with propionic anhydride (10 pts.) and sodium propionate (1 pt.) for 45 minutes (Gabriel a. Michael, B. 11, 1013, 1679). Slender needles. Converted by boiling KOHAq into phenyl ethyl

ketone o-carboxylic acid. Reduced by sodiumamalgam to C.H. -CH.C,H,.CO,H [140°] which yields BaA', and AgA' and is converted by boiling baryta-water into oxy-carboxy-phenylbutyric acid CO_H.C.H.CH(OH).C.H.CO.H. H,SO, at 100° forms C, H, O, [237°].

Salt .- AgA': white powder. Amide C, H,O,NH, [195°]. Leaflets.

PHYCITE v. ERYTHRITE.

PHYLLIC ACID $C_{:2}H_{6i}O_{16}$ (?). [170]. S.G. 1.014. Extracted by alcohol from the leaves of the cherry-laurel, apple, almond, and elder (Bougarel, Bl. [2] 28, 148). Crystalline granules, decomposing at 180°. The K salt crystallises in needles, sl. sol. water, sol. alcohol.

PHYLLOCYANIN v. CHLOROPHYLL.

PHYSALIN C, H, H, O, Occurs in the leaves of the winter cherry (Physalis Alkekengi), from which it may be extracted by chloroform (Desaignes a. Chautard, J. Ph. [3] 21, 24). Yellowish amorphous powder, with bitter taste, v. sl. sol. cold water and ether, v. sol. alcohol. Softens at 180°, and decomposes at a higher tempera ture. Sl. sol. acids, m. sol. NH₃Aq. Salt.—Pb₄(C₁₁H₁₅O₅)₂O₂: white pp., got by adding Pb(OAc)₂ and NH₃Aq to the alcoholic solution.

PHYSETOLEIC ACID C10 H30O2. [30°]. Occurs in sperm oil, and is perhaps identical with hypogwic a id (Hofstüdter, A. 91, 177). Stellate groups of needles. Not affected by nitrous acid.

BaA'2: crystals, sol. hot alcohol.

PHYSICAL METHODS USED IN CHE-MISTRY. The object of this article is to present a general account of the chief physical methods of inquiry which are made use of in attacking chemical questions. In each section of the article it has been sought to lay down the principles of the method discussed, and to present, in a general way, the more important results that have been obtained. No section claims to give a complete account of the subject with which it deals. The following articles, which are not specially referred to in their alphabetical positions in the present article, should be consulted: Aggregation, States of, vol. i. p. 87; ATOMIC AND MOLECULAR WEIGHTS. vol. i. p. 336; CHEMICAL AND PHYSICAL PRO-PERTIES OF BODIES, CONNECTIONS BETWEEN, vol. i. p. 730; Densities, relative, vol. ii. p. 370; Dissociation, vol. ii. p. 385; Molecular con-STITUTION OF BODIES, vol. iii. p. 410.

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271 (reference only).
I. CAPILLARITY, METHODS BASED ON. The term 'capillarity' is given to that property of bodies which is the cause of the rise of liquids in narrow tubes, the spherical shape of raindrops and soap-bubbles, the spreading of oil on the surface of water, and many other pheno-

The generally accepted theory by which these phenomena are connected and explained is due mainly to Laplace, and rests on the assumption that the parts of a body are held together by attractive forces which are insensible except at very small distances. We have evidence of the existence of these forces in the cohesion of bodies, in the latent heat of evaporation, which is merely the energy that has to be supplied to separate the parts from each other, and in the fact that at high pressures, when the parts of which a gas is composed are so near together that they never get altogether away from each other's influence, the compressibility is found to be greater than is required by Boyle's law. Though Laplace made no reference to molecules it is now usually supposed that the attractions in question are the forces acting between the molecules.

Imagine a molecule of a liquid surrounded by a sphere, whose radius is the distance at which the force ceases to be sensible. If the molecule is so far from the surface of the liquid that this sphere is entirely immersed, it will be on an average equally attracted all round, and no work will have to be expended to move it, but if it be so moved that part of the sphere is outside the surface, there will be a resultant force tending to draw it back again, so that to bring a molecule into the surface requires an expenditure of work. Now if we distort a given volume of liquid so as to increase its surface we bring i more molecules into the surface, and we increase the potential energy of the liquid by an amount proportional to the increase of surface, or the total potential energy arising from this source is proportional to the extent of surface. Hence, since in the position of equilibrium of any system the potential energy is a minimum, the liquid will of itself assume such a shape that the rurface is as small as possible consistently with other conditions, such as the action of gravity.

It is plain that what has been said is not restricted to liquids, but applies equally to solids and to the surface separating two different In the latter case a molecule at the surface of separation is acted on by both media. but unless the attractions are equal there will be a resultant force acting on it, and it will have potential energy by virtue of its position.

Capillary phenomena are often regarded as due to the external film of the substance being in a state of tension. It is not easy to imagine a tension at the surface of a solid, but the conception leads mathematically to the same results as the assumption of the existence of surface energy, and is practically only another way of stating the same thing, for we have seen that on the hypothesis of molecular attractions we arrive at the result that the surface tends to become a minimum, and this is equally well

described by saying that it behaves as though it were in a state of tension. Further, the measure of the tension - that is, the total force acting across a line of unit length-is numerically equal to the potential energy per unit area, which is easily proved as follows. Imagine a rectangular piece of the surface a cm. long and b cm. wide increase it to a rectangle a' cm. long and b cm. wide. Then we have produced (a'-a)b sq. cm. of new surface, and if E is the potential energy per sq. cm. we shall have done E(a'-a)b units of work. On the other hand, if T is the surface tension, the force acting on the side b will be Tb. and we have moved it through a'-a cm., and hence have done Tb(a'-a) units of work. These two measures of the work must be equal, and hence E = T; and since the rectangle can be taken anywhere on the surface and with its sides in any direction, it follows that the surface tension is the same at every point and in any direction.

It is to be observed that this tension differs from that of a stretched piece of indiarubber, for instance, in the fact that it does not depend on the amount of stretching. No matter how much a soap film is extended, the tension remains the same until the film becomes so thin that there are only a few molecules in the thick-

The surface tension, then, is a consequence of the molecular attractions which tend to draw the molecules as close together as possible. In order to balance this tendency and to allow the substance to be in equilibrium, Laplace imagined the existence of an internal hydrostatic pressure. which, from the value of the latent heat, is calculated by Stefan to be about 1300 atmospheres in the case of water. The potential energy due to this pressure is proportional to the volume, which is constant in most capillary phenomena, and hence has no effect on the equilibrium position.

The forms of crystals are probably conditioned to some extent by capillary forces. Most of the properties of crystals being different in different directions, the potential energy of a surface may be expected to depend on its direction, and those faces will be formed which have least energy. Further, as a large crystal has less surface in proportion to its volume than a small one, the familiar phenomenon of the large crystals absorbing the small ones is explained by the loss of potential energy resulting from the operation (v. Liveing, Camb. Phil. Trans. 14, 370).

If two immiscible fluids are in contact with a solid, the surface separating them meets that of the solid at a constant angle, called the angle of contact. The most important case is where one of the fluids is air and the solid is glass. Many experiments have been made to determine this angle, the conclusion being that in most Magie (W. 25, 429), Quincke (W. 27, 219), and Worthington (P. M. [5] 20, 65).

The constant which is most commonly used is the surface tension as defined above, but Quincke and some others use another called the specific cohesion, denoted by a2, which is twice the surface tension divided by the density of the liquid, or the height to which the liquid

would rise in a tube of unit radius.

The following are the principal methods that have been used in determining these constants: 1. By determining the rise of liquids in capillary tubes (Quincke, P. 139, 8; Frankenheim, J. pr. 23, 401).-2. By weighing or measuring the drops from a rod or pipette (Quincke, P. 135, 621; Duclaux, A. Ch. [5] 13,76; Linebarger, Am. S. 44, 83) .- 3. By measurement of large drops or bubbles (Quincke, P. M. [4] 41, 245; Eötvös, W. 27, 448; Worthington, P. M. [5] 20, 51).—4. By determining the force required to detach a disc or ring from the surface of a liquid (Weinberg, Z. P. C. 10, 34).

Mendeleeff states as one of the characteristics of a perfect liquid that its surface tension should be a linear function of its temperature, and Selby (P. M. [5] 81, 430) has given thermodynamical reasons for this relation. The subject has been investigated experimentally by Frankenheim, Weinberg, and others, and it is found that the equation $\gamma = a - bt$ holds approximately, where γ is the surface tension, t the temperature, and a and b are constants; hence by determination of y at two temperatures we can calculate roughly the

temperature $\frac{a}{b}$ at which the surface tension is

zero-that is, the critical temperature. Eötvös extends this result by showing that the rate of change with temperature of γv^{\dagger} , where v is the molecular volume of the liquid (and hence yv) is proportional to the energy of the amount of surface which contains a given number of molecules), has a constant value which is the same for all liquids.

The only measurements of the surface tensions of pure liquids which have been carried out extensively are those of Schiff (A. 223, 47; and G. 14, 368). Schiff determined the surface tensions of a large number of organic substances at their boiling-points, and divided the observed values by the molecular weights, denoting the quotient by N. This quantity was found to be in general unchanged by the substitution of one carbon atom for two hydrogen atoms, of one oxygen for three hydrogens, and similarly for other elements, so that each atom had its hydrogen equivalent, and compounds with the same total of hydrogen equivalents gave the same value for N. Taking N for ordinate, and x, the total hydrogen equivalent, for abscissa, Schiff plotted a curve from which he obtained the rela-

 $\log N = 2.8155 - .00728x - \log x.$ This equation enables us to calculate the surface tension of a liquid compound from its formula.

There are many exceptions to the law that each atom has a fixed hydrogen equivalent. For instance, C must be put equal to 3H in the free fatty acids instead of 2H as in most compounds; Ol generally has the value 7H, but when several chlorine atoms are attached to different carbons in a compound it has the value 6H; Br is usually equivalent to 13H, but sometimes to 11H, and so on.

A few preliminary measurements of the capillary constants of the surface separating water and organic liquids which do not mix with it, have been made by Linebarger (Am. S. 44, 83), by allowing the liquid to drop through the water, upwards or downwards, according to its specific

gravity, and counting the drops from a given volume. The results already published show that the introduction of two methyl groups in the meta- position into a benzene ring does not affect the surface tension, while if they are in the para-position the surface tension is greatly diminished.

· The surface tension of an aqueous solution of a salt is greater than that of water, and increases proportionately to the amount of salt present. Quincke (P. 160, 337, 560) found that for solutions of chlorides of equivalent concentrationsthat is, containing the same amount of chlorine per c.c.—the constant of proportionality is the same; but Volckmann (W. 17, 353), on repeating the work, concluded that the agreement is not within the errors of experiment. Traube (J. pr. [2] 31, 192) showed that the capillary constant of a 10 p.c. solution of water in alcohol is not raised, like that of water, but is lowered, by the presence of a dissolved salt.

Determinations of the surface tensions of solutions of organic substances in water have not hitherto led to any important general laws. Such substances lower the surface tension but not proportionally to the concentration, as appears from the work of Duclaux (A. Ch. [5] 13, 76), and of Traube (B. 17, 2294; J. pr. [2] 31, 177; 34, 292). The former gives the law that if aqueous solutions of two alcohols, or of two acids, have the same surface tension, the percentage compositions of the two solutions will have a constant ratio. Traube's work confirms this result, but leads to nothing farther of interest beyond the fact that solutions of isomerides have not generally the same surface tensions.

J. W. C. rally the same surface tensions.

II. CRYSTALLOGRAPHIC METHODS; v. CRYSTALLISATION, vol. i. p. 278; and Isomorphism,

vol. iii. p. 88.
III. DIALYSIS AND DIFFUSION, ME-THODS BASED ON. When a solid is dissolved in a solvent a movement of the particles occurs from the places where the solution is more concentrated to the places where it is less concentrated, and continues until the concentration is uniform throughout. Similarly when gases which do not react chemically are mixed, movements of the particles take place until the gases are equally distributed throughout the space. The mixing of gases or liquids, by reason of the movements of their particles, is called diffusion. When the diffusion of a liquid is accompanied by a total or partial separation into unlike bodies, the process is generally called dialysis; this process is usually effected by allowing the diffusion to take place through an animal or vegetable membrane. The chemical applications of diffusion are chiefly connected with the diffusion of substances in solution, and generally in solution in water.

Graham (T. 1850. 1, 805; 1851. 483) was the first to measure the rates of diffusion of different compounds, in aqueous solution, without a separating membrane. He nearly filled glass jars with the various solutions, carefully poured water on the top of the solutions, placed the jars 'n glass dishes, and filled these with water until the water extended in the dishes about 3 c. above the tops of the jars. The dishes were set aside for some time; when the process was to be stopped. glass plates were slid over the mouths of the jars,

which were then removed, and the quantities of substance in the liquids outside the jars, called the diffusates by Graham, were determined.

the diffusates by Graham, were determined. Graham found that the quantities which diffused varied much according to the compositions of the diffusing substances. The quantity of a specified substance which diffused in a determinate time was found to be nearly proportional to the concentration of the original solution. Graham also found that diffusion was able to effect a tolerably complete separation of two salts whose rates of diffusion differed considerably. He looked on his results as showing that nearly equal quantities of chemically similar salts diffused in equal times.

A few years after Graham's fundamental experiments, Fick, reasoning from Fourier's theory of the conduction of heat, came to the tentative conclusion that the quantity of a salt which diffuses through a stated area is proportional to the difference between the concentrations of two areas infinitely near one another. Assuming the truth of this statement, a definition was obtained for the diffusion-constant of a salt as the quantity of a salt which diffuses through unit area in unit time, when unit difference of concentration prevails throughout unit distance. A long series of researches by Belstein (A. 99, 165), Simmler a. Wild (P. 100, 217), Stefan (W. A. B. 79, 161), and especially by Weber (W. 7, 469, 536) and Graham (T. 1861, 183), has fully confirmed Fick's law, and has given measurements of the diffusion-constants of many substances. Attention should be drawn, in this connection, especially to Graham's method of allowing salts to diffuse in water gelatinised by starch, gum, &c. (T. 1861. 183; v. also Voigtländer, Z. P. C. 3, 316). In 1880, Long (W. 9, 613) made a number of determinations of rates of diffusion; he divided the numbers obtained by the molecular weights of the salts used, and thus obtained figures which represented the number of molecules of each salt which diffused under the same conditions. The results showed somewhat regular arrangements of the molecular diffusion-values. For instance, Long found that the haloid compounds of K had nearly the same value, that the sulphates of Mg, Zn, Mn, Co, Ni, and Cu had approximately equal values, and so on.

Marignac (A. Ch. [5] 2, 546 [1874]) followed up Graham's observations on the simultaneous diffusion of pairs of salts, and arrived at the important result that the order of the rates of diffusion of the salts of any acid is independent of the nature of the acid, and that the order of the rates of diffusion of the salts of a metal is independent of the nature of the metal. Marignac was thus able to construct a table showing the order of the diffusion-coefficients of acid radicles, on the one hand, and of metals, on the other hand. The table is as follows:—

CI, Br, I
NO, CIO₃, CIO₄, MnO₄
CrO₄
SO₄
CO₅
CO₆

H
K, NH₄
Ag
Na
Ca, Sr, Ba, Pb, Hg,
Mn, Mg, Zn
Cu
Al

Crystalloids and colloids. Graham observed that the rates of diffusion of different substances

differ much. He found certain substances which diffused in water with very great slowness; these substances included gums, tannin, albumen, caramel, &c. Inasmuch as the substances which diffused comparatively rapidly generally assumed crystalline forms when they solidified, while substances which diffused very slowly solidified in amorphous forms, Graham called the former crystalloids and the latter colloids. The solution in water of crystalloids is usually accompanied by thermal changes: the solution; boil and freeze at temperatures different from the boiling- and freezing-points of water, and the properties of the solutions differ considerably from those of the solvent. On the other hand, the solution in water of a colloidal substance is not attended with any marked changes.

The solution of a colloidal substance allows the diffusion through it of a crystalloid, in solution, but scarcely permits the diffusion of another colloid. If, then, a solution containing a crystalloid and a colloid is separated from water by a colloidal membrane, such as animal or vegetable parchment, the crystalloid will diffuse through this membrane into the water outside, but the colloid will be retained in the interior liquid; in this way colloids can be separated from crystalloids by diffusion; this process was called dialysis by Graham.

By means of dialysis, Graham prepared many compounds in a colloidal, or jelly-like form (T. 1861. 183). Most inorganic colloidal compounds were found to exist in two forms; one soluble in much water, and the other gelatinous and insoluble in water. For instance, an aqueous solution of silicic acid, containing 14 p.c. of this acid, was obtained by adding a solution of sodium silicate to excess of dilute HClAq, and dialysing (by pouring into a flat saucer formed of parchment paper which was floated on pure water) for some days, until the liquid inside the dialyser ceased to give a reaction with AgNO, Aq; the liquid in the dialyser was then concentrated by boiling in a flask. The solution of silicic acid gelatinises after a few days, or at once by addition of a trace of an alkaline or earthy carbonate, or by a few bubbles of CO₂, or by certain soluble colloids, such as gelatin or soluble alumina. The gelatinised colloidal silicic acid is insoluble in water.

Graham prepared soluble and gelatinised colloidal forms of Al₂O₃, Fe₂O₃, Cu₂FeCy₈, Cr₂O₃, stannic acid, &c. Other soluble inorganic colloidal compounds have been obtained in recent years.

Graham looked on colloids as very different in their constitution from crystalloids. He regarded colloids as prone to undergo changes which take place very slowly; he thought it possible that the molecule, or molecular aggregate, of a colloid is formed 'by the grouping together of a number of smaller crystalloid molecules.' Colloids, a sording to Graham, are capable of loosely combining with various proportions of water; this process of 'gelatinous hydration' was regarded by Graham as being 'as truly chemical as that of crystalline hydration.'

Graham's views on the nature of colloids have been confirmed, on the whole, by more recent work. J. M. van Bemmelen has especially studied the hydration of colloids. He gives the name hydrog. Is to those gelatinous hydrates which contain varying quantities of water not agreeing with any definite formula; he describes the reactions of hydrogels with gases and liquids to form what he calls absorption-compounds, and discusses the part played by such compounds in the soil (L. V. 35, 69; Abstract in C. J. 54, 985). For van B.'s work on various individual colloids v. R. T. C. 7, 37, 69, 75, 87, 106, 114; Abstracts in C. J. 54, 1157, 1162.

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Picton (C. J. 61, 137) and Picton a. Linder (C. J. 61, 114, 148) have recently prepared a number of soluble colloidal forms of metallic sulphides, such as CuS, HgS, As.S. colloidal solutions were obtained (1) by pouring solutions of the metallic salts into H. SAq, into which H2S was continuously passed, and dialysing, after removal of excess of II.S by a current of H; (2) by passing H2S into water with metallic hydrates in suspension; (3; by suspending freshly ppd. metallic sulphides in water and passing in H.S. · All the solutions contained combined H2S, and were therefore solutions of hydrosulphides. The solution of As, S, contained about 6 g. As, S, per litre, and that of HgS about 10 g. per litre. These colloidal solutions were shown to contain solid particles. In some cases the particles were visible through a powerful microscope; in other cases the particles were proved to be present by passing a ray of bright light through the liquids, and showing the scattering of polarised light which thus occurred. Solutions of 'colloidal molybdic acid.' and colloidal silicic acid containing free HCl. seemed to be free from solid particles. Solution of colloidal antimony sulphide showed no particles under the microscope, but the presence of particles was revealed by the passage of a beam of light; after keeping for about ten days, par-ticles had formed sufficiently large to be seen by the help of the microscope; and after some weeks the Sb was all ppd. as Sb.S₃. In this case the passage could be followed from a liquid containing very minute particles, whose presence was detected only by the fact that they scattered light, to a liquid containing particles sufficiently large to be seen under the microscope. On the other hand, a solution of CrCl, in water containing a little chromous acetate was able to scatter light, and therefore contained solid particles; but after a few days the particles were no longer present. In this case the passage could be traced from a liquid containing very minute particles to a liquid free from such particles.

The colloidal solutions did not diffuse, with one exception—namely, arsenious sulphide. The diffusible solution was obtained by running As,O,Aq into H₂SAq, into which H₂S was continuously passed, and removing excess of H₂S by a current of H. This solution showed no particles under the microscope, but as it scattered polarised light particles were present in it. The liquid was put into a small wide-mouthed bottle, which was placed in a beaker and covered with water; a distinct amount of As,S, had diffused in one day, and after eleven days about 12½ p.c. of the As,S, was found in the diffusate. This colloidal solution therefore presented the interesting phenomenon of a liquid containing solid particles capable of scattering polarised

light from a beam passed through, and yet able to diffuse in exactly the same way as true solutions undergo diffusion.

Picton a. Linder consider that their experiments establish 'a good prima facie case for the belief that there is a continuous series of grades of solution passing without break from suspension to crystallisable solution.' They look on the very small particles in some of these colloids solutions as large molecular aggregates, and they think that these aggregates become very small in the solutions which can diffuse, and that the forces by which the aggregates are held in solution 'become more definitely those of chemical attraction.' (In connection with colloidal solutions v. Paterno, Z. P. C. 4, 457; and Barus a. Schneider, Z. P. 6. 8, 278.)

Diffusion of gases. The fact was observed by Dalton (P. M. 24, 8) that if a heavier gas is placed in a bottle which is connected with another bottle containing a lighter gas, and placed beneath the first bottle, after some days the gases will be equally mixed in both bottles. The same fact was observed, and some measurements were made, by Berthollet (Mém. S. d'A. 2, 463). Graham (Q. J. S. 1829, 74; P. M. 1833. 175, 269, 351) made a great many measurements of the rates of diffusion of different gases. For most of these he employed a diffusiometer, which consisted of a glass tube about 20 cm. long and about 11 cm. diameter, having a plug of plaster of Paris in one end extending inwards about ½ cm., and graduated from this end downwards. The tube was filled with the gas under examination and placed in water; when the level of the water in the tube had become constant, the total volume of gas now in the tube was measured, and the amounts of air and original gas contained in the tube were determined. With gases lighter than air there was a decrease in the contents of the tube, as the lighter gas passed out through the porous plate more quickly than air passed in; with gases heavier than air there was an increase in the gaseous contents of the tube, as air passed in more quickly than the heavier gas passed out.

The conclusion which Graham arrived at was that 'the diffusion or spontaneous intermixture of two gases in contact is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas.'

Modifications in Graham's apparatus have been made, and many determinations of the rates of diffusion of gases have been conducted; the results have fully confirmed Graham's law, which may be stated in the form $c:c' = \sqrt{d}': \sqrt{d}$, where c and c' are the diffusion rates of two gases whose relative densities are d and d'.

It is evident that Graham's law of diffusion gives a means for finding the molecular weights of gases; inasmuch as the law enables measurements to be made of the relative densities of gases, and the density of a gas, referred to hydrogen, multiplied by 2 is (approximately) the molecular weight of that gas. For a description of an instrument for this application of the law of diffusion v. Bunsen's Gasomet. Methoden, p. 160.

3. M. P. M.

IV. DYNAMICAL METHODS. Several methods used in attacking chemical problems may be put together under this general title : v. CHEMICAL CHANGE, vol. i. p. 731; AFFINITY, vol. i. p. 67; AGGREGATION, STATES OF, vol. i. p. 87; DISSOCIATION, vol. ii. p. 385; EQUILIBRIUM, CHE-MICAL, vol. ii. p. 434; MOLECULAR CONSTITUTION or Bodies, Theories of, vol. iii. p. 410.

V. ELECTRICAL METHODS.

Historical .- The history of the science of electricity divides itself into two well-defined periods, the boundary between which lies at the close of the last century, and is marked by Volta's discoveries concerning the production of electricity when different substances are brought into contact. The investigations in the older period, when only the phenomena of frictional electricity, characterised by small quantity and high tension, were known, showed no connection with chemical problems. It is true, Deimann and Paets van Trostvijk had decomposed water by means of the electrical machine; this effect was, however, assigned as due more to the high temperature of the electric spark than to a specific property of electricity.

It is only with Galvani's discovery of the electricity which appears when different substances are brought into contact, and with the scientific investigation of this discovery by Volta, that the period of electro-chemistry begins. This branch of science is thus of nearly exactly the same age as the current century. It was by means of the pile as constructed by Volta that chemical changes were recognised to be essential phenomena concurrent with the passage of an electric current through certain substances. . Directly this apparatus became known, Nicholson and Carlisle (1800) used it for the decomposition of water, and since then the fact that there is a close connection between chemical and electrical phenomena has always been present to the mind of investigators. The mysterious and unexpected mode of action of this apparatus soon revived the hope that by means of it the problem of vital activity might be fathomed. Consequently, the electric current was made to pass through various animal fluids, such as blood, protein, &c., with the object of following the changes produced by this influence, and thus obtaining information concerning the processes taking place in the organism. It was found that, along with other effects, a basic reaction was always observed at one pole, and an acid reaction at the other. On further investigation it was found that the acid and the base still appeared. even when water was taken instead of the animal fluids, and thus the electric current seemed to be a means for producing acids and bases from pure water. This is the point at which the classical researches of Humphry Davy began. In order to decide whether acids and bases were really produced from pure water by means of electricity, he repeated the experiments. He soon recognised that the vessels in which the water was contained exerted a determinant influence on the results; he proved that very small quantities of the substance of the vessels were always dissolved by the water, and that vessels of glass, clay, basalt, &c., were subject to this influence. The electric current had the power of decomposing the very small quantities of saline matter

present into acids and bases, and of accumulating these at the poles, where they could be detected ensily. Only ressels of gold proved to possess the necessary resistance, and when these were used not the least quantity of either acid or base was obtained from pure water.

After Davy had thus become acquainted with the great power of decomposing compounds possessed by the electric current, he proceeded at once to submit the most diverse substances to its influence. By means of the large batteries of the Keyal Institution, which had been constructed according to his plans, he succeeded in obtaining great effects; he decomposed the alkalis, and isolated the metals potassium and sodium.

At the present day it is difficult to imagine the impression which this discovery made on his contemporaries. It was not scientific circles only that were full of it; the public at large and the daily press occupied themselves most diligently with this fact. Everyone who could procure some dozens of copper and zinc plates tried to repeat the experiment, and gave an account of it. Napoleon, who then had just nearly reached the zenith of his power, proceeded at once to have larger batteries constructed in order to smooth the way for similar discoveries by the French scientists. He also offered great prizes for scientitic works dealing with voltaic electricity.

Davy's discovery was of great importance for the development of the science of chemistry, because it enabled the alkalis to be classed with other basic metallic oxides. Chemical classification was thus simplified considerably. The investigations of Davy were, however, without influence on the knowledge of chemical affinity, sound as were the views held by this man of genius concerning the relation between chemical and electrical processes.

It was at this same time that the two Swedish naturalists Berzelius and Hisinger carried out work which then, it is true, did not attract anything like the same attention as had justly been aroused by Davy's investigations, but which had an even more lasting influence on the later development of scientific chemistry. Davy's experiments dealt chiefly with the fact that the electric current split compounds into their constituents, and aimed at the isolation of these constituents. Berzelius and Hisinger went a step farther; they tried to grasp the laws underlying this decomposition, and from these they developed a theory concerning chemical compounds. The generalisations under which Berzelius and Hisinger comprised their results were as follows:

(a) Chemical compounds are decomposed by the electric current, and their components collect at the poles.

(b) The combustible substances, the alkalis, and earths go to the negative pole; oxygen, the acids, and oxidised substances go to the positive

The fact that Berzelius had experimented chiefly on the salts of the alkalis determined the theoretical conception of electrolysis. Since acids and bases appeared at the poles when alkali salts were electrolysed, acids and bases were considered to be the components of salts. Berzelius assumed further that a similar binary division prevailed throughout the whole domain of chemical compounds. He conceived every atom as endowed with a definite quantity of positive or negative electricity, and this led him to distinguish between positive and negative elements, and to arrange the elements in a series, beginning with the most positive down to the most negative. It was thus that for Berzelius the combination of elements with each other was simply an act of electrical attraction; according to him the thermal and optical effects which are produced along with chemical combination are due to the same cause as the corresponding plienomena which accompany the electric spark. It is true that at this point Berzelius, with the caution peculiar to him, himself brings forward the objection that when the opposite electricities have neutralised each other a further cause of their keeping together is no longer present. It seems, however, that he did not consider this difficulty of sufficient importance to give up his theory for it.

When a positive and a negative atom interact, their electricities, according to Berzelius, are in general not completely neutralised, as the quantities of electricity present differ according to the nature of the atoms. The compound formed thus retains a surplus of positive or of negative electricity, and acts therefore similarly to an element, but less intensely. It is in this way that compounds can again combine with each other to form compounds of a higher order, and so on, and thus is brought about a binary

constitution of all compounds.

This electro-chemical theory of Berzelius, which he developed more fully at a later time, has exerted a very marked influence on the progress of chemistry, since it has impressed on this science the form which was the only one recognised from 1810 to 1840. It was characteristic of this phase that after this first investigation Berzelius did not again undertake any experimental work on the action of electricity on chemical compounds. The places wherein the Berzelian theory was weak from the physical point of view were not considered at all, as the theory was used only for the purposes of chemical classification; no attempt was made to explain by means of it the problems of chemical affinity.

After an almost uncontested reign of twenty years' duration the theory of Berzelius proved itself insufficient to follow the progress of the science. Since it was deduced from the phenomena of the decomposition of compounds by electricity, it was not surprising that it could not represent the chemical relations of organic compounds, which, as a rule, are not decomposed by electricity. Investigations on this subject proved more and more conclusively that in chemical compounds individual atoms could be substituted by other atoms or groups of atoms, quite independently of the 'electro-chemical' nature of the elements; in the most conspicuous and best-known examples it was a question of the substitution of 'positive' hydrogen by 'negative' chlorine. Such a process Berzelius considered to be quite impossible in the light of his theory.

But it was not this proposition of the electro-chemical theory alone, but the whole foundation of Berzelius's system, which was made doubtful and proved to be untenable by the newer development of organic chemistry. The

theory of the binary constitution of chemical compounds was no longer capable of being brought into accord with facts, which rather led to the unitary conception of substances. Closely connected with this development is the establishment of the conception of the chemical molecule, a conception which assigned a sharply-defined existence to the combinations of the elementary atoms, and which led to the view that these structures would split up in the most diverso ways, according to the nature of the influences to which they were subjected, although no such division appeared pre-existing in the molecule.

At the same time (after 1840) at which purely chemical facts had proved Berzelius's system insufficient for the domain of organic chemistry, the insufficiency of its physical foundations was also made apparent. This happened in consequence of Faraday's funda-

mental work.

A lively discussion concerning the cause of the production of electricity in the galvanic pile had been carried on ever since the days of Volta. While Volta and his successors sought for the cause of the electric tension at the extremities of the pile in the contact of the metals, a number of other workers held to the opinion, as first expressed by Fabbroni, that the cause of galvanic electricity was to be found in the chemical processes which take place in the pile. It is not possible to enter here into the history of the contest which has lasted up to the present day. Faraday attempted to solve the problem, and in so doing he discovered the electrolytic law (1834) which goes by his name.

This law affirms, firstly, that when electricity passes through a body which is decomposed by it—that is, through an electrolyte—the quantity of substance decomposed is proportional to the quantity of electricity that has passed through. Secondly, the law affirms that when the same quantity of electricity passes through different electrolytes, the quantities of the different substances which are thereby decomposed are to each other in the ratio of their chemical equiva-

lents.

These two generalisations primarily supported the chemical theory of galvanic electricity, as according to them a galvanic current is never possible without a corresponding chemical process. At the same time, however, they were in unresolvable contradiction to the foundations of the theory of Berzelius as conceived by him; since, if one and the same quantity of electricity is always necessary in order to decompose chemically equivalent quantities of any substances, it cannot be true that different quantities of electricity cause their combination, in which act they neutralise each other. Berzelius was keenly alive to this contradiction, but as he did not wish to doubt his own theory he preferred to doubt the laws of Faraday, and he continually argued against them.

It was through the work of Daniell (T. 1839. i. 07, and 1840. i. 209), which followed up the researches of Faraday, that the electro-chemical theory was fought on the very ground from which it had sprung. The results of the electrolysis of neutral salts, such as potassium sulphate or sodium chloride, when, the two elec-

trodes of the electrolytic cell were separated by a porous diaphragm, showed that detonating gas (or hydrogen) was formed in the same quantity as in a voltameter with dilute sulphuric acid inserted in the circuit, and besides this an equivalent quantity of the salt was decomposed into acid and base. This phenomenon cannot be brought into accordance with the law of Faraday otherwise than by assuming that electrolysis does not split up the salts into base and acid, but rather into the metals and into the elements (such as Cl) or radicles (such as SO₄) combined with these. Thus, when potassium sulphate is electrolysed, hydrogen and oxygen are only secondary products, just as the free acid and the base are only secondary products; the salt K2SO, splits up rather into free potassium K, which acts on the water, forming potash (K2+2H.O = H2 + 2KOH), and into the radicle SO4, which with water gives sulphuric acid and oxygen $(SO_4 + H_2O = H_2SO_4 + O)$. Correspondingly, when copper sulphate is electrolysed we obtain, not copper oxide and sulphuric acid, but on the one side metallic copper, and on the other side SO, which gives sulphuric acid and oxygen. Thus Daniell arrived at the conclusion that the conception of salts as consisting of base and acid would have to be given up, and that they rather consist of a metal and a simple radicle (Cl, S, &c.), or a compound radicle (SO, NO, &c.), and he further pointed out that Davy had already expressed similar ideas.

The same result to which the application of Faraday's law led in this case had meanwhile been arrived at by chemical methods. Graham (T. 1833, ii. 253) had reduced the differences exhibited by the salts of phosphoric acid to differences in the amounts of water held by the acid, and had thus founded the theory of the polybasic acids, Liebig (1838), in his celebrated paper (A. 26, 113), enunciated the theorem that all acids must be looked on as hydrogen compounds, and that the formation of salts consists in the replacement of this hydrogen by metals or metallic radicles. By means of this conception the unnatural division between the salts of oxyacids on the one hand, and the halogen compounds of metals on the other, was again put aside. The necessity for such a division had been felt by Berzelius to be a great trouble, and to do away with it he had for long clung tenaciously to the assumption that the halogens were

oxygen compounds.

The first attempt to utilise the facts of galvanism for chemistry had failed. In 1850 Berselius's electrochemical theory had but few supporters left. Still the consciousness survived that the mistake had lain in the form in which the relation between chemical and electrical properties had been represented; and it continued to be recognised that this relation actually did exist, and that it was of the greatest importance. A sign of this recognition is found in the fact that although Berzelius's theory had been rejected, the elements which form bases were still called positive and those which form acids were called negative. In fact, the electrochemical contrast of the two constituents of salts is a fact which becomes obvious with each electrolysis, and which, therefore, cannot be doubted. It was only necessary to modify the view of Berzelius YOL IV.

and to say that it is not the acids and bases for more correctly their anhydrides) which are the constituents of salts, but rather it is the metal and the acid radiole. This modification of the electrochemical theory has, however, scarcely left any traces in the development of the chemistry of that time. The reason of this is that compounds of the nature of salts receded quite out of the foreground of interest. Organic chemistry, which at that time developed brilliantly dealt with substances very few of which could be decomposed by the electric current, which were not electrolytes, and for which, therefore, the electrochemical contrast did not exist. unitary conception was consequently involuntarily extended to the salts, and the important distinction between electrolytes and non-electrolytes was not at all taken into account by chemists. It is true that Faraday attempted to account for these two classes of bodies by supposing that in the one case the number of positive and negative atoms was the same, but in the other case these numbers were different; but this rule proved to be incorrect, and for a long time these relations were neglected because they could not be grasped scientifically. After the refutation of the erroneous views of Berzelius. people thought themselves justified in altogether ignoring the electrochemical relations.

This was the condition of electrochem.stry till quite recently. The only attention it received was from the hands of some physicists, and it is only natural that purely chemical problems did not fare particularly well under these circumstances, the more so as even up to the present day it often happens that from this side the electrolysis of dilute sulphuric acid is represented as the electrolysis of water 'which has been made conductive by an addition of sulphuric acid. Although the direct furtherance thus given to chemistry was insignificant, yet the indirect effects were important. If it is possible to speak to-day of the development of a new electrochemical theory, it is almost exclusively to these physicists that we owe the means for so doing.

The first investigator to be mentioned at this point is Hittorf. He connected his work with the experiments of Daniell, and took up the consideration of a phenomenon which had remained incomprehensible to the latter. Daniell experimented with sulphuric acid in his apparatus, he found that besides the electrolysis of the acid a change in the concentration had occurred; at the negative pole the acid solution had become more dilute, at the positive pole it had become more concentrated. It occurred to Hittorf that this phenomenon must be due to the different velocities with which the two constituents or ions of sulphuric acid-that is, 2H and SO,-travel through the liquid. If, for instance, the hydrogen remained at rest and the group SO, alone moved, it would follow that after the electrolysis of one molecular weight of sulphuric acid, there must be an increase, by that amount, in the concentration at the positive pole towards which SO, had travelled. If, on the other hand, the hydrogen alone travelled, the concentration would remain unchanged. Now, it had been found by Daniell that the increase in concentration at the positive pole was equal to less than a quarter of the quantity of soid electrolysed; the necessary conclusion was, therefore, that both ions travelled, but that 80, moved much more slowly than 2H. Hittorf proved by a great number of careful experiments (P. 89, 177; 98, 1; 103, 1; 106, 337) that this conclusion always agreed with observed facts. He then used the knowledge thus gained to answer chemical questions, for the solution of which no other means existed at the time. But in spite of their great importance, Hittorf's results have been all but completely ignored by shemists.

These experiments afforded verification of the conclusion that the more immediate components of salts - or what is the same, the ions of saltsreally are the metal and the acid radicle. At the same time electrolysis furnished Hittorf with the means of solving certain old problems. Thus, for instance, opinion was divided as to whether potassium platinichloride and similar salts should be considered as double salts—for example, as 2KCl and PtCl,-or as salts of chloroplatinic acid H,PtCl. Hittorf submitted sodium platini-chloride to electrolysis. If it consisted of 2NaCl + PtCl,, it followed that sodium and platinum were the positive ions and chlorine the negative; if, on the other hand, it was Na PtCl, the ions would be 2Na and PtCl.. In the first case, therefore, the platinum must travel to the negative pole, in the other case to the positive. Experiment decided for the latter view: the platinum did not go to the negative pole, as the metals generally do, but travelled with the chlorine to the positive pole, thus proving itself to be a constituent of the acid radicle. In a like manner Hittorf decided quite a number of similar questions.

During these investigations, Hittorf drew attention to another point, which at a later time proved to be of the utmost importance. The fact that electrolysis can be started by the weakest currents is in contradiction to the usual chemical views, according to which the constituents of salts, such as KCl, Na,SO, &c., are held together by very strong affinities. At the same-time, Hittorf emphasised the fact that those substances which conduct electrolytically are the most ready to interchange their constituents. This fact also is against the assumption of a specially firm binding together of the constituents of salts. Occasion will be found later to refer to this remark.

There are other parts of the science of electricity, besides the phenomena of electrolysis, in which the chemical nature of substances has to be considered. These are the electrical conductivities of electrolytes, the electromotive force of galvanic cells, and galvanic polarisation. These fields have been cultivated till quite lately only by physicists to whom purely chemical questions were foreign.

The electrical conductivity of an electrolyte is a quantity the determination of which was formerly attended with great difficulties. These difficulties occur because the ions which separate where the electric current enters or feaves the liquid 'polarise' the electrodes, and thus produce new and unknown electromotive forces. Details of the various attempts which have been made to overcome this difficulty will be given later. It was, however, only in 1880 that, after long and varied preliminary investigations, F. Kohl-

rausch (W. 11, 658) indicated a really practical and accurate method. As soon as the values of the electrical conductivities of electrolytes could be determined easily, by Kohlrausch's method. important relations soon came to be recognised between the conductivities and the chemical properties of electrolytes. The most important of these relations, the discovery of which was made by Arrhenius (Bigh. Swensk. Ak. 8, Nos. 13 and 14, 1884), lies on the path opened up by Hittorf. The fact that substances capable of conducting the current and of being electrolysed are also specially capable of entering into chemical reactions, which was emphasised by Hittorf, can now be made definite by saying that both powers are nearly proportional for different electrolytes.

From this discovery there has grown a new electrochemical theory, which, in its entirety,

will be expounded later on.

The other problem concerning the connection between the electromotive force of galvanic cells and the chemical processes within them was solved by Helmholtz (Die Erhaltung der Was solved by Heinmonz (Lee Market, 1847), and later on also by Sir William Thomson (P. M. December, 1858), and this was done primarily on the basis of a hypothetical assumption. According to Faraday's law, when equivalent quantities of different substances are used in the galvanic cell, equal quantities of electricity are always put into motion. being so, the intensity of the motion, or the electromotive force of the galvanic cells, must be proportional to the quantity of heat produced by the chemical processes within the cell. The supposition is made here that all heat is used for electrical work-a supposition which Thomson found verified by an experiment of Joule. Meanwhile it has been proved, however, that the heat produced in chemical changes is not generally completely transformed into electrical work, and Helmholtz (B. B. 1882) himself has worked out the formula representing the general relation between these two quantities.

To these problems are joined those concerning the nature and the value of galvanic polarisation. In this province investigation has, however, made so little way as yet that it suffices to point out that most important problems here await their solution.

The foundations of the science of electricity. General considerations.—If a bar of perfectly pure or amalgamated zinc is placed in dilute sulphuric acid, no chemical action takes place, nor is there any such action if a bar of platinum be introduced into the acid. But as soon as the two metals are made to touch each other an action occurs; the zinc is transformed into zinc sulphate by expelling the hydrogen from the sulphuric acid, which hydrogen, however, is evolved at the surface of the platinum bar.

Direct contact of the two metals is not necessary. If, for instance, the zinc is touched with the end of a copper wire and the platinum is souched with the other end, the same effect is produced. On the other hand, there is no effect if the connection is made through glass, wood, or sight like substances.

The copper wire which connects the two metals has acquired special properties which remain as long as the chemical action of the tulphuric soid on the sine lasts. If the wire is held parallel to a movable magnetic needle at a short distance above it, the needle will be deflected; further, the wire becomes heated; and finally, if the wire is cut in one place, and the two ends are placed close to each other on a paper moistened with solution of potassium iodide and starch, it can be perceived that a chemical decomposition of the potassium iodide has occurred, since a blue spot of iodide of starch appears under one end of the wire.

Work, or speaking generally, energy, is gained by the chemical action between the zinc and the sulphuric soid; the energy usually appears in the form of heat. The arrangement described shows that it is possible to conduct this energy away from the place where it is set free—that is, from the point of contact between zinc and sulphuric acid—and to make it effective at any point of the connecting wire we please. And further, we can obtain this energy at will in the form of thermal energy, chemical energy, or mechanical energy.

The sole difference that can be perceived between the metals in their usual state and when dipped into the acid is that they have become electric; the platinum shows itself charged with positive, and the zinc with negative, electricity. By means of a suitable electrometer this electric charge can be measured. It appears to be dependent on the nature of the metals, as well as on that of the acid.

Hence we conclude that the chemical action between the zinc and the acid does not, as usual, give out its energy in the form of heat, but in that of electrical energy. As to whether the transformation from chemical to electrical energy is complete or partial, and, if the latter, by what this partial amount is determined, these are questions with which we can occupy ourselves only at # later stage.

As is generally the case with all forms of energy, electrical energy allows itself to be resolved into two factors, one of which is a capacity, and the other is an intensity. For these factors the general law holds, that a system can be in a state of rest only if the intensity of the energy is the same throughout the whole. An exception to this occurs only if different kinds of energy are present simultaneously in one system; then there can exist a difference of one intensity, if a compensation is produced by a corresponding difference of the after intensity.

The two factors of electrical energy are called quantity of electricity and electromotive force or potential; the first is the capacity, the second the intensity. In accordance with the above-mentioned law, we shall therefore say that in a system in which electrical forces alone act there is equilibrium if the electromotive force or the potential is the same throughout. This is the well-known law for conductors of electricity.

With substances which do not allow of any motion of the electricity—that is, with nonconductors—the potential can, it is true, be different in different places. But then, owing to the striving for equalisation on the part of the presential, small displacements are produced in the body, and the reacting forces of elasticity which accumpany these form the compensation

for the inequality of the electric intensity or potential.

When contact between two different substances occurs, a mutual action at the surface of contact is generally set up, and a displacement of energy is thus brought about. The changes in the surface-energy which thus occur seem to be generally compensated by corresponding differences in the electric intensity, i.e. the surfaces of different substances in contact attain different potentials. If the substances are conductors of electricity, each of them must be at a uniform potential at every point within it; hence a difference of potential exists at the surfaces of contact only.

Electrical measurements. In order to examine systematically the nature of electrical phenomena we are at the very beginning obliged to find a measure for them. We generally start from a definition of quantity of electricity, since the historical development of the science has led to the notion that this is one of the most important factors in the phenomena. And yet we have no proof that such things as the hypothetical electric fluids actually exist. What we do know of electrical phenomena are the mechanical, thermal, and chemical effects, i.e. the manifestations of the electrical energy, and it is this which is the real thing underlying the electrical phenomena. Quantity of electricity is a magnitude of the same order as perhaps a volume, and one which can be increased or decreased at will. But electrical energy cannot be destroyed, nor can it be produced; it can only be changed into, or obtained from, other forms of energy.

Electrical energy is then to be measured by the same units as other forms of energy, mechanical energy especially. The unit used for kinetic energy, which is represented by the for-

mula $\frac{m}{2}v^2$ (where m stands for the mass, v for

the velocity), is double that energy which the mass of one gram possesses when moving with the velocity of one centimetre in one second. This being so, the unit accepted for electrical energy is that quantity of energy which is obtained by the transformation of the above-defined quantity of kinetic energy into electrical energy. And further, since, as has been already mentioned, electrical energy has to be looked upon as the product of two factors, the quantity of electricity Q and the potential E, the unit by which the product QE must be measured is thus also fixed.

The units of the two factors Q and E are still arbitrary, in so far as we can choose one of them at will, that for the other being then fixed. In fact, different units have been chosen for different purposes, and accordingly different systems of electrical magnitudes have been obtained. Faraday's law, that equal quantities of electricity travel with equivalent quantities of separate igns, supplies the chemist with a natural unit for quantity of electricity. Hence that quantity of electricity which is combined with one gram of hydrogen as ion will serve as unit of quantity of electricity. Then the unit of potential would have to be the potential at which the above-defined quantity of electricity must be in order to produce unit of work.

This system of units has not become general;

it has been displaced by a system which is derived in a somewhat complicated manner from the action of current electricity on magnets. This system also has not been retained unchanged, but another one has been deduced from it, in which instead of the unit of length of 1 cm. a 10°-fold value has been introduced, while instead of the unit of mass of 1 g. a value 10°-11 times as small is accepted; the second has been retained as the unit of time. Hereby the unit of electrical energy has been changed also; it no longer coincides with the mechanical unit, but is 10° times greater.

In this system the unit of potential is called a volt; in order to get a conception of its magnitude it is to be remembered that the difference of potential at the ends of a Daniell cell is about 1-1 volt.

The unit of quantity of electricity has been called a coulomb. When a coulomb is forced through a volt a quantity of work equal to 10° mechanical units is done.

In order to fix the relations of these units to other units of energy, we must first remember that the work necessary to move 1 g. through 1 cm. against gravity is equal to 980 mechanical units, approximately. The above-defined unit of electrical energy would therefore be equal to 107

 $\frac{10^{\circ}}{980}$, or approximately to 10200 gravitation-units.

Further, the unit of thermal energy is the quantity of heat which raises the temperature of 1 g. of water by 1°C., and which, according to the measurements of Joule, is equal to 42350 gravitation-units, i.e. 42350 g. would on falling through 1 cm. give up 1 calorie of heat, or would heat 1 g. of water by 1° C. Hence this magnitude is equal to 4.15×10^{7} mechanical units. Since the unit of electrical energy amounts to 107 mechanical units, it follows that I calorie is equal to 4.15 electric energy units, or 1 volt × coulomb is equal to 0.241 calories. A number obtained more recently by Dieterici by direct measurements is probably more accurate. According to him, the energy of 1 volt × coulomb is equal to 0.2356 cal.; the unit of quantity of heat here used is 100 of the quantity of heat given out by 1 g. of water in cooling from 100° to 0°. This factor is important for the relations between the heat produced in chemical changes and the corresponding electrical phenomena. Finally, we know from measurements by F. Kohlrausch and Lord Rayleigh that 1 g. of hydrogen as ion carries with it 96540 coulombs. The same quantity of electricity is carried by each equivalent of any other ion, for instance, by 107 g. of silver, $\frac{1}{3} \times 63.4$ g. of copper, $\frac{1}{8} \times 27$ g. of aluminium, &c.

Electric currents. If the potential of electricity is different at different places of a conductor, a movement of the electricity is produced in the same way as motion is produced in a mass capable of moving freely when it is at a higher level than its surroundings. If the difference of potential is maintained, the movement is maintained also.

The compensation of a difference in electric potential necessitates a decrease in the electric energy, which in this process changes into another form. The form most easily produced is thormal energy, but, as has been mentioned

above, it is possible also to obtain mechanical or chemical work.

The measure of the quantity of energy changed into another form is given by the product of the quantity of electricity moved into the decrease of the potential. If the differences of potential are distributed over measurable distances the process is called an electric current The term has been taken from the analogy which in fact does exist between currents of water and currents of electricity. The level of the water corresponds to the potential of the electricity, and the quantity of water corresponds to the quantity of electricity. In both cases the transformable energy, or the available work, is equal to the product of the quantity (of electricity or of water) into the difference of level or of potential, and a current sets in when a difference of level exists. It must only be borne in mind that the phenomena which are brought about by the kinetic energy of the moving masses in water currents have no analogy in the domain of electricity. The electricity behaves as if it possessed only an inappreciably small velocity or mass. Therefore, when the electricity has sustained a definite decrease in potential, it has lost the whole corresponding quantity of energy, while the water can retain a part of it in the form of velocityenergy.

Electric currents are measured by their intensity. By this is understood the quantity of electricity which flows in the unit of time through a cross-section of the current-path; hence the intensity I has to be put as $\frac{Q}{t}$, where t stands for the time. Since electricity moves only when using energy, a loss of electrical energy corresponds to every current, the lost energy generally reappearing as heat. When heat is the only form into which electric energy is transformed, the following equation must hold; W = EQ, and $\frac{W}{t} = EI$, where E stands for the loss of potential between the two ends of the path of the current considered.

Experience has further shown that different conductors when introduced into a circuit cause different losses of potential along their lengths. This property has been ascribed to a resistance of the conductor to the motion of the electricity, in a way similar to that wherein tubes of different bore offer different resistances to the motion of water within them. In accordance with this, the resistance R is defined as the ratio between the difference of potential E and the quantity of electricity forced by means of it, in unit time, through the conductor, or, what is the same, the intensity I. Here we have $R = \frac{E}{I}$ or $I = \frac{E}{R}$. This is the

celebrated law of Ohm, that the intensity or the strength of the current is equal to the ratio between electromotive force and resistance.

Combining this law with the preceding one, it follows that $\frac{W}{t} = 1^{\circ}R$. This expression is the law arrived at experimentally by Joule, according to which, for currents of equal strength, the heat evolved in unit of time is proportional to the resistance, and for equal resistances it is proportional to the square of the current strength.

It is easy to deduce from the units already given the values for the units of the two new terms introduced when defining electric currents. namely, the strength of the current S and the resistance R. The unit of intensity I is that strength of current at which, in every second, one coulomb flows through the cross-section of the conductor; the unit of intensity is called an ampere. The unit of resistance is that resistance by means of which a current of unit intensity (1 ampère) produces in unit of time the unit of heat. As we have seen above, this last is equal to 10' mechanical units, or to 0.2356 calories. An attempt has been made to represent this resistance with the utmost possible accuracy, and it has been found that it equals the resistance of a column of mercury of 1 sq. mm. section and 106.3 cm. in length, at the temperature of melting ice. This unit of resistance has the name ohm. Slightly different to this is the legal ohm, which has been lixed arbitrarily as equal to the resistance of a column of mercury 106 cm. long and 1 sq. mm. section, the exact determination of the true ohm being a very difficult operation. The commercial resistances are graduated according to the legal ohm, and in scientific works in which the absolute value of the ohm comes into consideration, this difference of 3 per thousand must be taken into account. In most cases this is not necessary, just as in most cases it is immaterial whether or not a set of weights is made according to exact grams, as long as it is only made exact in its proportions.

The Law of Faraday. Those substances which allow a movement of electricity through them, i.e. conductors of electricity, are divided into two classes. In the cases considered so far, the assumption has been made that the only form of energy into which the electric energy of the current is transformed is heat. Conductors which undergo no change other than that they get heated when the current passes through them are called conductors of the first class or metallic conductors. To this class belong the metals, their alloys, carbon, and certain compounds.

Now, there are many substances which permit a movement of electricity through them, but in so doing themselves suffer chemical change. To these belong aqueous solutions of acids, bases and salts, as also salts in the molten state, and a few other compounds. Such substances are called conductors of the second class or electrolytes.

The movement of electricity in electrolytes takes place in such a manner that the components of the electrolyte move independently of each other. Hydrogen, the metals, and the metallic radicles move with the positive electricity, or, according to the usual designation, from places of higher to places of lower potential. The halogens, the acid radicles, and hydroxyl, on the other hand, travel with the negative electricity, or from places of lower to places of higher potential.

According to Faraday's nomenclature the components of electrolytes—that is, on the one hand the metals, hydrogen, &c., on the other hand she halogens, the acid radicles, &c.—are called ions. The first named, which travel down with the current are called cations, those which travel up anions.

In a circuit consisting exclusively of an electricity, a motion of electricity can take place without the corresponding chemical action being apparent. But if a conductor of the first class directly touches an electrolyte, whenever there is a movement of electricity there is also a production of the ions at the surface of contact, and the chemical effects become apparent. As proposed by Faraday, the surfaces of metallic conductors, where they touch the electrolytes, are called electrodes. The surface at which the anions appear is called the anode, and that whereat the cations appear is called the cathode.

Faraday also formulated the general law to which all movement of electricity in electrolytes is subject. In every electrolyte the quantity of ion separated out is proportunal to the quantity of electricity which has passed through, and the same quantity of electricity passing through different electrolytes separates quantities of the different ions that are in the ratio of the chemical equivalents of those ions. In these propositions it has been assumed for simplicity's sake that the ions are actually separated out at the electrodes. but this is not essential for the truth of Faraday's law. The following wording completely expresses the actual meaning of Faraday's law: Electricity can move in electrolytes only simultaneously with the ions, and so that chemically equivalent quantities of the different ions carry with them equal quantities of positive or of negative electricity.

We arrive at a perfectly appropriate conception of the nature of electrolytic conduction if we assume that each equivalent of the different ions possesses an equally large capacity for electricity, or, to use the words of Helmholtz, 'the electricity in electrolytes behaves as if it

were divided into equal atoms.'

In applying Faraday's law, it is important that we should keep in mind the difference between the equivalent and the atom; the equivalent weight is equal to the atomic weight divided by the valency. Thus the same quantity of electricity travels with 107 g. of silver, \(\frac{1}{2} \times 0.65 \) G. of zinc, and \(\frac{1}{2} \times 27 \) g. of aluminium; also with 355 g. of chlorine there travels only half as much electricity as with 96 g. of SO. As an amplification of the illustration used above, we must assign to each atom as many equal capacities for electricity as the number of valencies it possesses. Perhaps this is the path by which in the future we may arrive at a elucidation of the nature of chemical valency.

The truth of Faraday's law was tested by its discoverer himself in many ways (Exp. Res. vii. ser.). He convinced himself that the same quantity of dilute sulphuric acid was always decomposed by the same current, whether the electrodes, or the E.M.F., were large or small. Nor did the strength of the acid exert any influence. Finally, he introduced into the same circuit dilute sulphuric acid and tin chloride, lead chloride, or lead borste, or he led the same current through different beakers with dilute sulphuric acid, using electrodes of different metals; in all cases he found his law verified. Later on, other investigators have tested whether part of the electricity is not perhaps conducted through electrolytes in the same way as through metals, but no trace of this has been discovered: in

every case the electricity passed through has compound substance, since otherwise its parts been strictly proportional to the quantity of ion or ions could not transport the electricity in both separated out. And the law of equivalency has also proved itself so correct that it has been used lately as a means for determining equivalent

weights, and hence atomic weights.

The cases in which the same element exhibits different valencies according to circumstances are of special interest. Many such cases have been examined by Regnauld (A. Ch. [4] 11), who formed cells by taking platinum and different metals, along with the corresponding electrolytes. and then determined the quantities of metal dissolved when equal quantities of electricity had been allowed to pass. Thus it was found that mercury in dilute nitric acid has the equivalent 200, since it is changed into HgNO3, a compound of mono-valent mercury; in a solution of potassium cyanide it has the equivalent 100, because it becomes Hg(CN)2, in which the mercury is divalent. Similarly, copper in hydrochloric acid forms CuCl and has the equivalent 63.4; in nitric acid it forms Cu(NO_s)₂, and has the equivalent 31.7. Tin scarcely ever passes into solution except as a di-valent element; it is only in alkaline polysulphides and in a solution of caustic potash containing nitre that it acts as a tetra-valent element. Tellurium also can be made to act as a di-valent and a tetra-valent element. It is known that the elements mentioned show quite different reactions in their solutions, according as they are present as mercurous or mercuric, as stannous or stannic compounds, &c. Hence in these cases the nature of the chemical reactions depends on the quantity of electricity with which the ions are combined.

This is the place to refer back to a misunderstanding concerning the law of Faraday into which Berzelius first fell, and which has recurred many times since. As has been mentioned, Berzelius saw in this law a contradiction to his theory, and tried to refute it by the following argument: if equal quantities of electricity were required for the decomposition of equivalent quantities of the most diverse compounds, it would follow that these could be decomposed by equal forces; this, however, is not possible, since the different substances are evidently held together by quite different forces of affinity. From the illustration given above it can be seen that, contrary to the assumption of Berzelius (which, however, was very excusable, considering the state of electrical science at that time), Faraday's law does not in any way deal with forces, but rather with quantities of electricity. Comparing electrical decomposition to the raising of water out of wells by means of buckets, Faraday's law asserts that in spite of the differences in the depths of the wells, the size of the buckets is always the same. We would fall into an error similar to that of Berzelius if we concluded from the equal size of the buckets that the work necessary for raising the water out of all the wells of different depths was the same. The illustration also shows directly wherein the differences in chemical work, corresponding to the different depths of the wells, assert themselves, namely not in the quantities of electricity required, but in the differences of potential

Electrolytes and ions. It follows from the nature of an electrolyte that it must be a

or ions could not transport the electricity in both directions. Yet all compounds do not possess the power of conducting electricity. In particular, we do not know of any substance liquid at the ordinary temperature which is an electrolyte; amongst pure substances it is only the salts melted at a higher temperature which conduct at all appreciably.

On the other hand, all substances having the character of salts, acids, and bases possess electric conductivity when in aqueous solution. In these cases the water exerts a specific influence, since solutions of the same substances in alcohol conduct much less if at all; and solutions in ether, carbon disulphide, and similar solvents are scarcely conductive.

There are two factors, therefore, which are necessary for the production of electric conductivity, i.e. the nature of the substance and the condition in which it is.

In electrolysis the molecule of the conducting compound appears to be split into two parts. There can be no doubt as to what these parts are with substances such as chloride of silver or potassium iodide: since they consist of two elements only, the metal must be one ion and the halogen the other. The question gets more doubtful with ternary compounds, such as nitrie acid, sodium acetate NaCO₂CH₃, or ammonium chloride NH,Cl. Since, however, no important distinction manifests itself in the behaviour of these substances and those mentioned above, it is simplest and most obvious to assume that their ions correspond to those of the substances first named. Hence the ions of nitric acid are H and NO₃, those of sodium acetate Na and CO₂CH₃, and those of ammonium chloride NH, and Cl.

It is possible to examine this assumption on the basis of Faraday's law. In the electrolysis of potassium sulphate as much oxygen and hydrogen are obtained as from the electrolysis of dilute sulphuric acid by means of the same current, but in addition to this there is found at the anode an equivalent quantity of free sulphuric acid, at the cathode a corresponding quantity of free caustic potash. If we assume with Berzelius that the current has decomposed the potassium sulphate into potassium oxide and sulphur trioxide, K₂O and SO₃, which combine with the water to form 2KOH and H₂SO₄, we should have to assume further that the same current had in the same electrolyte simultaneously decomposed an equivalent quantity of water. But this is in contradiction to the law of Faraday. If we assume, however, that the ions are K2 and SO4, it is comprehensible that the potassium separated out should act on the water of solution, evolving hydrogen, according to the equation $2K + 2H_2O$ = 2KOH + H.; in like manner the ion SO, acts on the water and forms sulphuric acid and free oxygen, according to the equation H2O + SO4 = H.SO. + O. With those metals which do not decompose water, such as zinc, copper, and silver, we actually obtain the metal only at the cathode; and similarly, solutions of chlorides, bromides, and iodides do not generally give free oxygen, but free halogen.

It is necessary, therefore, to distinguish carefully between the primary and the recondary effects of electrolysis. The primary effects consist In the separation of the ions at the electrodes. But since the ions do not continue to exist as such after having given up their electricity, they undergo further changes according to circumstances. The simplest case is that of the metallicions, when these cannot act on the water; they simply become solid or liquid metals. So also the separated atoms of the halogens pass on, combining into gaseous chlorine, Cl., or into the molecules of the dissolved bromine or iodine.

The metals which decompose water can still be obtained in the metallic state when water is excluded or reduced to as small a quantity as is possible. A classical example of this is furnished by the electrolysis of slightly moistened potash, by means of which H. Davy discovered potassium. The electrolysis of molten salts, that of the chlorides especially, furnishes a means for preventing the secondary reaction of the metals; such electrolyses, which had first been used by Bunsen for scientific investigations, have obtained at the present time great technical importance in the production of magnesium and aluminium.

Complex cations of the type of ammonium, NH_a are very unstable, and until recently it was doubfful whether the so-called ammonium amalgam, which is obtained on using a mercury cathode in the electrolysis of ammonium chloride, really contained the compound radicle NH_a. By measurements of another kind (viz. of the electromotive force) the existence of ammonium in the amalgam has now been placed beyond a doubt.

The compound anions as such are all of them very unstable. Many of them, such as the anions . of the nitrates, phosphates, sulphates, &c., simply act on the water by taking up from it the hydrogen required to produce acids, and liberate the oxygen. The latter, which appears in the nascent state, is capable of bringing about powerful oxidising effects. If, for instance, lead or manganeso salts are electrolysed, the oxygen acts on the dissolved metal and separates it at the anode as peroxide. In other cases the anion splits up into more stable compounds. Thus in the electroly is of formates we obtain carbon dioxide and hydrogen from the ion HCOO, according to the equation $2H600 = H_y + 2CO_{\infty}$ The acctates give carbon dioxide and ethane $2CH_1CO_2 = C_2H_0 + 2CO_2$, and similarly the salts of the higher fatty acids give the corresponding paraffins.

In some cases the secondary action can take place in another direction; in this manner the formates can produce—instead of hydrogen and carbonic acid—water, carbon dioxide, and carbon monoxide, as is shown in the following equation, $2H \cap O_1 = H_1O + CO + CO_2$. In most cases such secondary processes take place along with the primary actions, and the proportion between the two depends on external circumstances, temperature, concentration, current-density, &c.

In a few cases it is somewhat difficult to recognise the primary or secondary character of a product of electrolysis. On electrolysing potassium silver cyanide or sodium platinichloride, silver or platinum separates at the cathode, so that it seems as if the silver oyanide or the platinichloride were decomposed primarily. This, however, would be an erroneous view, since the

ions of the salts are K and Ag(CN),, and Ma, and PtCl, respectively, and the heavy metals are only scondarily reduced from the sclutions by the alkali metals. We can convince ourselves of this by using small electrodes and strong ourrents, when the salt near the cathode is soon used up, and potassium (or sodium), or, more correctly, hydrogen which has been formed secondarily, separates. More distinct proof of the nature of the ions is, however, obtained by studying the migration of the ions, to be discussed later.

So far the assumption has been made that the ions exert no action on the metal of the electrode; this, however, is not always correct. Only a few metals when used as anodes offer resistance to the chemical attack of the anions. If the metal can combine with the anion it forms the corresponding sait, which either dissolves in the water of solution, or, if insoluble, remains attached to the electrode and often interrupts the current. But also when used as cathoden the metals often combine with the cation; thus mercury forms amalgams, and the hydrogen separated at the cathode is occluded in greater or smaller quantities, especially by palladium and platinum, and also by iron. In other cases the cathode simply becomes coated with a layer of the corresponding metal, which separates more or less uniformly according to its nature and that of the electrolyte. These processes are used for coating substances which are conductors, or if non-conductors, whose surfaces at least have been made conductive; such processes have also been employed for galvanoplastic coating with gold, silver, copper, &c.

The constitution of electrolytes. It has already been remarked that all compounds are not electrolytes, and that some substances which do not conduct electrolytically by themselves obtain this power when dissolved in certain solventa, especially in water. From this it follows that electrolytes have a special constitution with which their special property is connected. question as to what this constitution is has scarcely been raised yet, much less has it been answered. This is because most of the com pounds known in the days of the electrochemics system of Berzelius were electrolytes, and late on, when many organic compounds, which ar mostly non-electrolytes, were discovered, th electrochemical theory had been given up, an the interest in it had disappeared. The fire investigator who proposed the question clearly and who, as far as he could, answered it-wa Hittorf. He it was who established the proposi tion 'electrolytes are salts.' Under the nam of 'salt' Hittorf comprised all those compound which are capable of exchanging their consti tuents within the shortest time. Hence alon with the salts proper must be classed acids an bases.

By enunciating this law, Hittorf was the first to draw attention to a most important relation which has become the starting-point for the due-comprehension of the constitution of electrolytes. The power to conduct electricity and the power to exert chemical reactions are so closely parallel that both must be considered as the outcome of the same cause. This cause, however, has to be looked for in the constitution of the electrolytes themselves.

Electrolytic conduction is brought about by the positive and negative electricities moving through the conductor bound to their ponderable carriers, the ions; it is necessary, therefore, to assume a considerable mobility of the ions.

And, further, electrolytic conduction occurs in consequence of any difference in potential, however small. It is necessary, therefore, as was already pointed out by Clausius (P. 101, 338), that in every electrolyte there should be present a certain number of ions capable of moving freely, i.e. in every electrolyte a portion of the salt-like compound which produces the conduction must be partly split up into ions. Clausius left undecided how great this portion is, as he possessed no means to determine it. To the chemists who, in consequence of a peculiar shifting of judgment, considered electrolytes generally as specially stable compounds, he made the concession that this portion might be very small. In the imagery of the kinetic hypothesis he conceived that, owing to the collision of the molecules of the electrolyte with each other and with those of the solvent, one or other occasionally splits into its constituents, and so gives the necessary free ions.

It is now possible to urge similar considerations from the chemical side. While gaseous substances at the ordinary temperature react but seldom, acids, bases, and salts dissolved in water do so instantaneously. A mixture of oxygen and hydrogen does not form water until it has been heated to between 400° and 500°; a mixture of hydrochloric acid and potash, however, when in aqueous solution, passes so quickly into potassium chloride that it has been found impossible as yet to determine the time required for the change, and yet in the first case 68,000 cal. of heat are produced, while in the second the heat produced, or the energy liberated, is only 13.700 cal.—that is, five times less. In general, non-electrolytic solutions also react with each other extremely slowly. An example of this is afforded by the means which must be taken to hasten the reactions of non-electrolytes, and especially of organic compounds; this has to be done by heating the reacting mixtures, often under increased pressure. For the formation of scetic ether from a mixture of alcohol and acetic acid-that is, for a process intimately connected with that of the formation of salts-at least ten years are needed, at the temperature of the room, before it has approximately attained the end which under these conditions it can reach. From the chemical point of view, therefore, it is necessary to suppose that compounds which react instantaneously—that is, electrolytes—possess a special mobility of their parts or ions; and that it is the constituents of 'salts'-the term being used in the widest sense -which are the ultimate causes of electrolyses as well as of chemical reactions. These constituents of salts are, on the one hand, the metals, the metallic radicles, and hydrogen; on the other hand, the halogens, the acid radicles, and hydroxyl. It is possible, therefore, to apply to substances which react rapidly -that is, to salts, as this term was used by Hittorf- the same kinetic considerations as were made use of by Clausius to show the presence of ions in electrolytes.

We are now confronted on both sides by the

question of how great is the proportion of free ions, or of decomposed molecules, in solution of electrolytes. The fact that a maximum reacting power exists for a given class of substances is in contradiction to the assumption that this proportion is inappreciably small. It has already been explained (compare the article Appinity) how the substances which have been most carefully examined from this point of view—the acids—exert their chemical reactions according to a definite co-efficient which is characteristic of each acid. This co-efficient-which can be determined, for instance, by merns of the velocity of inversion of cane sugar-cannot be increased at will. and does not exceed a definite maximum value, which maximum is possessed by hydrochloric acid, nitrie acid, benzenesulphonic acid, &c. All the conditions-such, for instance, as the introduction of oxygen, sulphur, or halogen into the molecule --which increase the velocity of reaction of weak acids are without any measurable effect on the strongest acids. From this it follows that the circumstance which is the cause of the velocity of reaction - that is, the unimpeded mobility of the ions—has in these substances alrealy reached its highest degree, or is at least very near to it, since, in opposition to Clausius and to the views current till now, we must assume that in aqueous solutions of these strong acids it is not, perhaps, a few hundredths or thousandths of the molecules present which are split into their ions, but rather that by far the greater part of the electrolyte is split into ions.

A similar conclusion can be drawn from the degree in which electrolytes conduct the current. The more detailed consideration of this subject will be taken up presently. Here it will only be mentioned that the results of these investigations agree completely with those on the velocities of reactions.

A third entirely independent verification of the unexpected conclusion that aqueous solutions of the strong acids are nearly completely dissociated can be gained from a study of the properties of these solutions.

Only so much of van't Hoff's theory of solutions (Z. P. C. 1, 481) as is necessary for understanding the constitution of electrolytes will be explained here,

The fundamental idea of van't Hoff's theory is as follows. The physical properties of gases, and especially the relations between pressure, volume, and temperature, are practically independent of the special nature of the substance, while such an independence does not exist with liquid and solid substances. The cause of this phenomenon may be sought in the fact that the smallest parts or molecules of gases are always at such a distance apart that they are not capable of exerting an action on each other. In liquid and solid substances, however, the molecules are in close proximity, and exert, therefore, their specific reciprocal actions. But there is another condition in which the molecules of a substance are relatively distant from each other, namely, when the substance is present in a solvent in the state of a dilute solution.

We should expect, therefore, that in this state matter would be subject to laws analogous to those which hold for gases.

The first property characteristic of gases is

their power of extending uniformly through any given space. Solutions exhibit the same pecu-When the pure solvent is placed over the solution of any substance, the substance begins directly to enter into the solvent (the pure solvent playing the part of a vacuum), and the movement does not cease until, as with gases, the substance is uniformly distributed through the whole space. The only apparent difference is that in the case of gases this process is completed in a very short time, while with solutions months, and even years, are needed in order to bring it, practically speaking, to an end. This movement can be impeded by introducing between the solution and the pure solvent a partition which allows the passage of the latter but not of the former. Such a 'semi-permeable' partition can be produced by saturating a porous clay cell, for instance, with a solution of copper sulphate. washing the cell, and filling it with a solution of potassium ferrocyanide. A pp. of amorphous copper ferrocyanide is thus formed in the pores of the clay, and this pp. allows the passage of water through it, but does not allow various other substances to pass. In order to arrive at a conception of the cause of such a property we can imagine that the pp. of copper ferrocyanide acts as a filter which allows the passage of the smaller water molecules, while it retains the larger molecules of the dissolved substance.

W. Pfeffer, who has studied such cells very thoroughly, found that if the cells are closed a very considerable amount of pressure is produced in their interior. A 1 p.c. solution of sugar produces a pressure of more than 50 cm. of mercury; a solution of nitre of equal strength gives pressures of between three and four atmospheres. Pleffer also found that the pressures increased, at constant temperature, to maximum values, which remained constant as long as the partition remained intact. These pressures proved to be proportional to the concentrations, and further, they increased with a rise of temperature.

According to van't Hoff, this pressure, the 'osmotic pressure,' is to be looked on as analogous to the gaseous pressure. It is possible to form a similar conception of its cause as is formed of the cause of gaseous pressure; the molecules of liquids, like the molecules of gases, possess a quantity of kinetic energy which is proportional to the temperature. The solvent—for instance, the water—can pass through the semipermeable wall, and since it is present on both sides its pressure is the same on both. The substance dissolved, however, bombards the wall from one side only, and thus a pressure is set up. This view-which, however, is only hypothetical, and which can be accepted or rejected without the 'heory itself being called in question -has been objected to on the ground that if it were true a weak-walled vessel must needs be broken by a solution placed in it. But this assertion overlooks the important point that the osmotic pressure can exert itself only within the solution. If we imagine for simplicity's sake a drop of a solution floating in space, it is true that a pressure due to the substance dissolved will be exerted on the internal surface of the drop, which pressure may easily amount to 100 atmospheres. But to this pressure there is opposed the normal capillary pressure of the liquid, the magnitude of

which we do not yet know very exactly, but of which we can assert that it has to be measured by thousands of atmospheres (in the case of water it is approximately 20,000 atmospheres). Hence this pressure is under all circumstances quite sufficient to maintain equilibrium with the osmotic pressure, and the only effect of the latter is to slightly increase the volume of the solution.

It has been shown by van't Hoff that the laws of osmotic prossure exactly coincide with those of gases. Boyle's law enunciates that pressure and volume are inversely proportional. Pfeffer's law says that pressure and concentration (or density) are proportional; this agrees with Boyle's law. Further, the law of Gay-Lussac tells us that at constant volume (or at constant density) the pressure of a gas increases with the temperature, and that for each degree it does so by $\frac{1}{2}$ of the value at 0°. A similar thing has been proved by van't Hoff from the numbers obtained by Pfeffer. And finally for gases we have the law of Avogadro, that, temperature and volume being the same, equimolecular quantities of different gases exert the same pressure. Taking the molecular weights in grams, and taking for the common volume 1 litre, then at 0° this pressure is equal to 22.37 atmospheres. Now, it has been observed by Pfeffer that the osmotic pressure of a one per cent. solution of cane sugar, which therefore con-tains 10 g. in one litre, is 0.649 atmospheres at 0°. The molecular weight of sugar C, H, O,, is 342; a solution containing this quantity in grams in one litre would exert a pressure W times as great - that is, a pressure of 22.2 atmospheres. This number agrees within the limits of experimental error with that which holds good for gases; and hence Avogadro's law holds also for solutions, or, more correctly, so far, for solutions of cane sugar.

The question whether the law holds for other dissolved substances must be answered in the affirmative. It is true that only very few measurements of osmotic pressures have been made, but these phenomena are so closely connected with others to be considered shortly, that it has been possible to place the general validity of the law beyond doubt.

Let us imagine a solution poured into a vessel of the form of an inverted funnel, the opening of which is closed by a semi-permeable wall in contact with which is a quantity of the pure solvent. Then the solution will rise in the tube, because of the greater internal pressure, and equilibrium will be established only when the pressure of the liquid column in the tube has become equal to the osmotic pressure. Let this arrangement be covered by a bell-jar. from which the air has been completely expelled; the solution will then be surrounded by the vapour of the solvent only. But the pressure of the vapour is slightly smaller in the upper part of the bell-jar, at the level of the solution, than below at the level of the pure solvent, and it is smaller by an amount which is equal to the pressure of the weight of the vapour present between the two levels. Moreover, it is by this amount that the vapour-pressure of the solution must fall short of that of the solvent, because, if this were not the case, liquid would either continually evaporate, or condense, at the surface of the solution; in consequence of the osmotic pressure, the changes in level produced would always equalise themselves again, and we should have a perpetuum mobile, which is impossible.

It follows, therefore, that in general the vapour-pressure of a liquid must decrease when a substance is dissolved in it, and that this takes place according to laws which run parallel with those of osmotic pressure.

This theoretical conclusion is in accordance with observation. It has been found by Wüllner (P. 103, 529) that, at a constant temperature, the decrease of the vapour-pressure of an aqueous solution is proportional to the concentration of the solution. Babo on his part had established that the ratio between the vapourpressures of the pure solvent and the solution is independent of the temperature. Both results have been confirmed, on the whole, by later investigations. Raoult especially has occupied himself with this question; he has shown that this behaviour is general, and he has also found that equimolecular weights of different substances dissolved in the same solvent produce equal diminutions of the vapour-pressure, and finally that on using equimolecular quantities of different solvents the relative diminution in the vapour-pressures is the same. If f stands for the vapour-pressure of the solvent, f' for that of the solution, and if further N stands for the number of molecules of the solvent (in gram-units), n for the number of molecules of the substance dissolved, the general expression holds

$$\frac{f-f'}{f} = \frac{n}{N+n}.$$

 $\frac{f-f}{f} = \frac{n}{N+n}.$ While Raoult discovered this law empirically, van't Hoff has deduced it theoretically from the laws of osmotic pressure (Z. P. C. 1, 494).

This formula can be used for determining the molecular weight of a substance in solution. Let p grams of a substance with unknown molecular weight m be contained in 100 g, of the solvent, the molecular weight of which is M; then $\frac{p}{100}$ M = grams of substance dissolved in one molecular weight of the solvent; let this = s; then putting $n = \frac{s}{m}$, and N = 1, and solving the

equation for
$$m$$
, it follows that $m = \frac{sf'}{f - f''}$.

Finally, a third set of phenomena is known, governed by similar laws. It has long been known that salt water freezes at a lower temperature than pure water. As far back as 1788 Blagden (T. 1788) established the fact that the lowering of the freezing-point of a solution of salt in water is proportional to the amount of salt dissolved. Later on, Rudorff (Pal14, 63) rediscovered this fact, which had been forgotten, and de Coppet found that equimolecular solutions of salts having analogous constitutions exhibited equal lowerings of the freezing-points (A. Oh. [4] 23, 366). Raoult discovered that the same law held for the most diverse solvents. This law states that equimolecular quantities of whatever substances we take, added to a constant quantity of the solvent, lower the freezing-point by the same amount (C. R. 1882). Raoult thought for a time that the lowering of freezing-point was the same for equimolecular quantities of different

solvents, but this proved to be erroneous. Van't Hoff has deduced this important relation from the laws of osmotic pressure, and his formula agrees well with experiment (Z. P. C. 1, 481).

We can convince ourselves of the necessity of these relations by an argument similar to that used in order to prove the connection between osmotic pressure and change of vapourpressure. As the mechanical theory of heat tells us, below 0° the vapour-pressure of ice decreases more rapidly than that of over-cooled water. A temperature must therefore exist whereat a saltsolution, which has a vapour-pressure less than that of water, exhibits the same vapour-pressure as ice. This is the only temperature at which the solution can exist side by side with ice, as otherwise a perpetuum mobile would be possible. Since, therefore, this temperature, which is the freezing-point of the solution, is in inseparable connection with its vapour-pressure, the laws holding for the one must also hold for the other, and from this the laws already stated follow directly. Formulating these laws, we get $\Delta = r \frac{p}{ml}$

where Δ is the lowering of the freezing-point, lthe weight of the solvent, p that of the substance dissolved, and m the molecular weight of the substance, while r is a constant dependent on the nature of the liquid. From the formula it

follows: $m = \frac{rp}{\Delta t}$. Having, therefore, once for

all determined the constant for a solvent, it is possible to find the molecular weight of a substance by determining the lowering of the freezing-point of its solution in that solvent. Van't Hoff has shown that the constant can be deduced thermo-dynamically from the heat of fusion of the substance.

If we now apply these methods for determining the molecular weights of dissolved substances to solutions of electrolytes, we find that the molecular weights appear smaller, and hence the number of molecules in solution are greater, than correspond with the formule. In many cases the amount of this deviation is very considerable, and its existence at first proved a great obstacle in the way of van't Hoff's theory of solutions. To Arrhenius (Z: P. C. 1) we owe the means of accounting for the deviation. The views propounded by this investigator have shed such a flood of light over difficult questions in chemistry and physics that we must consider the work of Arrhenius to be one of the most important advances ever made in this and in allied domains.

Arrhenius' idea consists in ascribing the deviations of the observed from the calculated molecular weights, to a dissociation of the electrolytes into their ions. From the magnitude of this deviation a conclusion can be drawn as to the number of molecules which are dissociated; the problem which was left unsolved by Clausius thus receives its solution.

Reserving the numerical proofs of the truth of this view till later on, it is proposed to deal first with some possible objections and diffi-culties of a general nature.

The application of the hypothesis leads to the conclusion that in moderately dilute solutions of strong acids and bases, and also of normal salts, as much as 80 to 90 per cent. of the substance in solution is dissociated into its ions. Hence a solution of potassium chloride contains little else than ions of chlorine and potassium. How is it that the chlorine does not escape into the air as a greenish yellow gas, and the potassium does not act on the water?

The answer lies in the consideration that the chlorine which we know as a greenish yellow gas is the electrically neutral molecule Cl₂, and does not consist of the separate atoms of Cl which are charged with a large amount of negative electricity. The potassium again is not present as the compact metal, but in the form of strongly positively charged ions. Considering the great differences exhibited by allotropic forms of the same element (oxygen and ozone, red and yellow phosphorus, &c.), we cannot wonder that in these cases also considerable differences appear.

And it is further possible to produce solutions in which such ions -as, for instance, potassium-are present in excess, and therefore certainly in the free state. For this purpose, let us imagine two vessels filled with notassium chloride solution and placed on an insulating stand, and then connected conductively by means of a syphon filled with the solution. Let us now bring near to the one vessel a body charged with negative electricity. The vessel becomes charged positively by induction, and an equivalent quantity of negative electricity moves through the syphon into the second vessel. If we now remove the syphon, and then the body charged, the first vessel remains charged positively, the second vessel negatively. So far the experiment contains nothing that is new; it is the elementary . experiment used for proving the inductive effect of electricity. If, however, we pay attention to the fact that, according to the law of Faraday, electricity can move in electrolytes only simultaneously with the ions, the conclusion is inevitable that an excess of potassium ions must be present in the vessel charged positively, and the same excess of chlorine ions must be present in the vessel charged negatively. These excesses of ions are maintained as long as the electric charge of the vessels exists. On discharging the vessels the ions give up their electricity, and the substances appear at the point of discharge endowed with their usual properties.

Owing to the magnitude of the quantities of electricity contained in the ions, the question may be raised whether the experiment which has just been indicated really can be carried out. Ostwald and Nernst have shown (Z. P. C. 3) that this is actually possible. By means of a mercury electrode contained in a capillary tube, such small quantities of hydrogen can be observed that the experiment becomes quite feasible. Since under ordinary conditions one gram of hydrogen occupies a space of about 12,000 c.c., a small bubble of 0·1 mm. diameter, which one can still see with the naked eye, has a weight of only 10⁻¹⁰ g., and one of 0·0·1 mm. diameter, which can be seen

one of 0'01 mm. diameter, which can be seen

1 From the number, already given, of 96,540 coulombs,
which are combined with 1 g, of hydrogen and which are
also present in one litre of normal potassium chloride solution—as positive electricity on the potassium, or negative
electricity on the chlorine—it is possible to calculate that
this quantity of electricity would suffice to charge a sphere
of an approximate diameter of 10's cm.—which, therefore,
would be larger than the whole solar system—to a potential
effort one volk.

under a microscope, has a weight of only 10⁻¹³g. This is as small a quantity of matter as can be recognised in any way, and the electricity combined with it can be detected in an apparatus of very moderate dimensions.

Thus the experiment described above is not only conceivable, but feasible; and thus it is proved that free ions, such as those of potassium, can be present in aqueous solutions without acting on the water.

The assumption that some of the molecules of electrolytes are split into ions in solutions explains many properties of these solutions. In the following paragraph we will assume for simplicity's sake that the splitting up is complete—an assumption which is nearly correct in the cases of salts, strong acids, and bases; the modifications which must be introduced into these considerations by taking into account the portions not split up, will be considered afterwards.

Let us consider, first, the chemical reactions of electrolytes. As is well known, certain reactions are used in analytical chemistry for indicating definite substances. These reactions indicating definite substances. must take place quickly, as otherwise they would be of no practical use; hence they must be reactions between ions. If asked what it is that the ordinary analytical reactions allow us to recognise, we are inclined to answer, the different chemical elements. But this is not at all appropriate. A solution of a salt of silver is called a reagent for chlorine, and in fact by its help chlorine can be detected in metallic chlorides. But the chlorine in potassium chlorate or in monochloracetic acid cannot be detected by means of silver solution. In the same way chlorides indicate silver; but the silver in potassium silver evanide cannot be recognised by means of chlorides. The different oxyacids of sulphur also give quite different reactions, though they all contain the same elements; similarly, the reactions of iron, copper, mercury, tin, &c., are quite different, according to the degree of oxidation of the metal.

These examples prove that it is not the elements which are indicated by analytical reactions. A more careful consideration shows that since it is the ions which react, the ions are indicated by the analytical tests.

This simple proposition removes all the difficulties which confronted us. If a solution of silver is a reagent for chlorine ions, naturally it cannot indicate the chlorine in potassium chlorate, whose ions are K and ClOs; nor in monochloracetic acid, whose ions are H and CH2ClCO2. And, conversely, silver is indicated by chlorides only where it appears as the ion; but the ions of potassium silver cyanide are K and Ag(CN). The behaviour of chloroplatinic acid H.PtCl₆ towards silver solutions is specially remarkable, a behaviour about which an incredible confusion has reigned in chemistry, because it has always been believed that its chlorine must be precipitated by silver solution as silver chloride. matter was first cleared up by Jörgensen (J. pr. [2] 16), who found that no silver chloride is formed at all, but rather the silver salt of chloroplatinic acid Ag,PtCle; sodium platinichloride is completely precipitated by two equivalents of silver solution only, instead of by six, which correspond to the proportion of chlorine.

Thus the so-called anomalies of analytical reactions are fully explained. It is further explained why, for instance, all the different sulphates give the same reaction with barium chloride. The nature of the metal is of no account, because the reacting ion SO, is not combined with the metal at all, but exists by itself. It is a remarkable fact that similarly con-

stituted ions give, under certain conditions, different reactions. According to this view, the iron in a solution of FeCl_n, and also in a solution of FeCl_n, is contained as an ion; yet the two act differently. In like manner, solutions of K₁Fe(CN)_a, as well as those of K₂Fe(CN)_a, contain the same negative ion Fe(CN)_a, and those two substances give quite different reactions. The explanation lies in recognising that these similarly composed ions are endowed with different quantities of electricity according to their valency. Thus iron appears divalent and trivalent, mercury and copper monovalent and divalent, the atomic group Fe(CN)_a tetravalent and trivalent, in that they contain corresponding numbers of positive or negative electric units or 'atoms.'

If the theory developed so far is correct, then all properties of salt solutions must be of an additive nature with regard to the two ions—i.e. their properties must be made up of two parts, one of which depends only on the positive ion, and the other only on the negative ion. This fact was recognised before it found an explanation in terms of the hypothesis of the independent existence of ions in solutions. Arrhenius drow attention to this fact (Z. P. C. 1) when he was establishing his theory. Some examples will make the point clearer.

In 1874 Valson enunciated a law concerning the specific gravities of salt solutions (C. R. 73), which he called the law of the moduli. By means of it the specific gravity of a 'normal' solution-that is, of a solution containing one equivalent of the salt in grams in one litre-of any salt can be found by adding to the specific gravity of a solution of ammonium chloride (chosen as the standard) two values, one of which depends on the metal only, and the other on the acid radicle only. According to Valson, these moduliare (NH, ClAq of specific gravity 1015 being taken as the standard); -K = 30, Na = 25, $\frac{1}{2}Ca = 26$, $\frac{1}{2}$ Mg = 20, $\frac{1}{3}$ Sr = 55, $\frac{1}{3}$ Ba = 73, $\frac{1}{3}$ Mn = 37, $\frac{1}{3}$ Fe = 37, $\frac{1}{3}$ Zn = 41, $\frac{1}{3}$ Cu = 42, $\frac{1}{3}$ Cr = 61, $\frac{1}{3}$ Pb = 103, Ag = 105; Br = 84, I = 64, $\frac{1}{3}$ SO₄ = 20, NO₄ = 15, $\frac{1}{3}$ CO₂ = 14, HOO₄ = 16. To these are added the value zero for NH, and Cl. These values allow us to calculate the specific gravities of solutions of 14 × 7 = 98 salts, and the calculations agree very well with experiment. Later on (1883), the law was confirmed by C. Bender (W. 20, 560), and by Nicol (P. M. [5] 18, 179), and was also extended by the first named.

A similar law was established by Gladstone (Pr. 16, 439) for the refraction-equivalents of salts. Gladstone expressed his generalisation in the form that the difference between the refraction-equivalents of the salts of two metals with the same acid is always the same, and is independent of the composition of the acid. The following table shows how the values agree in the cases of salts of potassium and sodium with soids of different compositions:—

	Potassium	Sodium	Difference
Chloride	18-44	15.11	8.8
Bromide	25.34	21.70	8.6
Iodide	35.33	31.59	8.7
Nitrate	21.80	18.66	8.1
Hydrate	12.82	9.21	. 3.6
Alcoholate	27.68	24.28	8.4
Formate .	19.93	16.03	8.9
Acetate	27.65	24.03	3.6
Tartrate	57.60	50.39	8.6
Carbonate	34.93	28.55	2 × 3·2
Bichromate .	79.9	72.9	2 × 3·5
Hypophosphite .	26.94	20.93	2 × 3·0

A similar law exists for the salts of strong acids, but with the weak acids the differences are much greater. We are now in a position to account for this discrepancy, which was left unexplained by Gladstone. Since the weak acids are only very partially split into their ions, it cannot be expected that hydrogen as an ion should have the same refraction-equivalent as it has in the undecomposed compound.

Gladstone also enunciated the general law that the colour of the solutions of salts whose acid or whose metal form coloured compounds is independent of that of the other constituent (P. M. [4] 14, 418). If we consider how dependent colour is on constitution in other cases, this fact must be considered as a specially weighty proof of the mutual independence of the ions.

The knowledge of the fact that the characteristic colours of salts are dependent on the nature of the coloured ion only, and are independent of that of the other ion, has existed for a very long time, almost, as one might say, unconsciously. In green liquids we should always expect nickel, in red ones cobalt, in pale blue ones copper, &c. Some exceptions to this can easily be explained. One such exception is that most copper salts show the blue colour of the copper ions, while concentrated solutions of copper chloride appear green. The cause of this is that in concentrated solutions a considerable number of undecomposed molecules CuCl, are present, which molecules are coloured a deep yellow, as can be seen in dry copper chloride, which looks almost reddish brown. This yellow colour mixes with the blue colour of the copper ions, and produces the green colouration. From the fact that as the temperature is raised the green colour becomes more intense, it must be concluded that with rise of temperature more molecules CuCl, form at the cost of the ions (v. Ostwald, Z. P. C. 9, 579).

Another additive property has been found by Marignac (d. Ch. [5] 8, 410) in the specific heats of salt solutions. This property is, however, partly hidden by small deviations which, though capable of explanation, require the knowledge of some quantities the measurement of which has not yet been undertaken.

And, further, Ostwald (J. pr. [2] 18, 853) has proved such relations to hold in a fairly extensive manner for the volume-changes accompanying neutralisation. On saturating solutions of potash, soda, and ammonia by the same acid the total volume changes in a very different manner. These volume-changes are, however, governed by the law that on saturating two bases by the

same acid the difference of the volume-changes is independent of the nature of the acid; and in like manner the difference in the volume-change on saturating two different acids by the same base is uninfluenced by the nature of the base. Hence the volume-change always depends on two constants, one of which is determined by the acid only, and the other by the base only; the specific nature of the salt formed has no influence. The following table shows these relations:—

	Potassium	Sodium	Ammonia
Nitrie acid	20.0	19.8	- 6.4
Hydrochloric acid .	19.5	19.2	- 6.6
Hydrobromic acid .	19.6	19.3	- 6.6
Hydriodic acid .	19.8	19.6	- 6.4
Formic acid	12.4	12.1	-13.6
Acetic acid	9.5	9.3	-16.3
Monochloracetic acid	10.9	10.6	-15:1
Dichloracetic acid .	13.0	12.7	- 13.0
Trichloracetic acid.	17.4	17.1	- 8.7
Isopropionic acid .	7.8	7.7	-17.8
Butyric acid	7.0	6.8	-18.6
Isobutyric acid .	6.3	6.1	-19.3
(Hycollic acid	9.6	9.8	- 16.5
Lactic acid	8.3	8.1	-17.7
Sulphuric acid .	11.9	11.5	-14.4
Oxalic acid	9.9	9.7	-16.1
Succinic acid.	8.2	7.9	-17.6
Malic acid	8.6	8.5	-17.4
Tartaric acid	9.4	9.2	-17.0

The differences between the corresponding members of two horizontal or of two vertical columns in this table are seen to be constant within the limits of error. The all but complete equality of the values for the four first-named acids, which are almost completely split up into their ions, is remarkable.

The most striking case of the additive properties of salt solutions is, however, given by their thermal relations. Hess long ago established the law of the thermo-neutrality of salts: this law declares that there is no thermal effect on mixing the solutions of two salts provided that everything remains in solution. This fact is difficult to understand as long as eve assume the existence in an undecomposed state of normal salts in solutions, since the mutual changes of the salts would have to proceed without any energy-change, and this is a behaviour without analogy. If we assume, however, that the solutions of the salts contain chiefly the ions of the salts, the fact becomes explicable, because on mixing the solutions, the ions remain unchanged, they do not influence each other, and hence there is nothing to cause thermal effects.

More remarkable still is the explanation which the theory gives concerning the heats of neutralisation of acids and bases. At first sight it seems as if no action could take place between a ch compounds, if we consider the strong acids and bases to be almost wholly separated into ions. Because if the solution of the acid, of the base, and of the salt contains ions only, no change ought to occur when the acid and the base are mixed. If, however, we consider the reaction more carefully, we arrive at different results. For instance, let there be given soda

and hydrochloric acid; the reaction will be

Na + OH + H + Cl = Na + Cl + H.O

The ions sodium and chlorine remain unchanged; but since water conducts very badly, only a very slight separation of H.O into the ions OH and H can occur, hence when the ions OH and H meet they must combine to form H₂O.

Hence the process of neutralisation in aqueous solutions is not a combination of the constituents of the salt, but only a combination of the constituents of water.

It is true that this remarkable result is somewhat contradictory of the usual views on the subject, but it is in complete agreement with the facts. If the process of neutralisation between acids and bases decomposed into their ions really consists only in a formation of water from hydrogen and hydroxyl, then its concomitant phenomena must be independent of the nature of the acids and the bases.

The most impertant of these concomitant phenomena is the heat of neutralisation. This value has been determined by different observers, with special exactness by Thomsen (Th. 1). A number of measurements are collected in the following table, calculated for one equivalent; the unit used is the rational calorie, K=100 gram-units of heat:—

кон LIOH BaO H. CaO H. NaOH HCI. 137 137 187 139 139 HBr 137 137 HI. 137 136 HNO. 137 138 140 139 HClo, 138 138 140 HBrO. 138 138 HIO, 138 138 141 143 λΗ₂S₂Ò, 135 139 iΗ,PiCl.. 136

And, similarly, tetramethylammonium hydroxide, platinodiamine hydroxide, and triethylsulphine hydroxide give with hydrochloric acid 138, 137, and 137 K respectively.

From this table, which could easily be enlarged, it follows that the heat of neutralisation of the strong acids and bases is a constant, and is approximately equal to 13,700 cal. This number must be looked on as very nearly equal to the heat of formation of water from the ions

H and OH. (A more exact calculation gives 13,500 cal.) The small deviations which are still present originate in the fact that the splitting up of the acids and bases referred to, though very considerable, is yet not quite complete; it is in this undecomposed remnant that the individual nature of the two substances still asserts itself a little.

The conditions become quite changed when we consider the weak acids and bases. Here the constancy of the heat of neutralisation ceases completely, and values are observed which fluctuate between 163K and 10K. In these cases the quantities of heat which are concerned in the splitting up of the acid and the base into their ions must be taken into account, besides the heat of formation of water from its ions, and the heat

of neutralisation may be represented by an expression of the form N = 13,500 + A + B, where A + B is the quantity of heat necessary for decomposing the acid and the base into ions. As experiment has shown that the salts when in dilute solution are uniformly and nearly completely decomposed, their heats of decomposition need not be taken into account meanwhile. This formula also expresses a law which, discovered some time back by Favre and Silbermann (A. Ch. [3] 37, 486), has been confirmed by the younger school of thermo-chemists. This law is, that the difference between the heats of neutralitation of any two bases is always the same whatever acid is taken, and that likewise the difference between the heats of neutralisation of any two acids is independent of the base. This is only another expression for the proposition that the acid and the base each contributes towards the heat of neutralisation a definite portion, which is independent of the nature of the substance with which the acid or the base reacts.

Very similar facts may be noticed concerning the other phenomena which accompany neutralisation. A table has already been given (p. 189) showing that the same relations hold good for the changes of volume that accompany neutralisation; the strong acids and bases give, on neutralisation, very nearly the same change of volume, i.e. 20 c.c. per litre of normal solutions of acid and base. The same holds good for the changes in the refractive indices.

The electrical conductivity of electrolytes.—Ohm's law $\mathbf{I} = \frac{\mathbf{F}}{\mathbf{R}}$ gives a definition

of R, the resistance of a conductor. It has been shown that the resistance is dependent on the nature of the conductor, and on its dimensions, in that it varies directly as the length and inversely as the cross-section. It has been agreed to call the resistance of a conductor of cross-section 1 sq. millim, and length 100 centim, its specific resistance; this depends on the nature of the material of which the conductor consists, and on its temperature.

If we define a quantity $C = \frac{1}{R}$, and call it the

conductivity, Ohm's formula becomes I=EC. We may best regard C as the power of the conductor to allow the electricity to pass through, or the power to transport the electricity. In the illustration of a current of water in a tube, C would be comparable to the cross-section of the tube. The conductivity is the reciprocal of the resistance. In calculating the strength of currents it is more convenient to work with resistances; it these are connected end to end, the total resistance is the sum of the individual resistances; but if the resistances are connected side by side, the conductivities must be summed up. For electro-chemical purposes the idea of conductivity has always proved more useful than that of resistances.

Measurements of resistances or of conductivities are made according to different methods, all of which rest on the application of the formula above given. For instance, we can measure the current strength, I, using the same electromotive force E (from a constant cell, as, for in stance, a Daniell), there being included in the

circuit at one time the resistance R, which is to be determined, and at another time a resistance of known magnitude R_o . We then get the equation $I_1 = \frac{E}{R_1} \text{ and } I_o = \frac{E}{R_o}, \text{ and from these } R_1 = R_o \frac{I_1}{I_o}.$ It is not necessary to discuss here the various

methods of measuring resistances. As mentioned before, the unit of resistance used is the ohm-i.e. the resistance of a mercury column of 1 sq. mm. section, and 105 or 106.3 cm. length at 0°. The unit of conductivity is given by the same quantity; since this represents the reciprocal value of the resistance, it has been proposed to designate it by Mho, which is the name Ohm reversed, and for which Mo might be put shortly.

While so far the different powers for conducting electricity possessed by the metals have remained more a question of practical than of theoretical importance, the study of the electrical conductivity of electrolytes has led to most important and suggestive views as to their nature. These have only been arrived at quite lately, chiefly because until recently there existed no convenient and good method for determining the conductivities of electrolytes in solution.

The difficulty to be surmounted consists in the fact that the current must be conducted through the electrolyte by means of electrodes, and that these get coated with the ions which separate-i.e. they become polarised. In consequence of this the electrodes become the seat of new electromotive forces, the magnitude of which is variable, and therefore not capable of being determined exactly. One method only has been brought forward as yet in which this difficulty is completely obviated; it is due to Guthrie and Boys (P. M. 1880. 328), and consists in allowing a system of strong magnets to rotate rapidly round the axing a cylindrical vessel filled with the electrolyte and suspended by a long thin wire. By this means currents are produced in the electrolyte (as would be produced in every conductor), the electrodynamic effect of which tends to rotate the vessel in the same direction. The strength of these currents is proportional to the conductivity of the liquid, and the vessel is rotated until the torsion of the suspending wire becomes sufficient to maintain equilibrium against this rotatory effect. We are therefore justified in putting the deviation as proportional to the conductivity, the velocity of the magnets remain. ing the same. As the currents produced in the electrolyte occur exclusively within it, no polarisation is possible. The method has not been applied, because the apparatus required is expensive and difficult to handle.

Becquerel and Horsford tried to bring up polarisation to its highest value by using strong currents. In this method the current is led through the electrolyte, then through an adjustable resistance, and finally through an instrument for measuring currents (galvanometer, &c.), and its strength is determined. The distance between the electrodes is noxt decreased by an accurately measured amount, and resistances are inserted until the strength of the current has regained its value; then the resistance inserted is aqual to that possessed by the portion of the liquid taken out. The method suffers from the

disadvantage that it is difficult to keep the electromotive force of polarisation constant as presupposed; and, further, the liquid is changed at the electrodes by the use of the stronger currents required, so that what we measure is the resistance of the changed, and not that of the original, liquid.

By using electrodes of zinc, which in solutions of zinc salts give no polarisation, Beetz (P. 117, 1) was able to determine the conductivities of such solutions by the methods used for metals. Paalzoff showed (P. 136, 489) that the method can be applied to other solutions also if we bring the two zinc electrodes into two separate vessels, and establish conduction through a syphon filled with the liquid to be investigated. The process is based on the fact that no polarisation is produced when a current is passed through

the surface of contact of different liquids. But this method is again far surpassed in convenience by one given by F. Kohlrausch (W.11, 653), in which polarisation is made harmless by using alternating currents. Such currents, in which equal quantities of electricity flow alternately in opposite directions, are produced most easily by means of an ordinary induction apparatus. It is true that by such currents the electrodes are also polarised, but the polarisations occur rapidly in opposite directions, sothat the polarisation produced by the first current-impact increases the strength of the second current-impact which has the opposite direction, and the polarisation resulting from the latter adds itself on to the third current-impact, and so on. Kohlrausch has shown that by using platinum electrodes of ten sq. cm. surface coated with platinum black, the effect of polarisation may be reduced to less than 0.1 p.c. of the resistance. Kohlrausch uses for his method Wheatstone's bridge in Kirchhoff's arrangement. For details reference is made to Kohlrausch's memoir.

The definition of specific conductivity as given above, and as employed in physics, is not of practical use in considering electrical conductivity from the point of view of the chemist. Since, according to the law of Faraday, the ions alone conduct, and since each ion carries the same quantity of electricity, it is evident that the conductivities of different solutions must be referred to the same number of ions in order to obtain comparable numbers. That we may form a conception of equivalent conductivity following from this, let us imagine two electrodes of indefinite extension placed at a distance of 1 cm. apart, and let there be brought between them so much of a solution as contains the equivalent weight in grams of the dissolved electrolyte; the conductivity of such a system is the equivalent conductivity of the electrolyte. In order to find the relation between the specific and the equivalent conductivity, we bear in mind that the length of the solution of the electrolyte is 106 times less than 106 cm., which was the length of the conductor assumed in the definition of specific conductivity. When the solution is normal-i.e. contains one g. equivalent per litre—the cross-section is 1,000 sq. cm.; when the same weight is dissolved in v litres it is 1,000v

A detailed description of the method for carrying out such measurements is to be found in Z. P. C. 2, 868.

sq. cm.; this is 100,000v times greater than the cross-section for the specific conductivity, which is '01 sq. cm. Hence from the specific conductivity we obtain the equivalent conductivity is by the equation $\lambda=1.06\times10^{7}lv$. It should be remembered that the specific conductivity of an electrolyte is not usually referred to ohms, but to the unit of Siemens, formerly commonly employed, which is equal to the resistance of a column of mercury 100 cm. in length; hence instead of 106 we must put only 100, and the equivalent conductivity becomes $\lambda=10^{7}lv$.

In addition to the equivalent conductivity we can calculate the molecular conductivity, which is as many times greater than the equivalent conductivity as the molecular weight contains the equivalent weight. So the molecular conductivity of sulphuric acid is twice as great as the equivalent conductivity, that of aluminium

chloride three times as great.

For the general facts which have been established regarding equivalent conductivities we are specially indebted to Kohlrausch, and to several investigators who succeeded him. The most simple relations are exhibited by dilute solutions in which v is greater than 1 lit., and those will be considered first.

1. The equivalent conductivities of normal salts are of the same order of magnitude, but are not the same (Kohlrausch).

2. The conductivities of all salts increase slowly with increase of dilution, and generally reach a maximum value, which is not surpassed after dilutions of 20,000 to 50,000 litres per gram-equivalent (Koblrausch).

3. The increase of conductivity is least for salts which consist of two monovalent ions; it is about twice as great for salts which contain one divalent and one monovalent ion; and about four times as great for salts whose ions are both divalent (Ostwald).

4. The equivalent conductivities of equally concentrated solutions of the most different salts can be represented as the sum of two constants, one of which is determined solely by the positive ion, the other solely by the negative ion (Kohlrausch). This law agrees the better with experience the more dilute the solutions are.

In order to give an illustration of these laws, I append the equivalent conductivities of several normal salts as measured by Kohlrausch. The values are for 18°.

Dilution	KCI	NaCl	Lici	∯BaCl,	1K,80.	iMgSO
17 107 1007 1,0007 10,0007 50,0907 100,0007	91·9 104·7 114·7 110·3 120·9 121·7 121·6	69:5 86:5 96:2 100:8 102:9 102:8 102:4	59·1 77·5 87·5 92·1 91·3 95·5 96·5	65 8 86·1 100·6 109·2 112·6 114·4 114·2•	89·7 109·8 120·7 124·9 126·6 127·5	27.0 47.4 71.5 93.5 103.4 105.2 105.6

If we attempt to form a picture of the processes occurring in electrolytic conduction, we must first bear in mind that, according to the statements of Kirchhoff (P. 78, 506), free electricity must be present along the surface of each current-path; and the fall of this potential causes the motion of the electricity inside the conductor. Hittorf pointed out that the theories of electrolysis hitherto held could not satisfy this requirement. Assuming the presence of free ions,

it is evident at once that the surface charge is formed by these. Owing to the fall of potential which exists, the positive electricity is now driven to the one side, the negative to the other. Both are bound to the ions; which are, therefore, moved in the same way by forces that are of equal magnitudes on both sides.

The velocities acquired by the ions under the influence of these equal and opposite forces will not generally be the same, since it cannot be assumed that the resistances to motion encountered by the ions in the solution will be the same. But in dilute solutions, anylow, the nature of the second ion, travelling in the opposite direction, will have no influence on the velocity of any definite ion—such as, for instance, Cl. Hence the conductivities of salts, when referred to equal quantities of ions, can be represented as the sum of the migration-velocities of the positive and negative ions. Calling these migration-velocities u and v, we get

 $\lambda = u + v.6$ But this is exactly the relation discovered by Kohlrausch (p. 191), to whom also the argument

just given is due.

Viewed thus, the phenomena of electrical conductivity are brought into connection with another group of facts, the comprehension of which had presented great difficulties to the older naturalists. These are the phenomena of the migration of the ions.' It has been mentioned that Daniell observed the corresponding manifestations, but they were not explained till Hittorf did so.

From the table already given it follows that the different ions must possess very different migration-velocities. On comparing, for instance, KCl and LiCl, we find differences of 27 to 30 units. Since the chlorine must possess the same velocity in both cases, and hence participate to the same amount in the conductivity, the difference is due solely to the ions K and Li. In the same manner we can convince ourselves that different negative ions migrate with different

On electrolysing a substance whose ions travel with different velocities, different quantities of the ions will collect at the electrodes, and, in addition to decomposition, the liquid will undergo an unequal change of concentration at the electrodes. In order to get as good a representation as is possible for these relations, let the ions be represented in the figure in the next column by black and white circles. The different horizontal rows represent different phases of the electrolysis, these being such that between them there is a distance equal to the mean distance of the ions. It is assumed that the black ions migrate twice as quickly to the left as the white ones do to the right. At first there are seven ions on each side of the central line. At the end of the process six ions have been liberated at each end, and, in addition, five out of the seven pairs have remained behind at the left side, and two have disappeared; while of the equal quantity at the right side three have remained behind and four have disappeared. Hence the proportion of salt has decreased at the right side twice as much as at the left-that is, in the same ratio as that in which the two ions migrate.

Therefore in order to determine the ratio of

the migration-velocities of the two ions of a salt it is only necessary to determine the proportion of undecomposed salt at each electrode before and after electrolysis; the ratio of the decrease of this proportion at each side is equal to the ratio of the migration-velocities, or is the 'migration-measure.

This representation holds good on the supposition that the ions which separate at the electrodes do not again go into the solution. If, however, we electrolyse a solution of copper sulphate between copper electrodes, the copper, it is true, will leave the solution at the cathode, but the ion SO, will not separate out at the anode, but will combine with the copper of the anode to form copper sulphate, which will go into solution. The solution will, therefore, become, not more dilute, but more concentrated. It is, however, easy to take this circumstance into account. It is only necessary to determine the total quantity of electricity passed through the solution (for instance, by means of a silver voltameter); from this we can calculate how much copper has gone into solution, and we need then only deduct this quantity from the total quantity of copper at the anode, as determined by analysis. It is simpler still to weigh the cathode before and after the experiment: the



increase of weight is equal to the weight of copper which has dissolved at the anode.

Hittorf examined (P. 89 to 106) a great many salts and acids with respect to their 'migrationmeasures,' and established the fact that the current-strength has no influence on the ratio of the migration-velocities, the temperature has an inappreciably small influence, but the concentration exerts a changeable effect-in some cases it is inappreciably small, while in others it is fairly important.

Hittorf found, for instance, that the concentration of KClAq at the electrodes scarcely changes at all; hence chlorine and potassium must migrate with very nearly equal velocities. If we consider the solution v = 1.000l in the table given on p. 191, it follows that of the 119.3 units of conductivity of potassium chloride, 59.65 belong to the chlorine and the same number to the potassium. Knowing these numbers, we can calculate the velocities of migration of all the other ions in the table. NaCl has 100'8; on subtracting from this 59.7 for the chlorine, the velocity of the sodium ion becomes 41·1. Similarly, Li = 32·4, $\frac{1}{2}$ Ba = 49·5. As K = 59·7, and as $\frac{1}{2}$ K₂SO₄ = 120·7, it follows that ${}_{2}SO_{1} = 61.0$; hence ${}_{2}Mg = 32.5$.

From these numbers we can again calculate the migration-measures, or the changes of con-centration at the electrodes, of other salts.

Thus $\frac{\pi}{v}$ is for NaCl = $\frac{41.1}{59.7}$ = 0.69; for LiCl $\frac{32.4}{59.7}$ | preserving very dilute solutions of alkalis perfectly pure. =0.54; for BaCl₂ $\frac{49.5}{59.7}$ = 0.83, &c. It is evident

that when one migration-measure is known, the migration-measures of all corresponding salts can be calculated from the measured conductivities. And since, on the other hand, the conductivities of salts represent the sums of the velocities of their ions, we can realise the very great simplification which these considerations, due to F. Kohlrausch, have produced in the relations of electrical conductivity which formerly appeared so complicated. If, for instance, we know the conductivities of ten salts with the negative ion A and the positive ions B, to B, and of other ten salts with the ion B, and the ions A, to And and in addition to these the migration-measure of one salt, we can calculate from these 21 measurements the conductivities and the migration-measures of 100 salts - that is, we can deduce 200 data.

An extensive examination of these relations, undertaken by Kohlrausch (W. 6, 164), and later by Ostwald (Z. P. C. 1, 74), as well as by Loeb and Nernst (ib. 2, 948), has proved that they hold good with very sufficient accuracy for very dilute solutions. But deviations from these relations become apparent in concentrated solutions, and these leviations are greater the more con-centrated the solutions. And, further, different salts behave differently, inasmuch as salts consisting of two monovalent ions show the smallest deviations, salts with one monovalent and one divalent ion show greater deviations, and salts with two divalent ions show the greatest deviations. Now these are the classes of salts which exhibit differences in the changes of conductivity accompanying dilution (p. 191), and we are, therefore, led to the conclusion that the same cause underlies both phenomena.

The free acids and bases only partially conform to Kohlrausch's law. The following data, taken from Kohlrausch's determinations, exemplify this statement. Temp. = 18°:-

From these measurements it follows primarily that hydrogen and hydroxyl possess much greater migration velocities than the otherions - namely. 284 and about 150, respectively. It follows, therefore, that if the law of Kohlrausch were generally valid, the conductivities of all acids would be > 244. and the conductivities of all bases would be > 150. On looking at the numbers in the table, we find that phosphoric acid and acetic acid, as well as ammonia, are at a quite hopeless distance from these values. Sulphuric acid, also, does not obey the law. For SO, the value 61 0 was found above; on deducting this number from {H,SO, = 331.6, there remains II = 270.6, and the difference of this value from the one found before, 284, exceeds the limits of experimental error.

On carefully studying the table we now see that the acids and bases which form exceptions to the law exhibit the same peculiarity as the exceptional salts; they change their conductivities very markedly upon dilution. While the substances which follow the law have nearly reached the maximum of the equivalent conductivity at 1000/, the numbers show that this is far from being the case in the exceptional substances. We are thus led to inquire as to the cause which brings about the change in conductivity that accompanies dilution.

The arguments used so far have tacitly assumed that all the molecules of the electrolyte participate in the electrical conductivity, and that the electrolyte is therefore completely split into ions. This assumption is evidently arbitrary; and when we remember that aqueous solutions of ammonia and acetic acid exhibit nearly normal lowerings of the freezing-points, and that, therefore, dissociation occurs only to a small extent, if at all, we see that the assumption is completely erroneous in these cases. former equation $\lambda = u + v$, established without reference to the degree of decomposition, must be changed into $\lambda = x (u + v)$ where x represents the degree of decomposition-i.e. the ratio between the molecules decomposed and the total

Dilution	HCI	HNO.	JH,so.	₩,РО,	CH CO, II	Kon	NaOH	NH.OII
12	278·0	277.0	189·9	29·0	1·2	171-8	149·0	0.84
102	324·4	322.5	208·4	43·0	4·3	198-6	170·0	8.1
1002	341·6	339.5	285·5	79·0	13·2	212-4	187·0	9.3
10002	345·6	842.7	831·6	96·8	38·0	214-0	188·0	26.0

Among the substances quoted, HCl, HNO, KOH, and NaOH follow the law of Kohlrausch. Thus, if 59.7, which is the migration-velocity of K, is deducted from 118, which represents the conductivity of KNO, as determined by Kohlrausch, the difference, 583, is the velocity of NO. On deducting this number from the conductivity of nitric acid at 1000l - that is, from 342.7 -it follows that the velocity of hydrogen is 284·4. From HCl = 345.6 it follows that H = 285.9, since Cl = 59.7; these numbers agree to within less than one per cent. In the same way the difference between KOH and NaOH is equal to 26.0, thus approximating to equality with number of molecules orginally present. In doing this we make the most obvious, and probably only possible, assumption, that, cæteris paribus, the conductivity is proportional to the number of conducting particles or ions.

We may find a method for determining a in the deviations of electrolytes from the simple laws of solutions with respect to vapour-pressure and freezing-point. We have another and much more accurate method, however, in the determination of the electrical conductivity itself. As was found by Kohlrausch, the equivalent (and also the molecular) conductivity increases with rising dilution, reaching a maximum value in the that between KCl and NaCl, which is 19.2. The case of salts within limits which are still prac-larger difference proceeds from the difficulty of tically measurable. We can interpret this Vol. IV.

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behaviour from the standpoint now gained in the sense that the number of molecules split into ions continually increases with increasing dilution, and that the maximum value of conductivity corresponds to a (practically speaking) complete splitting up. Then x = 1, and the formula $\lambda =$ x(u+v) changes into the former, $\lambda = u+v$. Now, for most salts the maximum value is reached at a dilution of 1000l, and the decomposition is a dilution of 1000s, and the decomposition is nearly complete; it follows from this, that the law of Kohlrausch $\lambda = u + v$ holds good for this maximum dilution. This can be asserted for the strong acids and bases, such as HCl, HNO, KOH, and NaOH. On the other hand, as can easily be seen from the course of the numbers, the increase has not nearly reached its limit for acetic acid and ammonia at a dilution = 1000l: hence the value x is still very far removed from unity, and the law of Kohlrausch cannot hold in its simplest form.

On the assumption that the molecular conductivities of dilute solutions depend only on the number of ions present, the values of x can be easily calculated from a knowledge of the values of the conductivities at different dilutions, as well as of their maximum values; designating the molecular conductivity at the dilution of v litres by μ_{rr} , and the maximum value by μ_{ro} , then, according to the assumption made, v

Whether the above mentioned assumption is strictly correct cannot be asserted a priori. It must be looked upon as probable, since the resistances to motion which the ions experience, and which determine the velocities u and v, depend on the nature of the solvent, which in these cases is water; and considering the small differences which exist between the properties of very dilute solutions and those of water, no appreciable difference in the resistances to motion can be supposed to exist in those differently diluted solutions. But the admissibility of the assumption can also be put to experimental proof in-determining x on the one hand by the deviations from the laws of solution, and on the other hand by the equation just given.

If m_0 is the theoretical molecular weight, and m_0 -the molecular weight determined from the laws of solution (for instance, from the lowering of the freezing-point), then for electrolytes $m > m_0$; following van't Hoff, we put the ratio of

the two $\frac{m_0}{m} = i$. If, on the other hand, x is the

number of molecules split up, the total number of molecules being put equal to 1, and if n is the number of ions into which each molecule splits (for KCl n=2, for BaCl, n=3, &c.), the number of molecules in the solution will have increased in the ratio 1:1-x+nx, that is, in the ratio 1:1+(n-1)x, and we have, therefore, i=1+(n-1)x.

Arrhenius, to whom we owe this calculation,

has shown (Z. P. C. 1, 634) that in the greatest number of cases investigated there is an excellent accordance between the values of as calculated from the electrical conductivities and those deduced from the freezing-points. Individual cases which at first seemed to be exceptions have, on later investigation, also proved to be

subject to the law (Z. P. C. 2, 491), and the apparent deviations have been shown to be due to incorrect observations. It is only at greater concentrations, where the suppositions made in determining molecular weights from the freezing-points, and those made in determining x from the electric conductivities, become uncertain, and not applicable, that marked deviations are apparent.

In addition to this confirmation of Arrhenius assumption that in electrolytes a more or less considerable portion of the molecules is split up, a further confirmation has been found by W. Ostwald, which is based on the following considerations (Z. P. C. 2, 36, and 270). spontaneous decomposition which the electrolytic molecules undergo in solutions is of the nature of dissociation; and since, according to van't Hoff, the substances in solution are subject to the gaseous laws, it must be possible to represent the process by the same formulæ as hold for the dissociation of gases. Considering the simplest case, that each molecule splits into two parts, there holds for gases (vol. ii. p. 406) the relation $\frac{p_2^2}{}$ = constant, where p_1 is the partial p_1 pressure of the undecomposed portion, and p_2 that of the decomposed portion.

In order to apply this equation to electrolytes, we notice that the pressures are proportional to the numbers of the molecules, and inversely proportional to the volumes occupied by these. If x is the part dissociated, and v the volume, then $p_1 = a\frac{1-x}{v}$ and $p_2 = a\frac{x}{v}$; a represents a factor dependent on the units chosen. Further, according to the former equation, we have $x = \frac{\mu_v}{\mu_\infty}$; introducing these values into the dissociation equation, we get $\frac{1-x}{x^2}v = k$, where k is a constant,

and from this
$$\frac{\mu_v^2}{(\mu_\infty - \mu_v)\mu_\infty} = kv$$
.

This equation represents a relation between

This equation represents a relation between the conductivity and the volume, or the dilution, which must be followed by all binary electrolytes, if the assumptions made are correct.

The equation cannot well be tested in the case of salts, as these very nearly reach complete decomposition; the value $\mu_{\infty} - \mu_{\nu}$ thereby becomes very small, and the experimental errors exert a preponderating influence. Those electrolytes which are only partially dissociated, such as acetic acid &c., lend themselves much better to applying the test. Here also it seems as if a difficulty met us, the quantity \$\mu_{\infty}\$ not lending itself to direct measurement because, with the very great dilutions necessary, the inevitable impurities of the purest water make accurate measurements impossible. But the law of Kohlrausch provides us with a means for making the measurements. It appears that the salts of weak acids are dissociated to just the same extent as those of strong acids; it is possible, therefore, as was shown at pp. 192-8, to calculate the migration-velocity of the negative ion. On adding to this the migration-velocity of hydrogen. which can also be determined (p.493), the sum represents the conductivity of the completely

discociated acid—that is, μ_{∞} , the quantity sought (Ostwald, Z. P. C. 2, 840).

In this manner, then, we obtain all the data for testing the above equation, and it proves itself to be in direct accordance with the facts. The examination is best carried out by calculating the constant k for a number of values of \(\nu\) at different dilutions, and seeing whether it really is constant. In the following tables a few examples are given. The numbers hold for 25°, and are molecular conductivities referred to the mercury unit:—

Acetic acid, $\mu_{20} = 364$.

0	μ	100 <u>μ</u>	Ł
8	4.34	1.193	0.000180
16	6.10	1.673	179
32	8.65	2.380	182-
64	12.09	3:33	179
128	16.99	4.68	179
256	23.82	6.56	180
512	32.20	9.14	180
1024	46.00	12.66	177
			0.000180

The values of k, calculated from eight different measurements, agree within the limits of experimental error.

The osmotic pressure of acetic acid at v=8 corresponds to about three atmospheres, that at v=1024 to about $\frac{1}{45}$ atmosphere, or to 1.7 mm. mercury pressure. The dissociation law has, therefore, proved correct within these wide limits; no examination of the law so farreaching as this has ever been possible in the case of gases.

Further examples are: -

Cyanacetic acid, $\mu_{\infty} = 362$.

٠	μ	100 µ / µ ∞	*
16	788.0	21.7	0.00376
82	105⋅3	29.1	373
64	139.1	38.4	1° 374
128	176.4	48.7	861
2 56	219.1	60.5	362
512	260.9	72.0	361
1024	297.8	82.1	368
			0.00370

Here also the individual values of the constant vary irregularly about the mean value, so that the discrepancies have to be ascribed to experimental errors.

In the accompanying tables, which have been taken at random from a great number, the dissociation law proves itself everywhere to be accurate. It has, in fact, been verified in every case in the course of an investigation which, for reasons to be discussed later, has been carried out with more than 400 acids, and it can be looked upon as generally valid.

We must not omit to remark, however, that, as observed above in the cases of the very strong

Oxyisobutyric acid, $\mu_{\infty} = 855$.

	-	100 4 00	
32	20.05	5.65	0.000106
64	28.05	7.91	106
128	38.86	10.95	105
256	53.91	15.20	106
512	73.49	20.70	106
1024	99.52	28.05	106
	•		0.000106

Oxysalicylic acid, $\mu_{\infty} = 356$.

v	μ	100 µ	
64 128 256 512 1024 2048	84·1 112·5 147·0 187·0 230·0 270·4	23·6 81·6 41·3 52·6 64·7 76·0	0·00114 114 113 114 116 117
			0.00115

Orthochlorobenzoic acid, µ = 356.

υ	μ	100 µ µ ∞	Ł
64	89-2	25.1	0.00131
128	119.4	33.5	131
256	156-1	43.8	133
512	197.0 .	55.3	133
1024	238.7	67·1	184
			0.00132

acids, and the neutral salts, which are very nearly completely dissociated, the calculation of the constants becomes very uncertain, and that greater deviations exist between the observations and the formula than can be ascribed to experimental errors. Which of the assumptions already made will have to be modified in order to explain these small discrepancies cannot as yet be determined; but anyhow the discrepancies are so inconsiderable, and there are so many cases of agreement, that the deviations must be looked upon as of a secondary nature, and undoubtedly they will receive their explanation later on. It is well not to pass over in silence, nor to attempt to hide, such deviations from a law which is otherwise generally valid, since in most cases theoretical progress is connected with the investigation of the causes of deviations from general laws. Examples of this are found in the deviations of gases from the sin ple laws, and the theory connected with this by van der Waals, and in the deviations of some substances from the law of Avogadro and the elucidation thereof by the theory of dissociation.

Chemical applications.—The laws of electrical conductivity, as developed in the preceding pages, give us the means for solving many chemical problems. This they do, because they ive a deeper insight into the constitution of issolved substances than is afforded by the sual chemical methods. A series of such appliations is already contained in the preceding ages; others are considered in the following aragraphs.

The first of these applications is connected vith the question as to the nature and composiion of the current-conducting particles or ions of salts. The conception of Berzelius that these re the 'anhydrous' acid and base has, in the ight of Faraday's law, been recognised as erroieous. Afterwards, in analogy with the comounds of organic chemistry, the salts were looked ipon as having a unitary composition, and this riew is still generally held. But this conception cannot be regarded as quite correct, since it does not take into account the fundamental difference which undoubtedly exists between salt-like compounds and indifferent compounds, a difference which manifests itself chiefly in the capacities for reaction of the two groups. The conception of Berzelius rested on the correct recognition that salts are dual compounds; he had only misconceived their constituents.

The new electro-chemical theory of Arrhonius avoids both errors, and retains what is correct in each conception. The solid salts, and, according to concentration, a greater or smaller portion of the salts dissolved in water, 'salt' being understood to include acids and bases, have, it is true, a unitary composition; but that portion of them which is capable of reacting chemically, and which therefore is of preponderating interest to the chemist, is split binarily.

'Salts,' in the general meaning, are therefore substances which very readily undergo such a binary splitting, and herein lies their binary character, correctly recognised by Berzelius.

It is a most remarkable fact that in the splitting up of 'salts' their constituents appear in oppositely charged electrical conditions. This indicates that probably both phenomena stand in the closest connection. It may be asked whether the salts split up so easily because their parts readily acquire opposite electric charges, or, conversely, whether the parts are easily charged electrically because they are readily separated. Not less remarkable is the fact that whenever a salt molecule is split up an equal quantity of electricity is produced (or separated), independently of the nature of the parts. It is beyond doubt that this fact is of decisive importance for the recognition of the nature of electricity, as well as of that of chemical affinity; when the one is elucidated, the other will be so also. But which of the two will first be thus advanced cannot as yet be foreseen.

A further remarkable fact is, that pure salts at ordinary temperatures do not conduct appreciably; the ordinary solid salts do so as little as pure sulphuric acid, acetic acid, &c. Even the halogen acids HF, HCl, HBr, and HI, when liquefied by pressure or cold, are all non-conductors. According to the dissociation theory of electrolytes this is quite comprehensible; the pure substances do not conduct because they are not dissociated, and they are not dissociated because their molecules have no space wherein to dissociate, or because they do not possess sufficient mobility.

Whether dissociation occurs or not when salts are dissolved depends in a marked way on the nature of the solvent. Hydrochloric acid, which when liquid is not dissociated, dissociates at once when dissolved in water. But on using as solvent benzene, xylene, hexane, or ether, no dissociation ensues; these solutions are non-conductors (Kablukoff, Z. P. C. 4, 480). On using alcohols as solvent, methyl alcohol is found to behave almost like water; the solutions of hydrochloric acid in if have a molecular conductivity about three times smaller than aqueous solutions. The conductivities of the solutions become less and less as we use ethyl alcohol, isobutyl alcohol, and issantyl alcohol.

It is still quite unknown what the condition is which determines the property of different solvents to cause dissociation to a different degree, and it is not known whether, as is somewhat probable, these effects remain proportional in the cases of all salts. Here it seems, however, as if the capability of the solvent itself to separate into ions, even if to a small degree only, determined its power to cause the dissociation of substances dissolved in it.

Although the questions just mentioned still await solution, partly for lack of experimental researches in this domain, yet the new conception of the binary character of salts allows us to distinguish more sharply between the different classes of these compounds than was possible before. This is especially so in the case of the so-called double salts. This name is at present somewhat uncertain in its application. Potassium copper sulphate K2SO1.CuSO1 is called a double salt, but sodium platinichloride is also formulated as such, 2NaCl.PtCl.; the first formula is correct, but the latter is wrong. This is so because potassium copper sulphate gives all the reactions of potassium sulphate as well as those of copper sulphate, but from sodium platinichloride silver solutions do not precipitate silver chloride as from sodium chloride, but silver platinichloride Ag, I'tCl. (Jörgensen, J. pr. [2] 16, 345). It is probable, therefore, that sodium platinichloride is a salt of chloroplatinic acid H.PtCl_g. If this is correct, the ions of the sodium salt are 2Na and PtCl_g, and in electrolysis the platinum must not, like the other metals, go to the cathode, but as a constituent of the acid radicle to the anode. And, in fact, Hittorf has proved (P. 106, 520) that this is the case.

Similarly with other salts; for instance, that which is obtained from chromium oxide and potassium binoxalate, and which has the empirical formula 3K₂C₂O₄Cr₂(C₂O₄)₃. Since this salt gives no pp. with calcium salts it cannot be regarded as an oxalate. In fact, in electrolysis the chromium goes to the anode; the chromium is, therefore, a constituent of the acid radicle, and the salt must be looked upon as the potassium compound of a tribasic chromoxalic acid (HC₂O₄)₃Cr—that is, as K₁C₄O₁₂Cr (Kistiakowsky, Z. P. C. 6, 107).

Such salts, therefore, are not double salts, but are salts of complex acids; it is possible to test, in the way already indicated, in every cas, whether a definite salt is a true double salt or the salt of a complex acid. One xamination we find that, not a double salt, but a salt of a

complex soid is present whenever the reactions of the salt in question are not those of its constituents. This decision is specially convenient when the solution of the salt is coloured. Because, since the properties of the positive ions, and therefore their colour also, are independent of the negative ions, it will always be possible to conclude that the positive ions are no longer present when their colouration disappears. In the easily decomposable salt 2KCN.Ni(CN), we must not see a double salt, but the potassium salt of cyano-nickelic acid H₂Ni(CN), because its solution is yellow, and not green as solutions of the nickel salts are which contain nickel as an ion.

The line of demarcation between the two groups of salts, however, is not absolute, as many salts exist which in aqueous solutions are both double salts and also complex ones. This is the case with potassium ferri-oxalate, for instance. Since this salt is green, while all true ferric salts are yellow or brown, it may be concluded that it is a complex salt, the compound of a ferri-oxalic acid H, C,O12Fe analogous to the above-mentioned chromo-oxalic acid. The solution of this salt gives, however, a precipitate with calcium solutions, which proves it to be an ordinary oxalate, but on the other hand the iron goes to the anode. From this it is seen that the aqueous solution contains chiefly the ions 3K + C_sO₁₂Fe, but that a portion of the salt has split in the manner of a double salt into potassium oxalate and ferric oxalate, which on their part form the corresponding ions.

The study of such cases has as yet scarcely been begun, because until now we possessed neither theoretical nor experimental means for answering the questions which arise. The electrical methods, in conjunction with the methods for the determination of molecular weights arising out of the theory of solutions, flow afford casy access to these hitherto closed and uncultivated domains.

The dissociation-constants of organic acids. The only province of chemistry which has been studied somewhat thoroughly in the light of the new electro-chemical theory is that of the organic acids. We have seen above that the molecular conductivity of these can be

represented by the formula
$$\frac{\mu_v^2}{(\mu_{\infty} - \mu_v)\mu_{\infty}} = kv$$
.

This formula contains only the single constant k, which constant depends on the nature of the acid, the temperature, and the solvent, but is independent of the dilution. At a given temperature, and in the same solvent, the quantity k is therefore a measure of the electrical conductivity, and hence it is the capacity for reaction of the acid; for the substance considered, k therefore represents the long sought for numerical value of the chemical affinity.

It is remarkable that the two conflicting views concerning the nature of chemical affinity, as represented by Bergmann and Berthollet (cf. vol. i. 68) here coincide. Berthollet, who represented the affinity as dependent on the mass, was right, and so was Bergmann, who desired to represent it by a constant. By accurately formulating the idea of the influence of mass as given by Berthollet, we obtain in the equation for the

chemical effects a co-efficient independent of the quantity—that is, one referred to the chemical unit of quantity, which is Bergmann's measure of chemical affinity.

of chemical affinity.

It has already been shown (vol. i. 81) that the electrical conductivities bear a definite relation to the composition and constitution of the acids. But the law of dissociation of electrolytes had not been discovered at the time when the article referred to was written, and the observed relations could not be represented numerically. This has now become possible, by means of the vaffics of the constant k, which have been measured for about 400 acids (Ostwald, Z. P. C. 3, 170; Bethmann, ib. 5, 885; Bader, ib. 6, 289).

Before expounding these relations, it will first be shown how the laws which have been found empirically for the electrical conductivities follow directly from the above dissociation-formula. In order to make the consideration easier, the formula will first be somewhat simplified by substituting for the molecular conductivity μ_{ν} its value referred to the maximum $\frac{\mu_{\nu}}{\mu_{\nu}} = m$.

The equation then assumes the simple form $\frac{m^2}{1-m} = kv.$

In the first place, we see that as the dilution v increases infinitely, the quantity 1-m must approach zero. Hence m must approach unity; hence the electrical conductivity increases with dilution up to a maximum, as has been shown by experience.

Further, it was found that when at any dilutions, v_1 and v_2 , two different acids have the same (relative) conductivity, they also have the same at other dilutions v_1 and v_2 , as long as the new dilutions are in the same ratio as the old ones—that is, when $v_1: v_2=v_1': v_2'$. This follows from the formula in this way: on the supposition that the relative conductivities are the same,

we have first of all
$$\frac{m^2}{1-m} = k_1 v_1$$
; $\frac{m^4}{1-m} = k_2 v_2$;

therefore $k_1v_1 = k_2v_2$. And in the same way for the other dilutions, $k_1'v_1' = k_2'v_2'$, from which it follows directly that $v_1: v_2 = v_1': v_2'$.

In addition, F. Kohlrausch had already pointed out that in the cases of acids which conduct badly (which, therefore, are but little dissociated), the molecular conductivity increases nearly as the square root of the dilution. If in the equation $\frac{m^2}{1-m} = kv, m \text{ is very small, } 1-m \text{ differs little}$

from unity, and can be looked upon as constant; then approximately, $m^2 = kv$, or $m = \sqrt{kv}$.

Finally, on taking the logarithms of the dilutions as abscissmend the values of m as ordinates, we also get from the formula a curve resembling a tangent-function (vol. i. page 82); the interpolation-formula given in vol. i. must be replaced by the present rational formula.

As regards the meaning of the constant k, we recognise what this is on putting m = 0.5, when we get $2k = \frac{1}{v}$. 2k is therefore the reciprocal value of the volume, or the concentration at which the electrolyte is just half dissociated. This number is extremely characteristic for different contents of the concentration of the concentration at which the electrolyte is just half dissociated.

ferent acids, since its value may vary according to the nature of the substance between the limits 1 and 1,000,000.

The measurement of the quantity k for differacids has led to the following general law:— The constant k is approximately the product of a number of factors, each of which depends on the nature of the constituents of the acid and on their. position relatively to the carboxyl group.

In order to realise what this law implies, and in what manner it is applied, we will proceed to discuss in the following pages the most important groups of the organic acids. The relations, the main features only of which could formerly (vol. i. page 82) be investigated, can now be represented numerically with perfect exactitude. The numerical values for k have been multiplied by 100 in order to get rid of ciphers; they all hold for aqueous solutions at 25°.

The fatty acids. The following constants were measured:—

Formic acid has the highest constant; the replacement of its hydrogen by methyl reduces the constant to half its value. But on again replacing one hydrogen atom in acetic acid by methyl the constant only decreases to $\frac{1}{1.4}$ of

its value, and further similar substitutions no longer produce a weakening of the acid, but some of them even bring about a slight strengthening. These changes are, however, but small, so that the constants of acids of this sories having more than three carbon atoms vary irregularly about the mean value 0.0014.

It is evident, then, that the substitution of hydrogen by methyl acts quite differently, according as it occurs next to the carboxyl or at a greater distance from it. This is a result which will atterwards be shown to hold good in all cases; on the whole, the effect of each substituent is the smaller the more distant it is from the carboxyl. The inference that the interposition of even two carbon atoms nearly counteracts the effect is correct for methyl, for which it is relatively small. Other constituents of greater energy extend their action further, but yet not over more than three or four atoms of the 'open chains'; in the case of 'closed chains' other relations hold good.

Halogen derivatives of the fatty acids. The entrance of chlorine in the place of hydrogen in the fatty acids exerts very considerable influence. The constants are—

1:86:2840:67200. The ratio of the values of the constants for the different acids, referred to the entrance of each separate chlorine atom, is 84, 33, and 24. It is only the ratios of the constants, and not their differences, which are

important; the ratios, though not equal, are yet of the same order of magnitude, while the differences between 0.155, 5, and 121 are quite incomparable. Further, it follows that the relative change of the constants for the entrance of each chlorine atom is not of the same value; the first chlorine atom acts more intensely than the second, and the second more intensely than the third. We shall again meet with a similar relation when dealing with substitution in connection with the same carbon atom. From this it may be concluded that the first chlorine atom which enters into acetic acid exerts its influence under more favourable conditions, therefore probably from a less distance, than the second and third, and it becomes evident how well such measurements lend themselves to investigations and examinations of the relations in space of the atoms within the molecules. The action of other elements and radicles is very similar to that of chlorine.

Monobromacetic acid CH_Br.CO_H . 0.138 Cyanacetic acid CH_CO.H . 0.370 Thiooyanacetic acid CH_SCN.CO_H . 0.265 So-called 'carbamine thioglycollic acid 'CH_(SCONH_)CO_H . 0.0246 Isothiocyanacetic acid C_1H_O_S.N . 0.0000246 Thiacetic acid CH_COSH . 0.0469

The constant of monobromacetic acid does not differ much from 0.155, that of monochloracetic acid, hence both halogens exert about the same influence. Cyanogen acts much more intensely. The ratio of cyanacetic acid to acetic acid has risen to 205 (from 86). Thiocyanacetic acid also is stronger than monochloracetic acid. but not so strong as cyanacetic acid, though sulphur is generally a negative substituent-that is, one which augments the acid properties. The idea of relations in space at once suggests itself; by the introduction of sulphur there has, in fact, taken place, on the one hand, an increase in the acid properties, but on the other hand, since the cyanogen is removed to a greater distance from the carboxyl, there has been a weakening, and the latter effect preponderates over the former. By taking up water, thiocyanacetic acid easily passes into the acid CH. SCONH, CO.H, the group CN changing into CO.NH. This transformation is accompanied by a marked decrease in the conductivity, the constant falling to less than a tenth of its former value: The change can be conveniently studied in an aqueous solution of thiocyanacetic acid, by determining its electrical conductivity; the conductivity decreases continuously, and after even a few days the greater part of the thiocyanacetic acid is found to be changed. Finally, there is a compound isomeric with thiocyanacetic acid, which Volhard (J. pr. [2] 9, 6) obtained by the action of hydrochloric acid on sulphohydantoin, and which is isothiocyanacetic acid. The constant for this compound is 10,000 times smaller than that for thiocyanacetic acid; it is also smaller than that of any other carbon acid, so that the inference must be drawn that the substance is not a carbon acid at all. This confirms the view expressed by Liebermann, and the reasons for which were given by Hantzsch (B. 20, 3129), that the compound is a dioxy-

The feebly acid properties are ascribed to the hydrogen of the innide group. The thiacetic acid mentioned at the end of the last table contains sulphur in the place of oxygen in the hydroxyl of the carboxyl. In accordance with the negative nature of sulphur, this acid proves to be twenty-six times stronger than acetic acid, and this factor may be looked upon as the greatest to which sulphur can give rise when replacing oxygen, because in this case the sulphur atom acts from the most favourable position which is ever possible.

Oxyacetic acid and its derivatives.

Glycollic acid CH, OH.CO, H	0.0152
Methoxy-acetic acid CH, (OCH,)CO,H	0.0335
Ethoxy-acetic acid CH2(OC2H3)CO.H	0.0234
Phenoxy-acetic acid CH2(OC,H3)CO2H	0.0756
Glyoxylic acid CH(OH), CO, H	0.0474

The replacement of hydrogen by hydroxyl in acetic acid produces a rise in the constant of 9 times its former value; hydroxyl, therefore, acts much less intensely than the halogens. By introducing a second hydroxyl the constant again becomes greater, but only 3.1 times greater. Here we find quite the same effects as in the cases of mono- and di-chloracetic acid, the second substitution of the same substance acting less strongly than the first. In the numerical values, even, we cannot overlook a certain correspondence; in the case of chlorine the ratios are 1:86 and 1:33; in the case of hydroxyl they are 1:9, and 1:31. It may therefore be said that, using round numbers, in the derivatives of acetic acid chlorine acts ten times as intensely as hydroxyl. When the hydroxylic hydrogen of glycollic acid is replaced by radicles, the constant changes, and, strange to say, methyl acts in this case in a strengthening manner, the constant rising to a little more than twice its former value. The substitution of hydrogen in this methyl by methyl again has a weakening effect, as is the case with the fatty acids; ethoxy-acetic acid is 1.4 times weaker than methoxy-acetic acid. Finally, by the introduction of phenyl, the constant becomes appreciably greater; it is about five times as great as that of glycollic acid, and is 2.3 times greater than that of methoxy-acetic acid. The ratio is smaller than that between acetic acid and benzoic acid, which is 1:3.3, an indication that the exchange of methyl for phenyl has in the latter case taken place in greater proximity to the COOH group, a con-clusion which follows also directly from the

A number of other substances related to glycollic acid have given the following numerical values:—

vanues:—
Thioglycollic acid CH₄(SH)CO₂H. 0.0225
Thiodiglycollic acid S(CH₂CO₂H), 0.048
Dithodiglycollic acid S₂(CH₂CO₂H), 0.065
Digiycollic acid O(CH₂CO₂H), 0.11
As the constant of glycollic acid is 0152, we

As the constant of glycollic acid is 0152, we see that the substitution of S for O in hydroxyl has caused the constant to increase 1.5 times; now, as substitution of S for O in OOOH of acetic

acid increased k from 1 to 26, we see here also the great influence of the position occupied by the replacing atom.

The three other acids quoted in the last table are dibasic, and the question at once arises how their constants must be calculated, since the dissociation-formula has been developed for binary electrolytes-that is, for monobasic acids only, and not for ternary ones, to which class the dibasic acids belong. It can, however, easily be shown that, as long as the dissociation is not great, the weaker dibasic acids are not electrolysed according to the formula $2H+R^n$, but according to the formula H+HR. In other words, at first one hydrogen atom only is split off, and the dissociation takes place according to the binary scheme of the monobasic acids. This follows from the fact that the change in the molecular conductivity of such acids can be represented by the same formula $\frac{m^2}{1-m} = vk$, so

that k remains constant. But the formula calculated on the assumption of a dissociation according to the scheme $H_1 h^{n_1} = 2H + R$ does not represent the change in the conductivity of these acids as determined by experiment.

Malonic acid CH₂(COOH)₂ may serve as an example of dibasic acids. It gives:—

•		m	100#
16	53'1	0.149	0.159
32	72.3	0.202	0.159
64	97.1	0.272	0.158
128	128.5	0.359	0.157
256	165.9	0.464	0.157
512	208.8	0.586	0.162
1024	253.2	0.708	0.168
2048	294.2	0.823	0.187

The constant does not change till the value m=0.586 is reached—that is, till about half the acid has been dissociated according to the binary scheme; then it becomes greater—a sign that henceforward the formula loses its validity, and that the decomposition according to the ternary scheme 2H+R'' begins to assume an appreciable value.

If, on the other hand, we attempt to calculate the conductivity according to the formula corresponding to ternary dissociation $\frac{m_s}{(1-m)v^2} = k$, the values of k decrease very rapidly and are far from being constant.

The values for the constants of dibasic acids given in the table preceding the last one have been calculated on this principle, and refer, therefore, to the first stage of binary dissociation H.R = HR + H.

H.R=HR+H.

*Comparing thioglycollic acid with thiodigly-collic acid and dithiodiglycollic acid, we find that the constants do increase distinctly, though only slightly; they are 0 v255, 0 048, and 0 065, and are in the ratio of 1:2:1:2.9. When, therefore, the residue of acetic acid, CH_CO_H, enters thioglycollic acid, this process has no appreciable influence on the constant. On the other hand, the constant of diglycollic acid. From the fact that the same substituent produces such different

effects in glycollic acid and in thioglycollic acid, it may be presumed that in the first case the oxygen brings the negative substituent nearer to the carboxyl than the sulphur does in the second case, and this presumption may be further utilised for hypotheses concerning the configuration of the sulphur atom, and the arrangement of the allinity points on it. It has, however, not yet been established with certainty that the greater or less distance of the groups is the only cause of their different actions, and there are some circumstances which allow us to conclude that other conditions are effective also; therefore, until these have been cleared up, conclusions such as the above hold only hypothetically.

Derivatives of amido-acetic acid.

Phenylamido-acetic

acid CH_(NHC,H_)CO_H . 0.0039

Hippuric acid CH_(NH.CO.CH_)CO_H . 0.0222

Aceturic acid CH_(NH.CO.CH_)CO_H . 0.0230

Phthalvlamido-acetic acid

 $CH_2(NC_2O_2C_6H_1)CO_2H$. . 0-100

Amido-acetic acid has not the character of an acid; the basic NH₂ group completely removes the acid properties of acetic acid. But if negative radicles are introduced into NH₂, well defined acids are again obtained. Phenyl has this effect, the constant of phenylglycocoll is 2·2 times as great as that of acetic acid. The constants of the acids obtained by introducing CO.C.H. and CO.C.H. for H in NH₂ are 12 to 13 times greater than that of acetic acid. The substitution of the divalent residue of phthalic acid for the two hydrogen atoms in the NH₂ group raises the constant of acetic acid 55 times.

Derivatives of propionic acid.

Propionic acid CH_xCH_xCO_xH . 0.00134 Lactic acid CH_xCH(OH)CO_xH . 0.0138 β-Oxypropionic acid CH (OH).CH_xCO_xH 0.00311 Glyceric acid CH_xOH.Cli.OH.CO_xH . 0.0228 β-Iodopropionic acid CH_xLCH_xCO_xH . 0.0090 Trichlorlactic acid CCl_xCH.OH.CO_xH . 0.465

The constant of d-oxypropionic or lactic acid is 10 times greater than that of propionic acid, but the constant of \$\beta\$-oxypropionic acid is only 2.3 times greater than that of propionic acid. The difference in the action of the same substituent, according to its nearer or more distant position relatively to COOH, asserts itself most clearly. The ratio between propionic acid and lactic acid is slightly greater than that between the analogods substances acetic acid and glycollic acid (1:9); it is, therefore, not quite immaterial whether the substitution does or does not take place in the group CH3. influence of the more distant position of the substituent can be recognised in \$\beta\$-iodopropionic acid and trichlorolactic acid. The first is only 6.5 times stronger than the parent substance. No measurement of α-iodopropionic acid has yet been made, but there is little doubt that iodine In the α- position must act very similarly to chlorine or bromine, and must, therefore, increase the sonstant by 70 or 80 times. The effect in the 3- position is 10 to 12 times less than this. the same way the substitution of 3Cl for 3H in 3H2.COOH increases k about 67,000 times; but he introduction of 8Cl into CH, CHOH.COOH n the β - position increases k only about 33-7

times. The ratio of these effects is about 1:2000; calculated for each Cl atom the ratio is $\frac{\sqrt[3]{2000}}{2000} = 12.6$; this ratio comes very near that estimated for α - and β -iodopropionic acids.

Derivatives of higher fatty acids.

Oxylsobutyric acid (OH₂)₂CH.OH.CO₂H 0-0108

Mononitrocaproic acid O₂H₁₀(NO₂).CO₂H 0-0123

Dinitrocaproic acid O₂H₁₀(NO₂)₂CO₂H . 0-069

Lævulinic acid CH₂CO.CH₂CH₂CO₂H 0-00255

Since the constant of isobutyric acid is 0.00144, the hydroxyl in the a-position here causes the factor 7.4, whigh is somewhat smaller than 9, the corresponding ratio between acetic acid and glycollic acid.

The ratio between caproic acid and its mononitro-derivative is 1:8.5. Since, as will soon be shown, the nitro-group has a more strongly negative action than chlorine, NO₂ must, in the present case, be in the \$\beta\$- position. The same holds for the dinitro-compound; it is 5.6 times stronger than the mononitro-compound; it is again evident that the second negative group has less effect than the first.

Levulinic acid, or β -acetyl-propionic acid, allows us to recognise the smaller influence to be expected of the acetyl in the β - position; the constant is only 1.9 times larger than that of propionic acid.

Benzoic acid and its derivatives. The largest and most varied group of allied substances that has been investigated so far, is that of benzoic acid and its derivatives, and consequently it has been possible to trace here many and striking regularities.

Benzoie acid C_aH₄CO₂H . . . 0-0060
Salicylie acid C_aH₄(OH)CO₂H . . . 0-102
m-Oxybenzoie acid C_aH₄(OH)CO₂H . 0-0087
p-Oxybenzoie acid C_aH₄(OH)CO₂H . 0-00286
Oxysalicylie acid [1:2:3] C_aH₄(OH)₂CO₂H 0-114
Oxysalicylie acid [1:2:4] C_aH₄(OH)₂CO₂H 0-052
a-Resorcylie acid [1:2:6] C_aH₄(OH)₂CO₂H 0-052
a-Resorcylie acid [1:2:6] C_aH₄(OH)₂CO₂H 5-0
Protocatechuie

acid [1:3:4] C₄H₃(OH)₂CO₂H . 0.0033 m-Dioxybenzoic acid C₄H₄(OH)₂CO₂H . 0.0091 Gallic acid [1:3:4:5] C₄H₂(OH)₂CO₂H . 0.0040 Pyrogallic acid [1:2:3:4] C₄H₄(OH)₄CO₂H 0.055 Phloroglucin carboxylic

acid [1:2:4:6] C,H,(OH),CO,H 2·1

The numbers indicate the positions of the OH groups relatively to COOH supposed to be in position 1.

This table contains the constants of all hydroxyl-benzoic acids known up to the present time. These show such close connections with the their that, knowing the constants of benzoic each of the three monoxybenzoic acids, those acid and of the can be calculated approximately. of all the other can be calculated approximately. It is true the constitutions of the constants of the constants of the constants.

Between the consuche ratio is 1:17. This value ortho-oxy-derivative $t_{i,0}$ when OH is introduced is larger than the ratio, $t_{i,0}$ when OH is introduced in the a-position into red 10; in the β -position, the ratio did not exce he constitution of salicylie which corresponds to $t_{i,0}$ larger than 2.3. From this acid, the ratio was not larger than 2.3. From this

it appears that the ortho-position involves a much closer relation in the benzene nucleus than even the a- position in the open chain, a fact which later on will be confirmed in many ways, and which seems to be of great importance in dealing with the question concerning the constitution

of benzene.

The constant is increased but slightly by OH in the meta-position. But in the para-position the hydroxyl even produces a diminution of the constant to rather less than half the value. We deal in this case, therefore, not only as usual with a greater or smaller value of the influence exerted by a substituent according to its position, but with a reversal of the direction in which the influence is exerted. This fact, which has already become evident in the case of methyl, recurs with other feebly negative substituents in the paraposition of the benzene nucleus. This promises to become very important in the construction of a theory to explain these phenomena.

We have then the following factors for the

influence of the hydroxyl :-

Ortho 1:2 or 1:6 = 17 Mota-1:3 1:5 = 1.4 •• 1:4 = 0.5Para-

By their help we are able to calculate the constants of the di- and tri-oxybenzoic acids by multiplying the constant of benzoic acid by the corresponding factor for every hydroxyl intro-duced. It must be remembered that such a calculation can only give approximate results; for we have seen that substituents already present some-what influence the magnitude of the factor of a newly entering substituent, and that, generally, by decreasing it. It is, therefore, only the order of magnitude of the constants, and not their exact value, that we shall be able to find in the manner indicated.

Four dioxybenzoic acids can be derived from salicylic acid; the constants of these four acids are calculated thus :-

```
1:2:3 gives .0060 \times 17 \times 1.4 = 0.143
1:2:4
                 0060 \times 17 \times 0.5 = 0.051
                 0060 \times 17 \times 1.4 = 0.143
1:2:5
         ,,
                 .0060 x 17 x 17 = 1.73
1:2:6
```

The numbers observed are 0.114, 0.052, 0.108, and 50. In the case of the first and the third acid which both contain a hydroxyl in the m-position, a diminution of the combined effect therefore makes itself felt as usual. In the second acid 1:2:4, calculation and experiment completely agree; while the fourth acid 1:2:6, which contains two ortho- hydroxyls, shows a value about three times greater than is furnished by the estimation. We shall see later that this behaviour is common; two substituents in the orthe position do not, as is otherwise usual, weaken one another, but reinforce each other's

For the two dioxybenzoic acids still remaining we must expect the following constants:

```
1:3:4 gives .006 \times 1.4 \times 0.5 = 0.0042
1:3:5
          " .006 \times 1.4 \times 1.4 = 0.012
```

Measurement gives 0033 and 009, both constants being therefore as usual somewhat smaller, a consequence of the combined effect, yet being quite of the expected order of magnitude.

The six possible trioxybenzoic acids allow us to estimate the following constants:

```
1:2:3:4 gives .0060 \times 17 \times 1.4 \times 0.5 = 0.07
                 .0060 x 17 x 0.5 x 17 = 0.9
1:2:4:6
1:3:4:5
                 ·0060 × 1·4 × 0·5 × 1·4 = 0·006
1:2:3:5
                 ·0060 × 17 × 1·4 × 1·4 = 0·2
          ••
                *0060 × 17 × 0.5 × 1.4 = 0.07
1:2:4:5
1:2:3:6
                0060 \times 17 \times 1.4 \times 17 = 2.4
```

Of the six possible trioxybenzoic acids three are known and measured. The comparison between the observed and estimated constants gives 0.055 instead of 0.07; 0.004 instead of 0.006, where as usual the observed value is smaller than the estimated value; and in the case of the acid with two hydroxyls in the ortho-position we have 2.1 observed instead of 0.9 estimated, which therefore, as before, is about twice as great. In the same way we may expect in the cases of the three trioxybenzoic acids still unknown, that the real constants of the acids 1:2:3:5 and 1:2:4:5 will be somewhat smaller than the estimated values, and therefore about 0.15 and 0.05, while the third acid 1:2:3% with two ortho- hydroxyls will probably have a constant from 5 to 5.5. spite of the uncertainty of the estimation, the differences are so considerable that when in future one of these acids is prepared the determination of the conductivity of an aqueous solution will suffice to decide its constitution.

The constitutional relations of the oxybenzoic acids, as indicated by the dissociation constants, are therefore in complete agreement with those

deduced from chemical relations.

The methods just expounded may be directly utilised for elucidating constitutional relations. On heating orcin C_aH₂(OH),CH, with KHCO_a there is formed 'paraorsellic acid,' whose constitution must correspond either to that of a- or \$-resorcylic acid. On measurement, the constant appeared to be 4.1; the acid has, therefore, a constitution analogous to that of a-resorcylic acid, corresponding to the arrangement CO,H:OH:OH:CH, = 1:2:6:4.

Further substitution products of benzoic acid gave the following numbers:-

```
o-Chlorobenzoic acid C_0H_1Cl.CO_1H

m-Chlorobenzoic acid C_0H_1Cl.CO_2H

p-Chlorobenzoic acid C_0H_1Cl.CO_2H
                                                                         0.182
                                                                         0.0155
0.0098
o-Bromobenzoic acid C<sub>e</sub>H<sub>e</sub>Br.CO<sub>2</sub>H
m-Bromobenzoic acid C<sub>e</sub>H<sub>e</sub>Br.CO<sub>2</sub>H
                                                                         0.145
                                                                         0.0137
Monobromgallie
    acid CaHBr(OH),CO.H
                                                                         0.059
Dibromgallic acid C.Br. (OH), CO.H
                                                                         1.21
m.Fluobenzoic acid C.H.F.CO.H.
                                                                         0.0136
m-Cyanobenzoic acid C.H.ON.CO.H
                                                                         0.020
o-Nitrobenzoic acid C<sub>e</sub>H<sub>1</sub>NO<sub>2</sub>CO<sub>2</sub>H
m-Nitrobenzoic acid C<sub>e</sub>H<sub>1</sub>NO<sub>2</sub>CO<sub>2</sub>H
                                                                         0.616
                                                                         0.0345
p-Nitrobenzoic acid C.H.NO.CO.H.
                                                                         0.040
Bromonitrobenzoic
    acid [1:2:5] C<sub>e</sub>H<sub>s</sub>BrNO<sub>2</sub>CO<sub>2</sub>H
o-Amidobenzoic acid C<sub>4</sub>H<sub>4</sub>NH<sub>2</sub>CO<sub>2</sub>H
p-Amidobenzoic acid C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>CO<sub>2</sub>H
                                                                         0.0010
                                                                         0.0012
o-Acetamidobenzoic
acid C<sub>e</sub>H<sub>4</sub>(NHCOCI;<sub>2</sub>)CO<sub>2</sub>H
m-Acetamidobenzoic
                                                                         0.024
    acid CaH, (NHCOCH, )CO2H
                                                                         0.0085
p-Acetamidobenzoic
    acid C,H,(NHCOCH,)CO,H
                                                                         0.0052
   Acetoxybenzoic
    acid C.H.(OCOCH,)CO.H
```

Acetoxybenzoic acid C.H.(OCOCH.)CO.H 0.033.

0.0042

The same conclusion may be drawn from these numbers as to the influence of the halogens as had been deduced for hydroxyl-namely, that the ortho-position is that of greatest influence. The constant of benzoic acid rises to 22 times its value on the introduction of chlorine in the ortho-position, to 2.6 times its value when Cl is put in the meta-position, and to 1.5 times its value when Cl is put in the para- position. But along with this there is a remarkable difference between the behaviour of OH and that of Cl; hydroxyl acts much more strongly in the orthoposition of the benzene nucleus than in the a- position of the open chain, while chlorine, which in the a-position of the open chain in-creases the constant to more than 80 times its value, does so only 22 times when in the of thoposition in the benzene nucleus. For this discrepancy the explanation offers itself, on the one hand, that the system of carbon atoms which constitutes the benzene nucleus is not rigid, but alters its form according to the atoms present in it, and that if so, the difference in form must be especially great according as hydroxyl or chlorine enters near the carboxyl. On the other hand, the following possibility strikes us. According to the hypothesis of Kekulé, there are two sorts of ortho-positions, the one being represented by a double, the other by a single, linkage. Now it is quite possible that in benzene itself the change of the double or single linking to the right or the left takes place easily, but that when two adjoining carbon atoms have fixed different atoms or groups of atoms, only one sort of linkage, either a single one or a double one, is stable. Assuming that -in salicylic acid, for instance-double linkage exists between the carbon atoms, combined with COOH

carboxyl and hydroxyl respectively,

while in o-chlorobenzoic acid the single linkage

only is stable, CCl , the difference empha-

sised above can be understood, since in the first case the ortho-relation is a much more intimate one than in the second.

The small changes which the constant of benzoic acid undergoes in m- and p-chlorobenzoic acid correspond to the greater distance of the chlorine from the carboxyl. According to the usual representation of benzene, the influence of the para-position proves to be the smallest. But this behaviour is by no means general.

Bromine behaves very similarly to chlorine. The effect for the ortho-position is somewhat larger than for chlorine—i.e. 24 instead of 22; that for the meta-position somewhat smaller—2-3 instead of 2-6.

When hydrogen in gallic acid is replaced by bromine in the ortho-position, the constant increases to 15 times its value, therefore less than in the case of benzoic acid. This corresponds to the general rule that several substituents simultaneously present diminish each other's action. Only when two substituents, which are the same, occupy the ortho-position is an increase in the simultaneous effect to be observed; in fact, a second bromine atom which occupies the ortho-position brings about a greater rise of the constant than does the first —21 instead of 15.

Hydrofluor cacid being much weaker than hydrochloric acid, it was to be expected that the fluobenzoic acids would be weaker than the chlorobenzoic acids. In case of the meta-compound this occurs, however, only to a small extent; the constants differ but little, and are nearly the same for the bromo- and fluo- compounds. It would be of interest to determine whether in the ortho- position also fluorine acts as strongly as chlorine, but o-fluobenzoic acid has not yet been examined; m-cyanobenzoic acid. This completely corresponds to the fact that cyanacetic acid is much stronger than chloracetic acid.

From measurements of the nitrobenzoic acids, the group NO₂ appears to be the most effective negative substituent. The ortho-compound exhibits a 103-fold increase of the constant, the meta-compound an increase equal to 5-8-fold, and the para-compound a 6-7-fold increase. With regard to the influence of position, the numbers agree with those found for the ohloro- and bromo-compounds, in so far as the ortho-position is again that of greatest influence; but, on the other hand, the influence of the nitro-group makes itself more felt from the para-position than from the meta-position, in opposition to the relations found in the case of chlorine.

Bromonitrobenzoic acid contains the subtine constant is made up of that of benzoic acid, and of the factor of the o-nitro group 103, and that of the m-bromine 2·3, and is therefore calculated to be 1·38, which agrees well with 1·4, the value found by experiment. In this case, therefore, the mutual influence of the simultaneously present substituents is practically zero.

The constants of o- and p- amidobenzoic acid show that the amido- group considerably reduces the strength of the acid. But the values quoted can only be looked upon as approximations, since peculiarities appear in the determinations which are not yet elucidated.

But the numbers become regular when the basic properties of the amido- residue are compensated by the introduction of acetyl. Of the three acetamidobenzoic acids the ortho- compound is the strongest, it surpasses benzoic acid by four times its value. The meta-compound is only 14 times as strong as benzoic acid, and in the para-position the atomic group NHCOCH, acts similarly to hydroxyl—that is, it exerts a weakening effect—the constant is only 0-86 of that of benzoic acid. The acetyl-oxybenzoic acids behave quite similarly; their factors re-

latively to benzoic acid are 5.5, 1.6 and 0.76. On comparing with these and the former numbers the factors of the oxybenzoic acids-namely, 17, 1.4, and 0.5-it follows that the substituent which in the ortho-position acts most strongly also exerts the greatest weakening influence in

the para- position.

But this relation again is not universal. Replacement of hydroxylic hydrogen by methyl in salicylic acid produces a quite extraordinary weakening of the acid; instead of 17 times, the constant is only 1.4 times, as great as that of benzoic acid. In the para-position, however, the same change produces scarcely any effect; the constants of p-oxybenzoic acid and of p-methoxy-benzoic acid or anisic acid are nearly the same, and the decreasing effect of the group OCH, is much greater in the para- than in the ortho- position.

It is further remarkable that acetosalicylic acid is weaker than salicylic acid, in spite of acetyl being a negative radicle. It may be that the cause of this curious behaviour is to be found in a change of linkage similar to that mentioned

ahova.

Homologues of benzoic acid.

o-Toluic acid C,H,(CH,)CO,II .	0.012
m-Toluic acid C.H. (CII,)CO.H .	0.0051
p-Toluic acid C,H,(CH,)CO,H	0.0052
Phenylacetic acid C.H.CH.CO.H	0.0056
Phenylpropionic	
acid CH ₃ .CH(C ₆ H ₄)CO ₂ H	0.004
p-Phenylpropionic	
acid CH ₂ (C ₆ H ₅)CH ₂ .CO ₂ H .	0.0023
Cuminic acid C.H. (C.H.,)CO.H .	0.0050

A comparison of the constant of benzoic acid with those of the toluic acids shows that a doubling of value has occurred by the introduction of methyl into the ortho-position, but that, as usual, the methyl group in the meta or paraposition has a slightly weakening effect. The isomeric phenylacetic acid also has a very similar constant. This constant is 3.1 times greater than that of acetic acid—an indication that phenyl is a negative radicle - but it does not attain to the value of benzoic acid.

The constants for the two phenylpropionic acids show that, as in the case of a- and \$\beta\$- oxypropionic acids, the acid in which the phenyl is at a greater distance from the carboxyl is the weaker. The other relations to be expected are also found; between propionic acid and a-phenylpropionic acid there is the same ratio of the constants, 3.1, as between acetic and phenylacutic

Cuminic acid differs from p-toluic acid only in that it contains isopropyl instead of methyl. To this small difference in constitution correanonds as small a difference in the constants

sponds as small a difference in the con	ave	P11 60.
Hydroxylised homologues of benzoid	c a	cid.
Mandelic scid C.H. CH(OH)CO.H		0.0417
Phenoxy-acetic acid C.H.O.CH, CO.H		0.0756
o-Nitrophenylglycollic		
acid C,H,(NO,)O.CH,.CO,H .		0.158
p-Nitrophenylglycollic		
acid C _a H ₄ (NO ₂)O.CH ₂ CO ₂ H		0.153
Tropic soid CH ₂ (OH).CH(C ₆ H ₅)CO ₂ H	٠.	0.0075
Phloretic acid CH_CH(C,H,OH)CO,H	I	0.0020
Hydroparacoumaric		
acid CH ₂ (C ₂ H ₄ .OH)CH ₂ .CO ₂ H.	•	0.0017

Mandelic soid is phenylated oxyscetic soid; the ratio of its constant to that of glycollic acid is 2.7, while that between acetic acid and phenylacetic acid is 8.1; both values approxi-

mate closely to each other.

On introducing into the phenyl of phenoxyacetic acid a nitro-group in the ortho-position, the constant rises to double its value. The introduction of NO, in the ortho-position into benzoic acid raises the constant to 103 times its former value. This enormous difference exemplifies most prominently the influence exerted by the varying distance of the substituent from the carboxyl. The same thing is made evident by the constant of p-nitrophenylglycollic acid, which is scarcely different from that of the ortho- compound; the change from the ortho- to paraposition, which is generally so influential, is of scarcely any account at this distance from the carboxyl.

Tropic acid is a phenyl-B-oxypropionic acid. It is 2.5 times stronger than exprepionic acid. For the influence of phenyl in the a- position we have before found the factors 27 and 3.1.

Phloretic acid is phenylpropionic acid whose phenyl contains a hydroxyl in the para- position; its constant is half as great as that of phenyl-propionic acid; hence the para- hydroxyl here exerts its characteristic weakening effect.

In the same way hydroparacoumaric is hydrocinnamic acid which contains a parahydroxyl in the phenyl. This also has a decreasing action on the constant, but owing to the greater distance of the phenyl this effect is

not so great as in the preceding case.

Unsaturated acids. The affinity co-efficients of these substances present a special interest owing to their isomeric relations, which cannot be represented by the ordinary chemical formulæ. Following up an idea of van't Hoff, an explanation of these phenomena has lately been given by Wislicenus (Abh. König. Sáchs. Ges. der Wiss. 1887). In this explanation the cause of the chemical differences is supposed to lie in differences in the relative positions in space of the radicles linked to the carbon. Since the results so far obtained from a consideration of the affinity-constants invariably point to relations in space, it becomes possible to subject this hypothesis to an experimental examination. Acrylic acid CH,:CH.CO,H

Crotonic acid Cli(CII,):CH.CO.H 0.00204 Isocrotonic acid CH(CH3):CH.CO2H . 0.0038 Tiglic acid CH(CH₃):C(CH₃)CO₂H 0.00096 Angelic acid CH(CH₃):C(CH₂)CO₂H 0.0050 a Chlorocrotonic acid 0.0720 CH(CH3):CCl.CO2H.

allo-a-Chlorocrotonic acid CH(CH,):CCl.CO,H. 0.158 8-Chlorocrotonic acid

0.0144 CCl.(CH₃):CH.CO₂H allo-B-Chlorocrotonic acid

CCl.(CH,):CH.CO,H 0.0095 A consideration of these numbers shows that the unsaturated acids have in general greater constants than the saturated ones. We must, therefore, ascribe to hydrogen a strongly basic character. And, further, as in the case of the saturated fatty acids, the constants on the whole decrease as the carbon increases. And, finally, . 0.0017 we see that the isomeric acids for which, according to the views hitherto held, no difference of constitution could be formulated are in fact distinctly different.

Now Wislicenus represents the difference between crotonic acid and isocrotonic acid by the following formulæ:--

Crotonic acid

$$H>C=C< CH_3$$
 $H>C=C< CO_3H$

and

 $H>C=C< CO_3H$

In crotonic acid the methyl group stands nearer to the carboxyl, in isocrotonic acid the hydrogen. Since, in accordance with present experience, a methyl group linked to carbon which is also directly linked to CO,H decreases the constant, a smaller constant must be expected for crotonic acid than for isocrotonic, this difference being more pronounced owing to greater proximity in space. Experiment con-firms this conclusion, and thus proves the appropriateness of Wislicenus' assumption.

It may be asked whether we are not here dealing with one of the cases of which some were mentioned before, in which, as an excep-tional case, the methyl acts by increasing the strength. But this view is excluded, since both acids are weaker than acrylic acid. Methyl has, therefore, in both cases reduced the strength, but to a greater degree in crotonic than in the

iso acid.
Wislicenus assumes similar differences in constitution for angelic and tiglic acids. We get

Hence angelic acid again would have to be stronger than tiglic, as has been verified by experience. But it is remarkable that in this case the difference has been found to be much greater than in the first one. Angelic acid has a greater constant than isocrotonic acid, which contains CH, less than angelic acid, a fact as unusual as that tiglic acid exhibits a smaller constant than the corresponding saturated acid, valeric, which has for constant 0 00161.

In the same way the values found for the a-chlorocrotonic acids agree with experience. The constants are very nearly in the same ratio as that of those of the two crotonic acids themselves, and the rise effected by the chlorine introduced into the a-position is represented by the factors 36 and 44, which, though markedly smaller, are of the same order of magnitude as the factor for monochloracetic acid.

In opposition to the agreement holding hitherto between theory and experiment, in the case of the β-chlorocrotonic acids, the allo- compound proves distinctly weaker than the deriva-tive of crotonic acid. The cause of this discrepancy cannot yet be established. The ratio of the constants for crotonic acid and \$-chlorocrotonic acid is 1:7, which is nearly the same as the corresponding factor for propionic acid and β-iodopropionic acid, viz. 6.6. On the other hand, the ratio for the factors of isocrotonic acid and the allo-B-chloro- derivative is 1:2.6, and is, therefore, much smaller.

Tetrolic acid is formed from both \$-chloroerotonic acids by splitting off hydrochloric acid; the constant is Tetrolic acid CH, C:C.CO.H .

Though hydrochloric said is one of the strongest acids, yet the splitting off of its elements from the \$-chlorocrotonic acids not only has not lowered the constant, but has raised it This result makes evident the considerably. strongly acid nature of carbon and the basic nature of hydrogen; the removal of four hydrogen atoms from butyric acid, whose constant is 0.00149, has produced a rise in the constant of 160 times its value.

Of other unsaturated acids the following have heen measured ---

0.00241

Hydrosorbic acid C₅H₈.CO₂H Sorbic acid C₅H₇.CO₂H Parasorbic acid C₅H₇.CO₂H 0.00173 0.00178 Ethyl-methacrylic acid C,H,.CO,H 0.00111 Atropic acid CH.:C(C,H,)CO,H . Cinnamic acid CH(C,H,):CH.CO,H 0.0143 0.00355 Isocinnamic acid CH(C,H,):CH.CO,H 0.0156 p-Coumaric acid CH(CaH4.OH):CH.CO2H 0.0022o-Coumario acid CH(C,H,OH);CH.CO,H 0.0021 Umbellic acid $CH(C_0H_2(OH)_2):CH.CO_2H$ 0.00188 a-Bromo-cinnamic acid CH(C.H.):CBr.CO.H 1.44 8-Bromo-cinnamic acid CH(C₆H₅):CBr.CO₂H

Phenylpropiolic acid C,H,C:C.CO,H . 0.59 o-Nitro-phenylpropiolic acid C₈H₄NO₂.C:C.CO₂H In accordance with the general rule, hydro-

sorbic acid is stronger than the corresponding saturated compound, which is caproic acid (k = 0.00145), while sorbic acid, which contains 2H less, is not stronger but weaker than hydrosorbic acid. It is, therefore, probable that sorbic acid has not one treble linkage, but two double ones, oreit may have an altogether different constitution, perhaps one with a closed chain arrangement of the carbon atoms.

Sorbic acid is sometimes obtained in the form of an oil which only when treated with acids or alkalis passes into the crystalline acid. Since it did not seem impossible that this was a case of isomerism, such as that of crotonic and isocrotonic acid, the constant of the liquid parasorbic acid was also measured. It proved identical with that of sorbic acid, and hence, with Fittig and Baringer (A. 161, 325 [1871]), these substances must be considered, not as isomeric, but as chemically identical.

The constant of methylethylacrylic acid is remarkably small; it is smaller than that of the saturated fatty acid, and approaches that of tiglic acid. The acids a-phenylacrylic, or atropic, and \$-phenylacrylic or cinnamic, behave as we should expect; the phenyl group causes a much higher value of the constant when it is in the α - than when it is in the β - position. But it is remarkable that cinnamic acid is not only weaker than atropic acid, but even weaker than acrylic acid; in this case, then, the phenyl group lowers the constant.

In the case of cinnamic acid, two 'geometrically isomeric' compounds may be expected, namely-

$$\overset{H}{\underset{C_{\bullet}H_{\bullet}}{\sim}} C = C < \overset{CO_{\bullet}H}{\underset{H}{\sim}} \quad \text{and} \quad \overset{H}{\underset{H}{\sim}} C = C < \overset{CO_{\bullet}H}{\underset{\bullet}{\sim}}$$

Quite recently there has been discovered by Liebermann a second cinnamic acid which must be regarded as geometrically isomeric with the ordinary one; it has a much higher constant than the latter, and hence we may conclude that in the new isocinnamic acid the neg ative phenyl has a closer connexion with the carb oxyl than in the old one, and that the new acid may have the second of the above formulæ.

Similarly, there are known two isomeric bromocinnamic acids, which are produced from cinnamic acid dibromide by splitting off hydrobromic acid, and for which the same kind of isomerism holds. Nor can there be any doubt as to which acid corresponds to each formula, the differences in the constants being very great, and in fact it has been made known quite recently by Erlenmeyer that he has obtained Liebermann's isocinnamic acid from the stronger a-bromocinnamic acid.

The phenylpropiolic acid formed from the acid is stronger than the \$\beta\$- compound, but weaker than the isomeric \$\alpha\$- compound. The constant is also, as was to be expected, greater than that of tetrolic acid. In o-nitro-phenyl-propiolic acid the nitro-group in the orthoposition has again been able to exert but a slightly strengthening action, owing to its being at a great distance from the carboxyl.

On comparing einnamic acid with p-coumaric acid, we find that the hydroxyl introduced into the p-position again lowers the constant. But, strange to say, a similar effect is produced in the derivatives of cinnamic acid by hydroxyl in the ortho-position; o-coumaric acid is also weaker than cinnamic acid. It is in accordance with this that umbellic acid, which contains one hydroxyl in the ortho-position and a second one in the para-position, is weaker than all these acids. It is to be expected that these relations will prove of importance for the complete clucidation of the constitution of these remarkable compounds.

Dibasic acids. The acids of the oxalic series save the following constants:

Oxalie acid (CO,H),	. 10(?)
Malonic acid CH ₂ (CO ₂ H),	. 0.158
Succinic acid C ₂ H ₄ (CO ₂ H),	. 0.0066
Pyro artaric acid C.H.(CO.H).	. 0.0048
Adipio acid C ₄ H ₈ (CO ₂ H),	. 0.0037
l'imelic acid CaHie(CO,H).	• 0.0036
Suberic acid C ₆ H ₁₂ (CO ₂ H) ₂	. 0.0026
Sebacic acid C, H, (CO, H),	. 0.0023
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It has already been explained that the weaker dibasic acids H.R¹¹ split electrolytically according to the scheme H + HR¹¹, and that therefore constants may be calculated for these acids in a manner analogous to that adopted for the monobasic acids. In the case of oxalic acid, however, this is not possible, since the dissociation has proceeded too far; the constant is only estimated approximately, but beginning from malonic acid, the values of the constants can be very well determined.

We see that at first the constants decrease very rapidly; that of malonic acid is about 60 times smaller than that of oxalic acid. From malonic to succinic acid the step is much smaller, 24:1, and much smaller from the latter to pyrotamaric acid, 14:1, and henceforward

the numbers vary only by small amounts. The influence which one carboxyl group exerts on the hydrogen of the other decreases, therefore, very rapidly in consequence of the interposition of the carbon atoms; sebacic acid does not surpass by more than twice the fatty acids richer in carbon. Of the numerous isomerides with side carbon chains, the following have been measured:

Methylmalonic acid CH(CH₃)CO₂H
Ethylmalonic acid CH(CH₄),CO₂H
0-127
Dimethylmalonic acid C(CH₄),CO₂H
Methylsuccinic acid C₄H₄(CH₄),CO₂H
α-Dimethylsuccinic
acid C₄H₄(CH₄),CO₂H
β-Dimethylsuccinic
acid C₄H₄(CH₂),CO₂H
0-0343
β-Dimethylsuccinic
acid C₄H₄(CH₂),2CO₂H
0-0245

The three first acids appear at once to be derivatives of malonic acid; their constants do not differ much from that of their parent substance, but all are somewhat smaller. Similarly, the constants of the derivatives of succinic acid appreach to the value of the latter, but are all greater. The alcoholic groups have therefore acted in these cases in the ordinary way: an explanation of this has been attempted by Bethmann (Z.P. C. 5, 407).

The amido- group entering into one of the carboxyls of oxalic acid causes a weakening of the acid to one-twelfth its value; the much more weakly basic urea residue produces a much smaller weakening effect, viz. to about half the value. The decrease caused by the residue of aniline is smaller also, to about the eighth part; when chlorine enters into the phenyl of the latter, there again occurs an increase in the acid properties, which increase, however, in consequence of the greater distance, is much smaller than in benzoic acid. But a distinct difference between the ortho- and the para-position still asserts itself. Methyl in the para-position exerts a distinctly weakening effect.

Tartronic acid CH(OH)(CO,H), 0-107
Phenylmalonicacid (C,H,),C:(CO,H), 0-408
Malonanilic acid CH,CO(NHC,H,)CO,H .0-0196

Strange to say, in spite of the hydroxyl, tartronic acid is weaker than malonic acid (k=0.158). The replacement of both hydrogon atoms of malonic acid by benzylic radicles raises the constant. Finally, malonanilic acid is about eight times weaker than the parent substance.

 $\begin{array}{c|cccc} Derivatives of succinic acid.\\ \text{Malic acid $C_2H_4(OH)($\cup O_2H)_2$} & . & . & 0.0395\\ \text{Inactive malic acid $C_2H_1(OH)(CO_2H)_3$} & . & 0.0395\\ \text{Dextrotartaric acid $C_2H_2(OH)_2(CO_2H)_3$} & . & 0.097\\ \text{Lievotartaric acid $C_2H_2(OH)_2(CO_2H)_2$} & . & 0.097\\ \text{Racemic acid $C_2H_2(OH)_2(CO_2H)_2$} & . & 0.060\\ \text{Phenyl-succinamic acid $C_2H_1(CONHC_2H)_2(CO_2H)_3$} & . & 0.0020\\ \end{array}$

e-Chlorophenylsuccinamic
acid C.H. (CONHC.H.Cl)CO.H . 0.0021
m-Chlorophenylsuccinamic
acid C.H. (CONHC.H.Cl)CO.H 0.0021
p-Chlorophenylsuccinamic
acid C ₂ H ₄ (CONHC ₄ H ₄ Cl)CO ₂ H 0.0021
o Tolyl-succinamic
acid $C_2H_4(CONHC_7H_7)CO_2H$ • 0.0021
p-Tolyl-succinamic
acid C ₂ H ₄ (CONHC ₂ H ₇)CO ₂ H . 0.0020
Succinurio
acid C ₂ H ₄ (CONHCONH ₂)CO ₂ H . 0.00311
Thio-succinuric
acid C ₂ H ₄ (CONHCSNH ₂)CO ₂ H . 0.00333
Oxysuccinic, or malic, acid has a constant
six times as great as succinic acid. The factor
is somewhat smaller than for the monobasic
acids, which may be because a negative radicle
carboxyl is already present. The natural opti-
cally active acid has exactly the same constant
as the inactive acid got from monobromsuccinic
acid. The same relation recurs in fartaric acid
and racemic acid. Both the dextrorotatory and
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the levorotatory acid, as also the inactive raceinic acid formed by a combination of these two, are all of exactly the same strongth. This result is in accordance with the present views concerning the constitution of these compounds. dextrorotatory and lavorotatory acids contain their constituents in a perfectly symmetrical arrangement, and must, therefore, have equal co-efficients of affinity. It has been assumed that the optically inactive acids produced from the optically rotating ones consist each of two molecules of the active acids. This is probably correct for the solid crystallised substances, but not for solutions; in these, both compounds are present side by side, uncombined, a conclusion which has also been arrived at in another way by Perkin (C. J. 52, 362). The undecomposable inactive mesotartaric acid has, however, another, and that a smaller, constant; theory also ascribes to it a different constitution. In the preceding table are further contained

a number of derivatives of phenylsuccinamic or succinanilic acid. This acid itself is only 3.3 times weaker than succinic acid, while the introduction of the anilline residue into CO, H of malonic acid decreased the strength 8 times; this indicates that the position of the substituent at a greater distance weakens the effect. The almost complete equality of the constants for all substitution products of succinanilic acid is of great interest; the distance of the benzylic residue from the carboxyl is here too great to allow the substituents to exert their effect over it. The usual assumption, that the molecular forces cease to act at even very small distances, is thereby made more definite, in that such distances are already given by the molecular dimensions.

As already found, the introduction of the urea residue produces a smaller decrease than that due to aniline. Smaller still is the effect of the thio-urea residue.

Dicarboxylic acids of bensene.

o-Phthalic acid C.H.(CO.H).

m-Phthalic acid C.H.(CO.H).

Ovyterephthalic acid C.H.(CO.H).

Phthalamic acid C.H.(CONH.)CO.H.

Phthaluric acid C.H.(CONH.)CO.H.

Ov100

Ov250

Ov100

Ov200

Ov200

As we were led to expect, the entry of a carboxyl in the ortho-position produces a somewhat considerable rise in the constant—vis. to twenty times the former value. For the metaposition the factor is only 4.8. p. Phthalic acid is too insoluble to be measured. But assuming that in oxy-p-phthalic acid the hydroxyl acts as strongly as in salicylic acid, the constant of p-phthalic acid would be estimated as 0.014 to 0.015, and it would follow that, in accordance with the usual result, carboxyl in the para-position—i.e. in the distant one—exerts the least action. A weakening effect, such as is exerted by hydroxyl in the para-position, seems to be excluded.

The amide residue in phthalamic acid has lowered the constant to one-eighth its value, but the acid is yet stronger than benzoic acid, and the group CONH, must be looked upon as negative. The urea residue exerts, as it always does, a much less marked weakening effect.

Unsaturated dibasic acids. The dicarboxylic acids $CH_{2n-2}(COOH)_2$ exhibit very similar isomeric relations to those of the compounds of the acrylic acid series. The following were neasured:—

The isomeric compounds are seen to have widely different constants. These results agree very well with the views of van't Hoff and Wislicenus. For fumaric and maleic acids the following formulæ have been adopted:

$$\begin{array}{c} \text{Malcic acid} \\ H > 0 = C < \stackrel{CO_2H}{CO_2H} \\ \end{array} \qquad \begin{array}{c} \text{Fumaric acid} \\ H > C = C < \stackrel{CO_2H}{CO_2H} \\ \end{array}$$

According to this, the two carboxyl groups are much nearer to each other in maleic than in fumaric acid, and the first must be stronger, as is actually the case. Similarly, according to Wislicenus, the formulæ

$$\begin{array}{ccc} \text{Citraconic acid} & & & \text{Mesaconic acid} \\ H > C = C < & \text{CO}_2 H & & & \text{CH}_3 > C = C < & \text{CO}_2 H \\ \text{CH}_3 > C = C < & \text{CO}_2 H & & \text{CO}_3 H \\ \end{array}$$

hold, and for the same reason citraconic acid must be stronger than mesaconic acid, which conclusion again agrees with experiment.

CH,: C-CO,H

Itaconic acid has the formula

H.C-CO.H

and therefore no double linkage between the carbon atoms combined with carboxyl. Accordingly, its constant is much smaller; it is only twice as great as that of succinic acid.

It may be mentioned that acetylene dicarboxylic acid $\overset{C}{C} - CO_x H$ is so strong that a constant cannot be determined for the first stage of dissociation. The acid is but little inferior to sulphuric acid.

Lutidinie seid (e7) C.H.N.(CO.H).	•	0.60
acid (βγ) C _a H _a N.(CO _a H) _a .		0.21
Isocinchomeronic		
acid $(\alpha\beta)$ C ₃ H ₂ N.(CO ₂ H) ₂ .		0.43
Chinolinic acid (as) C, H, N.(CO,H),		0.80
ββ-Pyridine dicarboxylic		
acid C.H.N.(CO.H),		0.15
The replacement of the group C2H	, ir	benzoi c
acid by sulphur raises the constan	nt	to five
times its value, provided the carboxy		

acid by sulphur raises the constant to five times its value, provided the carboxyl is placed next to the sulphur. In the \$\mathcal{\theta} position the carboxyl is without doubt influenced less, but we have yet no measurement of the constant.

It is remarkable that a similar replacement of C.H. by oxygen, forming pyromucic acid, acts much more strongly than a replacement by sulphur. On account of the magnitude of the constant it is very probable that in pyromucic acid the carboxyl is in a position next to the oxygen.

Differently from sulphur and oxygen, the replacement of C₂H₂ by CNH has a strongly weakening effect on the constant. The values found for the monocarboxylic acids of pyridine correspond fairly with the assumptions which might be made on the basis of the constitutions of these substances; picolinic acid, which contains the carboxyl next to the nitrogen, is by far the weakest; but the β- acid is stronger than the γ- compound, so that in pyridine the β- position proves the place of smallest influence.

The behaviour of the dicarboxylic acids of pyridine is very unexpected. While all monocarboxylic acids of pyridine are weaker than benzoic acid. all dicarboxylic acids are stronger than the strongest dicarboxylic acid of benzene -that is, o-phthalic acid, whose constant is 0.12. A further difference is that the strongest dicarboxylic acids are those which contain carboxyl in the a- position—that is, next to the nitrogen. Then follow the acids which contain carboxyl in the γ - position, and lastly those with carboxyl in the β - position. These relations are the exact reverse of those observed for the monocarboxylic acids; where a decrease of the constant had been observed there, an increase is found here. No plausible hypothesis concerning the cause of these peculiar phenomena has yet been brought forward.

Oxycinchomerome		
acid C ₃ H ₂ (OH) N.(CO ₂ H) ₂ .	•	1.67
Methyl pyridine dicarboxylic		
acid C,H,(CH,)aN,(CO,H),		0.20
Dimethyl pyridine dicarboxylic		
acid C,H(CH,), an N(CO,H), set		0.34
Dimethyl pyridine dicarboxylic		•
acid C,H(CH ₃)2"N.(CO,H)2881		0.55
Australia 11 ""		

Owing to the entry of hydroxyl in the orthoposition, cinchomeronic acid has had its constant increased to eight times its value. The methyl groups increase the strength of the $\beta\beta$ -dicarboxylic acid, and they do so to a greater extent in the γ -position than in the α -position.

Further, several poly-carboxylic acids of pyridine were examined; the constants cannot, however, be calculated, because the dissociation assumes a somewhat complicated character. But it is evident that the relations found in the case of the dicarboxylic acids concerning the influence of the position of the carboxyl hold good in these cases also. The rules found for detailed discussion.

the dicarboxylic acids were also confirmed in the case of methyl derivatives of the tricarboxylic acids. On the other hand, phenyl on entering into lutidine dicarboxylic acid, whose constant is 0.34, has a weakening effect, the constant for the compound formed being only 0.012. The action here is the reverse of that observed in the case of the fatty acids.

Quinaldinic acid C.H.N.CO.H .	0.0012
Cinchonic acid C, H, N.CO, H.	0.0013
Dipyridyl monocarboxylic	
acid C ₁₀ II_N ₂ .CO ₂ H	0.002
Dipyridyl dicarboxylic	
acid C ₁₀ H ₀ N ₂ (CO ₂ H) ₂	0.082
o-Pyridine benzoic acid C ₁₁ H ₈ N.CO ₂ H	0.0005
Phenyl pyridine dicarboxylic	
acid $C_{11}H_1N_1(CO_2H)_2$	0.011

The quinoline carboxylic acids, which have a constitution analogous to that of the pyridine carboxylic acids, are somewhat stronger than these, as the naphthoic acids are stronger than the benzoic acids. Concerning the other acids but Ittle can be generalised.

Amidobenzene sulphonic acids and similar

ooney our wood		
o-Amidobenzene sulphonio		
acid C,H,NH,SO,H .	• .	0.330
m-Amidobenzene sulphonic	-	
acid C.H. NII2.SO3H .		0.0185
p-Amidobenzene sulphonic		
acid CallaNHaSOall .		0.0581

The results obtained from measurements of the amidobenzene sulphonio acids are somewhat remarkable. While benzene sulphonic acid itself is so strong an acid that its dissociation constant cannot be determined, its amido-derivatives can be measured with ease; the amido- group has, therefore, as it usually does, exerted a weakening effect. But in the case of the carboxylic acids the ortho- position was always that of greatest influence; here it appears as the position of least influence. The weakest of the three acids is the meta- compound, then follows the para- compound, and then the ortho- compound, which comes nearest to the parent substance. The assumption is thus suggested that, by the agency of the group SO, the hydrogen is brought to such a distance from the benzene nucleus that it is more influenced by the radicles in the meta- position than by those in the ortho-

position.			
Diamidobenzene sulphonic			
acid (2,3) C ₆ H ₂ (NH ₂) ₂ SO ₃ H		•	0.0050
Bromamidobenzene sulphonic			
acid (2,5) C ₅ H ₂ BrNH ₂ SO ₃ H	•	•	7.9
Bromamidobenzene sulphonic			
acid (3,6) C _s H ₂ BrNH ₂ SO ₃ H	•	•	0.072
Dibromamidobenzene sulphonio			
acid (3,4,6) C,H2Br2NH2SO,H			2.5
Toluidine sulphonic			
acid (3,4) C,H,(CH,)NH,SO,H		•	0.024
Xvlidene sulphoni c			
acid (4,2,5) C,H2(CH2),NH2SO,	H		0.044
→ • • • • • • • • • • • • • • • • • • •			

acid (4,2,5) C_sH₂(CH₂),NH₂SO₂H . 0.044 In indicating the constitution, the sulpho-group is put = 1, then follows amide, and then bromine or methyl.

These acids exhibit the usual relations to be expected from the nature of the substituents and their position, and thus do not call for any detailed discussion. General considerations. The properties of chemical compounds, which can be expressed numerically, may be divided into three groups—the additive, the cumulative, and the constitutive. The first are of such a nature that in chemical compounds their value is the sum of the corresponding values of the constituents; these values have led to the conception of the atomic theory—i.e. to the assumption that the components continue to exist in the compounds as such.

The cumulative properties exhibit the peculiarity that, independently of the number and nature of the constituents, their numerical value is the same for certain complex systems. These have led to the conception of the molecular theory—i.e. to the assumption that the components of chemical compounds primarily form similar groups or systems, which have an individual existence, and out of which the visible and ponderable substances are built up.

And, finally, there exists a third group of properties, which are neither additive nor cumulative, since even in the case of substances having the same composition they can assume different values. These have led to the assumption that, in addition to the nature and number of the composing atoms, the properties of substances are influenced by still another condition. This condition has, from the time of Berzelius, been considered to lie in the different arrangement of the atoms within the molecule—i.e. in the constitution.

Of all the constitutive properties hitherto known—such as boiling-point, melting-point, colour, crystalline form, &c.—not one affords a clear insight into the determining cause, the chemical constitution. It is possible, when the latter has been found, more or less approximately, by purely chemical methods, to establish empirical relations; but these lie on the surface only, and lack generality. The cause of this is the defective development of our conceptions concerning the kind and the amount of the influence which the arrangement of the elementary atoms in the molecule exerts on the properties mentioned.

I believe I am not deluding myself when I affirm that the affinity constants, which represent a property of eminently constitutive nature. are far superior to all others with respect to their theoretical applicability. The result that one and the same atom exerts quite different effects, ac-cording to the 'position' which it occupies in the molecule, and that these effects are the greater the more close is the relation of the atom to that of the acid hydrogen, leads to the general inforence that these effects are functions of the distance in space of the atoms in question. But thereby, for the first time, is gained a means of taking measurements in space of molecular structures. There is no doubt that long and laborious work is needed before such measurements will lead to results which will give an allsufficient representation of the form of molecules. But it already seems certain that this goal can be reached.

It has been mentioned, to start with, that k, the affinity co-efficient of acids, appears, generally speaking, as a product whose factors are given by the nature and position of the elementary

atoms composing the acid. This follows from the fact that with analogous changes in analogous substances the constants change in the same ratio-i.e. that in consequence of these changes the constants of the original substances must be multiplied by the same factor. But these factors are never exactly the same, just because two analogous changes are never exactly the same. If, for instance, we change acetic acid into glycollic acid, and propionic acid into lactic acid, the two changes are, it is true, very much alike; but in the first case the hydroxyl takes up a position next to two hydrogen atoms. in the second case next to one hydrogen atom and one methyl; the hydroxyl is therefore subject to a different influence, and will in consequence necessarily act differently on the carboxyl. The same holds for all corresponding cases. The approximate character of the general relation follows, therefore, as a necessity; the deviations from the type are caused by the nature of the subject, and themselves afford a means for bringing to light their cause, which is the secondary influence mentioned above. What has been said concerning the constitutive properties generally—that they can never be completely represented by a general scheme, because this is contradictory to their nature holds particularly for the affinity co-efficients. In them the whole variety of nature asserts itself, and within the framework of great and general regularities produces the finest individualisation.

The form of the dissociation-constant as the product of factors $c = c_1.c_2.c_3...$ has a deeper significance, which is recognised on going back to the dissociation-formula itself. This formula is obtained from the mechanical theory of heat in the following form:

$$\log \frac{p}{p_1 p_2} = \frac{\rho}{R\tau} + C$$

where p_i and p_i are the partial pressures of the products of decomposition, p the pressure of the undecomposed substance, p the heat of dissociation, τ the absolute temperature, R the gaseous constant, and C is a value which is a function of the temperature only, and which, therefore, at constant temperature can be looked upon as a constant.

In the case in point $p_1 = p_2$, and since p_1 and p must be put proportional to $\frac{m}{v}$ and $\frac{1-m}{v}$, it

follows that $\frac{p}{p_1^2} = \frac{(1-m)v}{m^2}$ and thence

$$\log \cdot \frac{(1-m)v}{m^2} = \frac{\rho}{R\tau} + C$$

$$\log \frac{m^2}{(1-m)v} = -\frac{\rho}{R\tau} + C^1.$$

Now the affinity co-efficient is $k = \frac{m^2}{(1-m)n}$; and since, on the other hand, quite generally $k = k_1, k_2, k_3, \ldots$ it follows that

$$\log k_1 + \log k_2 + \log k_3 + \dots = -\frac{\rho}{R\pi} + C^1.$$

The constant C' depends only on the unit adopted and on the point chosen as zero; if, therefore, there appears on the left side of the equation a sum of terms represented by log.k, there must correspond to each of these on the right side a term of the form $-\frac{\rho_n}{R\tau}$, so that $\frac{\rho}{R\tau}$ also resolves itself into a sum of corresponding terms $-\frac{1}{R\tau}(\rho_1+\rho_2+\rho_3+\ldots)$ in which one R_n and

one ρ_n always correspond to each other.

This means: The natural logarithm of the dissociation-constant or affinity-constant is (save for a constant) proportional to the heat of dissociation of the acid in splitting into ions. Since the value of the dissociation or affinity-constant is known from experiment to be the sum of a series of terms which depend on the nature and on the position of the constituent atoms, it follows that the electrolytic heat of dissociation also is the sum of a corresponding number of terms each of which is fixed by the nature and position of each individual atom.

Now in this case the heats of dissociation are the exact measures of the quantities of work which are done in the separation of the acid hydrogen atom from the negative ion. This is so because no external work has to be taken into account, and because the condition of the substances dealt with very closely approaches that of ideal gases. Hence the heat of dissociation measures the potential or the force-function of the atomic system at the corresponding point. and we see that this force-function is the sum of the values which, according to their nature and position, the individual atoms contribute to the total value. And thus elements which, like chlorine, sulphur, &c., raise the constant k, cause a decrease of the heat of dissociation, since log.k and p have different signs. The amide group. on the other hand, which decreases the constant, raises the heat of dissociation-i.e. it increases the amount of work necessary for splitting off the acid hydrogen.

It is by these considerations that the long-mooted question concerning the connection between chemical affinity and the thermal values of reactions has been decided in principle. In this result we see the eminently constitutive property of affinity-quantities brought back again to the additive form. This has been effected by introducing the influence of constitution, or of position in space, into the terms themselves. A similar development awaits the theory of all constitutive properties, as, in fact, we are forced to conceive the combined action of different elements as the sum of various effects.

Electrical theory of chemical affinity. Elsewhere (AFFINITY, vol. i. p. 67) the laws of chemical affinity have already been explained. Nothing definite could be stated concerning their cause; but it followed from the close connection which was shown to exist between the co-efficients of chemical reacting power of electrolytes, and the values of the electrical conductivities, that an intimate relation exists between these two properties. The prospect is thus opened of carrying out in an exact form the electro-chemical theory of affinity which was rather conjectured than worked out by Davy and Berzelius.

The new view which affords such a possibility is the common cause underlying electrolytic conduction and chemical reactions as recognised by Arrhenius, viz. the existence of free ions. On making the assumption, which is justified by Vol. 1V.

this concordance, that chemical processes between electrolytes take place only by the agency of the free ions, the laws of chemical affinity, which have been established empirically, can be deduces so as to be in accordance with experiment. To do this we only further need van't Hoff's theory of solutions, and the theory of the laws of dissociation as deduced for gases (v. Dissociation is vol. ii.), which laws, thanks to van't Hoff's theory can also be applied to substances in solution.

The general law of chemical affinity first recognised is that manifestations of this affinity on the part of a definite substance are expressible by a definite co-efficient, dependent on the temperature and dilution, but independent of the nature of the chemical reaction in which the substance participates.

Now, if the reacting power of a substance in solution depends on the number of dissociated ions which are present, it can be seen at once that the above-mentioned law must of necessity hold good. So, for instance, the state of dissociation of an acid determines the velocity with which it must act on methylacetate, acctamide, marble, &c. The nature of the other substance determines a factor only, which in analogous cases is the same.

Hence we must conclude that all acids, for instance, when completely dis-ociated are equally strong. The strong inorganic acids HCl, HBr, HI, HNO₂, HClO, must be classed here, as also the sulpho-acids and similar organic acids. No one of these substances exhibits any of the specific differences discussed in former paragraphs for acids of medium strength. They all exert a nearly equal effect when used in equivalent quantities, and approach the maximum conductivity even at moderate dilutions. At a time when the dissociation theory of electrolytes did not exist, the author of this article vainly tried to obtain from benzene-sulphonic acid, by all the means which make weak acids strongersuch as the introduction of halogens, nitrogroups, &c .- acids stronger than the parent substance, which may itself be ranged side by side with hydrochloric acid. This was not possible; all 'strengtheners' remained in this case ineffective. This remarkable fact shows that it is not its special nature, but its electrical condition, which is determinant for the chemical effect of a substance, especially if that substance be an acid.

The greater the number of the molecules which are split into their positively and negatively charged parts, the stronger is the acid; but any ion, when once present in the separated. electrically charged, condition, is as effective as any other. Here, then, we see that Berzelius' conclusion drawn from false premisses, by means of which he attempted to demonstrate the absurdity of Faraday's lar -that then the chemical affinity between the ions of all electrolytes would have to be the same-is perfectly correct. The affinity of the most diverse ions is really the same, because it does not depend on their nature but on their electrical charge, and this, according to Faraday's law, is everywhere the same. What does depend on the nature of the ions is the degree to which they dissociate, and herein alone lies the cause of the differences ₽

In the arguments used so far, it has been assumed that the state of dissociation of the reacting substances is determined by the volume and the temperature, and that the presence of other substances does not alter the state of the one considered. This case, however, only occurs when there are present either one dissociated substance and nothing but non-electrolytes besides, or when all the dissociated substances present are for all practical purposes completely split up. But as soon as several partly dissociated substances are present, the relations become much more complicated.

It is known from the theory of dissociation that when two gaseous substances are present, and the quantities of these substances vary, the product of their active quantities, or of their concentrations, must be constant, constant temperature being presupposed. If, for instance, a given space is filled with the gaseous products of decomposition of ammonium hydrosulphide, the addition of sulphuretted hydrogen will cause a decrease in the quantity of hydrosulphide dissociated, because on increasing the one factor the other must decrease in the same ratio. The same must evidently hold for electrolytes; on adding to a solution which contains the ions A + B an excess of ions A, the quantity of ions B must decrease until the product of the two quantities has again become equal to its original value. Now, it is not very well possible to add ions A only, but an electrolyte can be added which is dissociated, and which contains the ions A + B'; if B' is different from B, the two do not influence each other.

We may now ask how two solutions must be constituted in order that their state of dissociation shall not vary when the solutions are mixed. We have the solutions of the electrolytes A + B and A + B', which contain a common ion A; let their volumes be v and v'. Then, in accordance with the general law of the equilibrium of dissociation, the following equations will hold:

$$\frac{1-\xi}{v} = k\frac{\xi}{v} \cdot \frac{\xi}{v}$$
$$\frac{1-\xi'}{v'} = k'\frac{\xi'}{v'} \cdot \frac{\xi'}{v'}$$

in which the quantities of the electrolytes originally present are put as equal to 1, and the dissociated portions equal to ξ and ξ' respectively. On mixing the solutions, the volume becomes v+v', the dissociation ratios ξ and ξ' remaining unchanged, as supposed. The quantities of the undissociated portions are $1-\xi$ and $1-\xi'$, but the products $\xi.\xi$ and $\xi'.\xi'$ change into $\xi(\xi+\xi')$ and $\xi'(\xi'+\xi)$, since the ion A common to both substances participates in the equilibrium condition of both. We have, therefore,

$$\frac{1-\xi}{v+v'} = k, \quad \frac{\xi}{v+v'}, \quad \frac{\xi+\xi'}{v+v'}$$

$$\frac{1-\xi'}{v+v'} = k', \quad \frac{\xi'}{v+v'}, \quad \frac{\xi+\xi'}{v+v'}$$

On dividing each of these equations into each of the corresponding equations given above, it follows that $\frac{\xi}{\xi'} = \frac{v}{v'}$. Therefore, in order that the state of dissociation should not alter on mixing solutions of two electrolytes which have one ion

in common (for instance, two acids), the portions dissociated must be in the ratio of the volumes.

Writing the equation in the form $\frac{\xi}{v} = \frac{\xi'}{v'}$, the

law can also be expressed in this form; when the concentration of the common ion is the same in both solutions, these do not influence each other.

Arrhenius, to whom we owe these considerations, calls solutions which do not influence each
other in the sense just mentioned isohydric
solutions. Since, in accordance with the above
formula, it is only necessary for this that the
concentration of the common ion in the two
solutions should be the same, the ratio of the
quantities of the two solutions does not enter
into consideration; isohydric solutions can be
mixed in all proportions without mutually
changing their condition.

If, however, two non-isohydric solutions which contain a common ion are mixed, the process can be represented by saying that the one solution withdraws water from the other until both have become isohydric; then they leave each other uninfluenced. This withdrawal of water occurs in the following manner. First. the total concentration of the solution which loses water increases, and thereby the concentration of the ions increases also. But, owing to this, the state of dissociation changes directly, since, in consequence of the smaller volume, the dissociation decreases, and, therefore, the concentration of the ions increases more slowly than the total concentration. Conversely, the concentration becomes less in the portion which takes up water; but, owing to the increase in dissociation, it does so to a smaller degree than corresponds to the volume change.

Since the relation between the volume and the state of dissociation is known for binary electrolytes (p. 194), a formula can easily be deduced which allows us to calculate the characteristic quantities for a mixture of several electrolytes. But it is generally simpler to proceed by way of successive approximation.

Two solutions which are isohydric with a third must be isohydric with each other; because, in order to be isohydric with the third, there must be in both the same concentration of the common ion as is in the third solution.

These laws were all established empirically by Arrhenius (W. 30, 51), and it was only lately that he deduced them theoretically from his theory of dissociation (Z. P. C. 2, 284 [1888]). The examination of these relations is best conducted by making measurements of electrical conductivities. Since the conductivity of a compound in solution is proportional to the number of free ions, it can easily be recognised whether two substances with a common ion-two acids. for instance -- are isohydric; if the conductivity of the mixture is equal to the sum of the conductivities of the components, the solutions are isohydric; if this is not the case, the two numbers differ from each other more or less. To quote an example: with a phosphoric acid solution, of specific conductivity l=225.6, was mixed an equal volume of hydrochloric acid solution 1-225.9; the mixture gave 21-4690, while the sum of the two values is 4515; the observed conducivity was too great by 17.5. Further, the same shosphoric acid solution mixed with an equal rolume of a more dilute hydrochloric acid, =1851, gave for the conductivity of the mix-ure 2l = 4074; this is smaller by 3.3 than the sum 410.7. Finally, hydrochloric acid of l = 168.8gave for the mixture 2l = 394.4, the sum being 194.4; both solutions were isohydric. By such experiments as this Arrhenius arrived at the aws stated above.

It need scarcely be mentioned that any other property of solutions which depends on the molecular condition of the dissolved substance sould likewise have been used for determining the relations of isohydricity. The best of these properties would be measurements of the velocities of reaction for instance, those of the inversion of sugar - these being proportional to the state of dissociation; but the freezingpoints, vapour pressures, &c., could also have been used.

So far the only case considered has been that in which the mixed electrolytes contain a common ion. If this is not the case, new phenomena appear, which we will now consider in greater detail. It has already been pointed out that the theory of free ions leads to a view of the processes of the formation and mutual decomposition of salts which is very different from that generally accepted. It has been shown that, neglecting the small undissociated portions, the process of neutralisation between the strong acids and bases consists exclusively in the formation of water from the ions H and OH. The cause why these ions coalesce to form undissociated water lies in the fact that water is an extremely stable compound, which, under ordinary circumstances, is only very slightly split into ions. If, therefore, such ions anywhere appear simultaneously, they combine directly to form undissociated water.

The phenomena take a quite similar course when a strong acid-hydrochloric, for instanceacts on the salt of a weak acid-sodium acetate. for instance. The former solution is almost exclusively composed of ions II and Cl, the latter of ions Na and CH, CO, Since the sodium chloride also is almost completely dissociated when in dilute solution, the ions Na and Cl are already present in the same condition as in sodium chloride solution, and there exists no tendency to the formation of this compound. But, in addition, there are present the ions H and CH, CO, and these cannot exist side by side without for the most part combining. Hence a corresponding quantity of undissociated acetic acid will be formed, as is actually shown by experiment. But while formerly this fact was ascribed to a specially great affinity between the chlorine and the sodium, and the acetic acid was allowed to play a passive part, being supposed to be 'expelled' by the hydrochloric acid, we now see that the entire cause of the process lies in the action of the acetic acid. Owing to the great affinity of its ions, it is formed whenever its ions meet, while the components of the 'strong' reagents, chlorine and sodium, remain perfectly indifferent in the process. •

The conditions under which chemical equilibrium is established between four substances.

formed by a combination in pairs of two positive and two negative electrolytes, must now be established in a general manner. We assume we have produced four solutions of the substances A,B, A,B, A,B, and A,B, so that those solutions which contain a common ion are isohydric. When this is the case we can, it is true, mix the isolydric solutions in all proportions; but if we mix all four solutions the simple law stated above evidently no more holds, and we must ask in what proportion the mixture must be made in order that no change in the state of dissociation should occur. Let a, b, c, and d be the relative volumes of the four solutions in which this occurs, and let α , β , γ , and δ be the undissociated quantities of the four substances. We can represent the dissociated quantities by ha, hb, hc, and hd, since, in consequence of the assumption made, there must in all cases be equal concentration of the ions. The equations of dissociation of the solutions thus become

$$\frac{a}{a} = k_1 \binom{ha}{a}^2 \qquad \qquad \frac{\beta}{b} = k_2 \binom{hb}{b}^2$$

$$\frac{\gamma}{c} = k_3 \binom{hc}{c}^2 \qquad \qquad \frac{\delta}{d} = k_4 \binom{hd}{d}^3$$

or, $a = k_1 h^2 a$, $\beta = k_2 h^2 b$, $\gamma = k_3 h^2 c$, $\delta = k_4 h^2 d$.

If we suppose the four volumes to be mixed. new equations will make their appearance which

have the form $\frac{a}{a+b+c+d} = k \frac{h(a+b)(a+c)}{(a+b+c+d)^2} &c.$, and which can be brought to the form

$$\mathbf{c} = \frac{k_1 h^2 (a^2 + ab + ac + bc)}{a + b + c + d},$$

$$\mathbf{\beta} = \frac{k_2 h^2 (b^2 + ab + bd + ad)}{a + b + c + d}, &c.$$

The quantities α , β , γ , and δ are to remain unchanged, according to the assumption. Now, by dividing the corresponding equations by each other, the same equation follows from each pair ad = bc,

i.e. the volumes a, b, c, d of the four solutions must be such that the products of the volumes of such pairs of solutions as contain no common ion must be equal to each other.

Now, the volumes a, b, c, and d are proportional to the active or dissociated portions of the four substances present. Calling the total quantities of the latter, p, p1, q, and q1, the values a, b, c, and d are proportional to $m_1 p$, $m_2 p_1$, $m_3 q$, and $m_1 q_1$, and hence we get from ad = bc the equilibrium formula

 $m_1 p \cdot m_1 q = m_1 p_1 \cdot m_4 q_1$ This equation represents not only Guldberg and Waage's formula for chemical equilibrium, but it also contains the extension, made by Ostwald, that every co-efficient of the Guldberg and Waage equation, $k_1pq = k_2p_1q_1$, is made up of two factors each of which depends only on the nature of the ions.

But the equation goes still further than this extension. In the theory of affinity the co-efficients m1, m2, &c. have been considered as constant to a first approximation. But from what has been said it follows that they are not con-stant; they depend on the state of dissociation of the four substances, and are rather com-plicated functions of the dissociation-constants, of the quantities, and of the total volume. The

various deviations from the simple laws which were brought to light by experiment find here their appropriate explanation. Thus it follows that in the case of slightly dissociated acids the degree of dissociation must be considerably lowered by the presence of the normal salts of these acids, which salts are themselves considerably dissociated. The corresponding fact, that such mixtures act much less strongly than the quantity of free acid present in them would do, was known long before theory explained it.

Arrhenius has subjected his investigations on the saponification of ethyl acetate by means of ammonia in the presence of different salts (Z. P. C. 1, 110) to an examination from the standpoint of these newly-established ideas (ib. 2, 289), and has everywhere found them to be in complete agreement with experiment. He has also re-examined a great number of older investigations on conditions of chemical equili-brium in the light of his theory (ib. 5, 1), and here also the discrepancies found when considered from the point of view of the older theory have for the most part disappeared (v. also Z. P. C. 9, 487).

Electromotive forces. Contact theory or

The laws of electromotive force, or of differences in potential produced on the contact of different substances, are not nearly so well known as those of electrical conductivity. It is true the knowledge of the phenomenon itself is as old as that of galvanic electricity, since Volta had already carried out the first approximate measurement of it, but up to the present day no agreement has been arrived at between the different investigators concerning even the chief phenomena.

Volta screwed a disc of zinc coated with isolating varnish on to his straw-electrometer; on the top of this he placed a similar disc of copper, connected the two discs metallically, and after the connection had been broken he took off the copper disc by means of an insulating handle. The electrometer then proved to be charged; examination showed that the straws were charged with positive electricity.

This phenomenon indicates that the substances used-that is zinc, copper, and the isolating coating-charge each other electrically on contact. Volta assumed that, of the three contacts, only the one between copper and zinc was electromotively active; the contact between the metals and the isolating layer of resin was regarded by him as indifferent. Though neither then, nor up to the present day, has a proof of this assumption been brought forward, it has yet met with fairly universal acceptance, and it often passes as a fact not to be doubted.

On the further assumption, which certainly is incorrect, that liquids also-such as water or salt solutions - show no differences of potential with the metals, Volta constructed his electric pile by superposing alternately two metals and a moist card disc. By this he expected an intensification of the electrical effects, since the electricity of the metal lying underneath was to communicate itself through the moist discs to the one lying above, without any change, and so

¹ A complete discussion of this question by O. Lodge is to be found in P. M. [5] 18,

the effects of the individual pairs of metals were to be added together. Volta did, in fact, obtain the expected intensification- a proof that great discoveries may be made on the basis of quite

false hypotheses.

Fabbroni first refused to accept the assumption that the tension of the voltaic pile has its seat only at the point of contact of the metals, and numerous other investigators have taken the same line. Faraday especially, whose work in electrochemistry ranks with the most important done in this subject, was an opponent of Volta's views. He attributed the production of the electric current solely to the chemical processes present, and transferred the cause of the production of electricity to the places at which these processes occur-i.e. the point of contact between the metals and the electrolytes.

The contention thus aroused between the contact theory and the chemical theory of the galvanic cell has lasted to the present day, and even now it is not completely decided. But most of the discussions raised have certainly originated in the insufficient lucidity with which the questions have been stated.

In so far as a galvanic current can be produced only by using electrical energy, it can be maintained, to begin with, that in order to cause a galvanic current there must be present a corresponding source of energy. If other kinds of energy are excluded, as is the case in an ordinary galvanic cell, it can further be said that chemical energy changes into electrical energy, and that, therefore, a theory of the electric currents produced by the voltaic cell must in any case be a chemical one.

But to an electric current there appertain two factors: a quantity of electricity, and a difference of potential. The first is given by the law of Faraday. Since in electrolytes the motion of electricity takes place only simultaneously with the motion of the ions, equivalent quantities of the different ions carrying equal quantities of electricity, a current in a galvanic cell can again not be produced without a corresponding chemical process. From this point of view, also, the theory must be a chemical one. As regards the other factor of the current energy-i.e. the difference of potential-an unequivocal decision, as in the preceding cases, can certainly not be pronounced easily. The experiments on this subject, taken alone, have proved that all substances. when separated from each other after close contact, show themselves to be electrically charged. The smallest differences suffice for this. It has been long known, for instance, that black and white silk stockings which have been pulled over each other are electrically charged after separation. Even in such homogeneous materials as crystals of mica or calcite, the two parts obtained by cleavage of the layers are found to be in different electrical conditions at the original point of contact.

It is imperative, therefore, to accede to the proposition of the 'contact theory,' in so far as to admit that a process occurs at the surface of contact when two surfaces touch, in consequence of which the surfaces are at different potentials after separation. We do not know what the nature of this process is. Helmholts supposes the different substances to possess a different

attraction for electricity, in consequence of which there is brought about a separation of the electricity at the planes of contact; then when the bodies are separated they appear electrically charged. A difficulty with respect to this theory is found in the electrical phenomena attending the cleavage of crystals, where a difference in attraction seems excluded.

In order that the equilibrium of electricity may be changed when two bodies charge themselves oppositely on contact, the expenditure of a certain quantity of energy is required. The source of this energy has to be sought in the change which the surfaces of the bodies undergo

owing to their mutual contact.

In order that this difference of potential may cause an electric current, two things are needed. Firstly, the bodies touching must be conductors, as otherwise the electricity cannot move: and secondly, a cause must be present which will maintain unchanged the condition of the surfaces in contact, in consequence of which condition the arrangement of the electricity is changed; otherwise a charging motion of the electricity could take place once only, but not a continuous current. The current can be produced by mechanical action, and then the phenomena of frictional electricity appear, or the renewal of the surfaces occurs by chemical action, and we deal with galvanic cells.

When considered from this point of view also, the chemical processes appear as the causes of galvanic currents, and a final theory of these currents will doubtless be much more a 'chemi-

cal 'than a 'contact' theory.

Galvanic cells. The simplest conditions for examining the relations between chemical and electrical energy are found in the so-called constant galvanic cells, of which the Daniell cell is a type. This cell consists of a copper plate in a solution of copper sulphate, and a zinc plate in a solution of zinc sulphate; both solutions are in contact with each other. Such a galvanic cell has an electromotive force of about 1.09 volts, which does not change appreciably when the metals are connected by a conductor, and the galvanic current is thus allowed to pass for a longer or a shorter time.

The chemical process in such an element is also of the simplest kind: zinc dissolves to zinc sulphate, while copper is separated from the copper sulphate. Hence the same process takes place as when a piece of zinc is brought into

a copper sulphate solution.

The chemical energy which is available in this process can easily be measured by experiment; it proves to be 50,100 cal. for the reaction

 $Zn + CuSO_1Aq = Cu + ZnSO_1Aq.$

Now, since (p. 180) the unit of electrical energy, volt × coulomb, is equal to 0.2356 cal., this quantity of heat corresponds to 212,600 electrical units.

Now, of the two factors making up the electrical energy of the voltaic cell, one is given by Faraday's law. One gram-equivalent of a metal carries (p. 180) 96,540 coulombs. Since copper and zinc are divalent, the above equation refers to 2 gram-equivalents; when, therefore, 65 g. of sinc dissolve in the Daniell cell, 193,080 coul. are transferred. Dividing this value into the a reversible cycle taking place in the temperature-

| number 212,600 (volt × coulomb), we get 1.10 volts for the electromotive force of the Daniell element, a number which agrees well with the observed value.

This calculation was first carried out by W. Thomson with the help of numbers due to Joule. From the agreement between observation and calculation, the inference was drawn that the assumption made in this case-namely, that the chemical energy transforms itself completely into electrical energy—was universally correct. From this was deduced the possibility of calculating, on the basis of thermochemical data, the electromotive force of all constant elements, and further, the electromotive force of all elements in which the chemical process is known. It was only necessary to multiply the heat of the reaction referred to one equivalent (not molecular

weight) by $\frac{0.2356}{96540} = 0.00000214$. It would also

follow that the electromotive force of all cells would be proportional to the heat of the chemical reaction.

This theory could not, however, be maintained. On the one hand, theoretical doubts were raised, and that specially by Braun (W. 5. 188), against the premisses that the chemical energy of the galvanic cell was always completely transformed into electrical energy; and, on the other hand, experience proved that as a rule the assumed proportionality between heat of reaction and electromotive force did not exist. Raoult (A. Ch. [4] 4, 392) discovered a number of cells, some of which produced less, and some produced more, energy than corresponded to the heat of reaction of their chemical changes; and at a later time it was provedchiefly by F. Braun and Alder Wright (P. M. [5] 19, 1), by means of direct measurement -that only in rare cases do the chemical and electrical energy exactly correspond to each other.

The simple theory must, therefore, be abandoned, and without assuming that the chemical energy is wholly transformed into electrical energy, we must seek to discover a relation between the two. Such a formula has been found by W. Gibbs and H. von Helmholtz (B. B. 1882). The following statement is a simple way of deducing this equation. Let there be given a galvanic cell whose heat of reaction calculated for one equivalent is W. Let its electromotive force at the absolute temperature τ be On raising the temperature by dr the

electromotive force is changed by de.

Now let us carry out the following cycle. The cell is heated from τ to $\tau + d\tau$. Then let the quantity of electricity q, by means of which one equivalent of the reacting substance undergoes chemical decomposition, pass through the cell, the electromotive force remaining + + de, and the temperature being kept constant. Now let the temperature be brought to \u03c4 and, the electromotive force being e, and the temperature being constant, let the same quantity of electricity q be passed through the element in the opposite direction. Thereby the element returns exactly to its initial condition.

According to the mechanical theory of heat, the portion of heat transformable into work, in interval $d\tau$, is $\frac{d\tau}{\tau}$ of the total quantity of heat

produced. Now, the work is given by $qd\epsilon$, and the total heat which has been communicated to and taken from the cell is $\epsilon q - W$. If an electric current alone were produced, the quantity of heat would be ϵq . But since a chemical process also takes place, which yields a portion of the heat—namely, the heat of reaction, W—it is only necessary to communicate the difference $\epsilon q - W$.

We have then the equation -

$$\frac{d\tau}{\tau} = \frac{q d\epsilon}{\epsilon q - W}$$

$$\epsilon = \frac{W}{q} + \frac{1}{\tau} \cdot \frac{d\epsilon}{d\tau}$$

The former equation was $\epsilon = \frac{W}{q}$; we see, therefore, that a correcting term must be added, and that this term is dependent on $\frac{d\epsilon}{d\tau}$, that is, on the change of electromotive force with change of temperature. In the case that $\frac{d\epsilon}{d\tau} = 0$, the new equation is the same as the old one; in the

now equation is the same as the old one; in the Daniell cell the temperature co-efficient is, in fact, nearly equal to zero, and thus it is explained that in this case the chemical energy is equal to the electrical energy.

The equation has been examined in many ways. At first it gave only partially correct results, and in some cases observation and calculation differed from each other. The differences occurred, however, only in cells which contained mercury compounds, and the cause was the use of a wrong number for the heats of formation of these compounds. When this error was corrected by Nernst (Z. P. C. 23) the discrepancies disappeared; and a very careful investigation by H. Jahu (W. 34, 755), in which the thermal and electrical quantities were measured simultaneously, has fully confirmed the correctness of the Gibbs-Helmholtz formula.

The formula has been deduced primarily for constant galvanic cells, and when deducing it the conditions assumed have been expressed: the chemical process resulting from the passage of the quantity of electricity q (which, however, can be as small as we will) must be reversible, by allowing the same quantity of electricity q to pass through the element in the opposite direction. In order that a galvanic cell should fulfil this condition, it is generally requisite that each metal should be surrounded by its corresponding salt. Therefore, when the salt is soluble, the metal must stand in a solution of the salt. In the case of insoluble salts it generally suffices to cover the metallic surface with the solid salt; in this case, either the salt of another metal with the same acid (which salt is not precipitated by the first metal), or the free acid itself, serves as the electrolyte.

The action in a Daniell cell is as follows. Individual atoms of the metal pass from the zinc as positively charged ions into the solution of the sulphate. Since no free electricity can exist within the solution, the copper ions of the copper sulphate must go to the copper plate, where they give up their positive electricity, passing lote ordinary metallic copper. Owing to this

action, a motion of the positive electricity from the zinc to the copper takes place in the solution; on connecting both metals by a wire the current passes continually through it, corresponding quantities of zinc and copper being dissolved, and precipitated, respectively. If the cell is not closed, the zinc becomes charged negatively, owing to the exit of positive ions, and the copper positively, owing to their entrance; and this goes on until the attraction of the zinc for the positive ions, and their repulsion by the copper, is so great that neither can zinc pass into solution nor can copper separate out. The capacity of the ions being enormous, this is brought about by even extremely small numbers of them.

Nernst, who has studied these changes in detail (Z. P. C. 4, 129), assigns to the metals which are in contact with electrolytes definite solution pressures, just as volatile liquids or solids have definite vapour pressures. This pressure is the cause of zinc tending to pass into solution. The solution pressure of copper is very much smaller than that of zinc. Hence when the Daniell cell is newly set up, both metals will at first send positive ions into the solution. But, since no free electricity can exist in the interior of the solution, that metal which has the greater pressure will maintain the preponderance; its ions will pass into solution, and, in order that no free electricity may accumulate in the liquid, an equal number of copper ions must leave the solution, and be precipitated in the metallic state.

Similar arguments hold for all reversible elements. By their help, and with the help of the theories of electrolytic solutions expounded above, a great number of special cases referring to galvanic cells can be deduced theoretically. The results thus obtained have, on the whole, been confirmed by experiment; but details cannot be entered into here.

Besides the constant galvanic cells of the type just described, which are reversible, there still exists a great number of cells which, though practically constant, are not reversible. The constancy of these cells rests on the fact that the nature of the surfaces in contact is not altered by the chemical processes. When metal dissolves at the surface of the zine, and when metal deposits at the surface of the copper, the nature of the bounding surfaces is not thereby influenced; this cell is also reversible, because on sending a current through in the opposite direction zine is precipitated and copper dissolved, but the surface again undergoes no alteration.

Cells of the type of that of Grove, which consists of zinc in sulphuric acid and platinum in nitric acid, are also constant. On working this cell, zinc dissolves, expelling the hydrogen ions from the sulphuric acid; these hydrogen ions go to the nitric acid, whose own hydrogen ions go to the platinum; at the moment when they give up their positive electricity there, and pass into ordinary hydrogen (which, however, is in the nascent state), they are oxidised by the nitric acid to water, and the platinum surface remains unaltered. But such elements are not reversible. When an opposite current is passed through the cell, since the platinum ions cannot pass into solution, the ions NO₂ of the nitris

seid separate out at the platinum, while hydrogen appears at the zine; both these actions change the condition of the bounding surfaces, and thereby simultaneously change the electromotive force also.

Finally, there still remains the large group of the non-constant cells. These are distinguished by the fact that even when the current passes through them in the direct way, the ions separated out produce an alteration in the bounding surfaces, or in one of them at least. To these belongs Volta's cell, which consists of zinc and copper in salt water, and all the other similar combinations. A type still in use is Smee's cell, which consists of zinc and platinum in dilute sulphuric acid. On closing the circuit, zinc ions enter into the solution, expelling the hydrogen, which gives up its electricity at the platinum, whereby it first combines with or dissolves in the metal, and when that is saturated escapes in the gaseous form. In consequence of this, the surface of contact between the acid and the platinum is altered, and the electromotive force also changes, until saturation with hydrogen has taken place; after this point has been reached the electromotive force of Smee's cell remains practically constant. If the cell is left with the circuit open, the hydrogen gradually disappears, partly through diffusion into the air, partly through combination with the free oxygen of the air, induced by the catalytic action of the platinum. Thus, the cell again gradually resumes its original electromotive force. Such cells are, therefore, quite workable in cases where only small quantities of electricity are required at long intervals.

The seat of the electromotive forces. Volta found that no galvanie pile, giving a current, could be produced from metals only. When considered from the point of view of the principles of energy, such behaviour follows necessarily, because, no continuous source of energy being present in a circuit of metals alone, no current can be produced.

The cause of this may be of a two-fold Either there exist no differences of potential between metals, or these follow a definite law, which involves that in a closed circuit these differences just neutralise each other. With Volta, we will assume the latter alternative, of which the former is only a special case. If, then, we have several metals A, B, C. . . and if we call the differences in potential between A and B, A and C, B and C, &c., in succession (a-b), (a-c), (b-c)... the law is that we must always have $(a-b)+(b-c)+(c-d)+\ldots+(y-z)=(a-z)$. The difference of potential of a series of metals depends only on the nature of the first and the last metal, and not on the nature of the intervening metals.

This result necessarily follows if the values $a, b, c \dots$ in the quantities (a-b) &c. are considered as the potentials of the individual metals referred to a zero value which must be fixed arbitrarily. For the zero value of potential we generally use the potential of the earth, or, more correctly speaking, that of a large metallic mass which is in connection with the earth, as are, for instance, iron water-pipes. It can, therefore, be assumed that every metal con-

nected with the 'earth' assumes a definite value of potential which depends only on the nature of the metal. These values of potential are the same for every metal, whether the different metals are in contact with each other

In order to measure these differences of potential, the experiment of Volta mentioned before (p. 212) has been improved upon, in that instead of a dividing layer of resin one of air is used; and, dating from the time that R. Kohlrausch (P. 75, 88) thus carried out the first experiments, a great deal of similar work has been done. But in this case also we are dealing, not with one, but with three separating surfaces-namely, copper-zinc, zinc-air, air-copper, and only when we make the assumption that the differences of potential at the last two surfaces are zero. are we enabled to judge from the measurements of the total difference of potential as to the

difference between the metals.

The legitimacy of this assumption has formed the subject of much discussion. Considering the universality of differences in potential between heterogeneous substances, the absence of a difference between metal and air would be very strange, and we are quite entitled to demand a proof of it from the champions of this view. But, on the contrary, it seems as if the following fact proved the existence of such differences of potential. All the investigators who have undertaken such measurements complain of the extraordinary inconstancy in the differences of potential observed. On placing two freshly-cleaned plates opposite to each other and measuring their difference, one is sure to find different values after a little time. If the surfaces are again cleaned, the original values approximately recur. Therefore, it is not the point of contact of the two metals (besides, this can be made unalterable by soldering), but their surfaces with respect to air, which are the seat of the changes. Let us now assume that at a definite moment the difference of potential of both plates towards air is equal to zero; since another value is observed after some time, the difference of potential of the metals towards air cannot now be zero, i.e. between metals and air there exist differences of potential. How great these are cannot as yet be determined. There is nothing against the assumption that these make up the greatest part of the apparent differences of potential between the metals (measured in air). It is true an attempt has been made to eliminate the influence of the air by making the experiment in vacuo. But since we have learned by observation of the electrical phenomena in vacuum tubes, how difficulthow impossible, even-it is to withdraw from a substance the last remnants of air condensed on it and in it, these experiments cannot be looked upon as affording any conclusive proof.

Other methods for solving the difficulties must be sought. Unfortunately, there does not exist a single process quite free from objection. The following consideration still appears to be

the best :-

When a given quantity of electricity e is brought from a potential A to a higher potential A + a, a quantity of work aq is required. There-

Compare O. Lodge, La.

fore, when we lead a current through two metals which touch in one place, and which there exhibit a difference of potential a, an absorption or a production of energy will occur at the place of contact, according to the direction of the current: and, if there is no other source of energy, this energy-change will be produced from, or will be added to, the heat which is present, as the case may be. In the case of metals such a phenomenon is actually known; it is the effect discovered by Peltier (A. Ch. 56, 371 [1834]). If the strength of the current, and the total heat produced, are measured, the corresponding difference of potential can be calculated. Such experiments have been made by Le Roux, and again quite recently, with great accuracy, by H. Jahn (W. 34, 755), and the results have shown the values to be very small; they are mostly only a few thousandths of a volt.

It is true we must not pass over in silence the following objection made against he validity of this argument. Since we know nothing definite concerning the nature of the electric current. the possibility is not excluded that it may be connected with movements of energy of other kinds. It has been especially assumed as probable by several authors that, simultaneously with the electric current, a heat-current flows through the conductor. If so, the quantity of heat flowing with the unit quantity of electricity might be different in different conductors; and at the point of contact of the metals, in addition to the thermal exchange resulting from the difference of potential, there might occur a further exchange of heat resulting from the difference in the 'thermal capacity of electricity.' Since these two quantities need not have a necessary connection, it would not be permissible to draw any conclusion from the Peltier effect-that is, from the sum of two independent effects -as to the magnitude of the difference of potential.

Without attempting to decide this difficult question here, I should like to draw attention to a circumstance which makes it probable that the second effect, if present at all (which so far has not been proved), must probably be of the same order of magnitude as the difference of potential corresponding to the Peltier effect. According to the second law of the mechanical theory of heat, the carrying of a definite quantity of heat Q from a lower to a higher temperature involves

work which is given by $Q^{\frac{\tau_1 - \tau_2}{\tau_1}}$. If, therefore,

we pass an electric current through a wire whose temperature varies, it follows that, if heat is carried with the current, in places of rising temperature a corresponding quantity of work must be expended, i.e. an opposing electromotive force must there assert itself. Indications of such a force appear to manifest themselves in the so-called Thomson effect (supposing that this effect does not find its explanation in differently heated portions of one metal having differences of potential to each other), but in any case the quantities of work, or the differences of potential, indicated by this phenomenon are extremely small (of the same or of a smaller order of magnitude as those corresponding to the Peltier effects), so that the assumption of an appreciable carrying of heat by means of elec-

tricity (for which, at any rate, we lack the power of forming a conception) seems excluded.

From this it is evident that though nothing quite certain is known concerning the differences of potential between different metals, yet preponderating reasons favour the assumption that such a thing does exist, but that its magnitude does not exceed a few thousandths of a volt, and particularly that it does not attain the order of magnitude of 1 volt. But, varying slightly with the nature of the metals, such a value has been observed by means of the air-condenser method.

As regards differences of potential between various electrolytes, such differences certainly do exist. This can be inferred from the fact that there exist 'liquid chains,' i.e. combinations of different liquids, which produce an electric current. If, for instance, we put into a series of beakers water, concentrated hydrochloric acid, concentrated soda solution, and water, and if we connect these by small syphons or by moist threads, then the two quantities of water at the ends exhibit a difference of potential which may attain to 0.5 volt.

In such liquid chains we have always to deal with three distinct differences of potential at least; designating the three liquids named above by A, B, and C, there exist in the chain the differences of potential (a-b), (b-c), and (c-a), whose sum is observed. There is no combination of the liquids by which we could succeed in obtaining as many independent observations as there are differences of potential, so that it is impossible to determine by measurements on liquid chains only the individual differences of potential.

This determination has, however, been achieved in another way. Since in electrolytes the electricity moves only with the ions, differences in potential between two liquids in contact can only be produced if the different positive and negative ions distribute themselves unequally. A cause for such an inequality lies in the different velocities of migration of the ions (p. 92), and, in an extensive investigation, W. Nernst has shown (Z. P. C. 4, 129) how thereby the actually observed differences of potential can be theoretically calculated in a great number of cases. The fundamental idea of these calculations is the following. When any solution is brought into contact with pure water, forces make themselves apparent at the surface of separation, which forces can be calculated by van't Hoff's theory (pp. 184-5); for 'normal' solutions (which contain one gram molecular weight per litre) they are equal to the pressure of about 22 atmospheres, and they are proportional to the quantity of substance in the solution. Owing to the osmotic pressure, the molecules of the substance are forced into the water. The velocity of their motion is determined by the resistance which they encounter, and this depends on their form as well as on the nature of the solvent.

This statement contains a physical theory of hydro-diffusion (Nernst, Z. P. C. 2, 613), and from it the law of Fick follows directly, that the velocity of diffusion at any point is proportional to the change in concentration at that point. From this we see at once how a separation must occur in the diffusion of dissolved substances,

because those molecules which are endowed with greater mobility or suffer less friction outstrip the slower ones. The same laws hold for each kind of molecules, only the constants are different.

These arguments can only be applied immediately to electrolytes in solution if both ions have equal rates of motion. This condition is very nearly fulfilled in the case of potassium chloride, and this substance conforms, therefore, to the simple law of diffusion.

It is now possible, in the case of electrolytes, to determine the resistances which the ions encounter, as well as to measure the impelling forces. If the ions are moved past each other by electrical forces of separation, they encounter exactly the same resistance, and since in the electrical conductivity we have a measure of the velocity of the corresponding motion of the ions, it is possible, as first shown by F. Kohlrausch (W. 6, 160), to calculate the magnitude of the resistances from a knowledge of the impelling force and of the velocity attained. On introducing this resistance (which, owing to the smallness of the molecules, is enormously great) into the equation for the velocity of diffusion, indicated above, Nernst has found (l.c.) that the velocities of diffusion agree very well with the results of experiment.

In the case of electrolytes whose ions do not migrate with equal velocities the phenomena become much more complicated. stance, we imagine hydrochloric acid, in which the hydrogen ion travels about six times more quickly than the chlorine ion, to be brought into contact with water, the quicker hydrogen atoms will, to start with, pass into water, and the chlorine atoms will remain behind. But since the hydrogen atoms are charged with positive electricity, the water will become positively electrified, while the acid, owing to the preponderance of chlorine atoms, becomes charged negatively. But the further exit of hydrogen atoms is thus rendered more difficult, owing to the electro-static effect, while from a similar cause the chlorine atoms are subject in addition to the osmotic pressure, and also to an electric impelling force, and are thus driven into the water. The consequence is that both ions influence each other's velocity until they again migrate at equal rates.

At the same time, we see that every electrolytic solution whose ions travel with unequal velocities on contact with water—or, speaking more generally, on contact with a solution of different concentration—at once acts as the cause of difference of potential, and also that the more dilute solution will always assume the sign of the ion which has the greater migration velocity. The exact expression which has been deduced by Nernst (i.e. p. 189) is

$$\epsilon_1 - \epsilon_2 = 0.0000860 \quad \tau \quad \frac{u - v}{u + v} \log_1 \frac{p_1}{p_2}$$

Where e_1-e_2 is the difference of potential (in volts) of two solutions in which the osmotion pressures of the (positive as well as negative) ions are p_1 and p_2 ; w is the velocity of the positive, w that of the negative, ion; τ is the absolute temperature, while log. stands for the natural logarithm.

We see that for u=v the electromotive force becomes zero, and it becomes the greater the greater the difference between the migrationvelocities of the two ions. Further, we see that as regards the electromotive force, only the ratio

 $\frac{\mathcal{P}_1}{\mathcal{P}_2}$ of the two pressures, and not their absolute

values, enters into consideration. By increasing the concentration n times in both solutions, the difference of potential does not change. If one of the solutions is pure water, we get $p_2 = 0$, and the electromotive force becomes infinitely great. Since 'pure water' in this sense does not exist, such values cannot come under our observation. But yet we see that liquid chains with 'water' can give very different values according to the degree of purity of this liquid.

The preceding formula is the fundamental expression for all kinds of liquid chains, since in the commination of any solutions the corresponding differences of potential are superposed. It would take us too far afieldeto enter into the different cases; in the memoir of Nernst, a number of cases are discussed theoretically as well as experimentally. But on the whole it may be concluded that the differences in potential apparent on contact of approximately equally concentrated solutions of the most varied kind, vary within fairly small limits, which probably do not surpass 0.01 volt.

Now, since we cannot suppose that differences of potential of the order of magnitude of those observed in galvanic cells exist either between metals alone, or electrolytes alone, we are obliged to regard the surfaces of contact between the metals and the electrolytes as the real seat of the electromotive forces. This result quite corresponds with what was to be expected from the relations between the chemical and electrical energies. This is so because these surfaces of contact are the only seat of the processes by which energy becomes available in the chains, i.e. they are the result of the chemical changes. Since, on the one hand, the cause of the galvanic current of the chains has to be sought in the transformation of chemical into electrical energy, and since, on the other hand, a galvanic current can be produced only when a difference of potential exists, it does not seem very logical to wish to separate in space, and in their nature, the more approximate and the less approximate causes of the same phenomenon, as is done in the assumption that the difference of potential is to be sought at the surface of contact of the metals.

The question now arises again, whether some means does not exist for directly measuring the differences of potential between metals and electrolytes. The answer is that up to the present only one such means is known. A second independent way for arriving at those numbers does not as yet exist, and hence it has hitherto been impossible to put to the proof the results obtained by that method.

The method in question is based on the phenomena exhibited by mercury surfaces when in contact with electrolytes. Lippmann (P. 149, 561; A. Ch. [5] 5,494) has shown that there is a close connection between the condition of the surface of mercury touching an electrolyte and

the electrical state of the system. If, for instance, mercury is covered with dilute sulphuric acid, and the surface of contact between the two is then increased, a galvanic curront is produced, because the mercury becomes less positive on expansion. This can be observed most easily by allowing mercury to drop out of a funnel with a small orifice immersed in dilute sulphuric acid. On connecting the mercury in the funnel and that collected below the sulphuric acid by means of a galvanometer, a current passes from the lower mercury to the higher; in the sulphuric acid the reverse occurs.

This phenomenon is reciprocal. On leading a current through the surface of contact between mercury and sulphuric acid the surface tends to diminish or to increase, according to the direction of the current—i.e. the capillary tension at this point changes. As is always tho case, both phenomena are in such a relation that they oppose each other—i.e. when the surface is made larger the current has the direction such that if it alone were active it would tend to make the surface smaller, and vice versa.

Helmholtz (W. 16, 35 [1882]) has given a theory of these phenomena which is based on the following considerations. When a metal and an electrolyte are in contact, they generally possess a varying difference of potential. Owing to this circumstance, the opposite electricities must accumulate on both sides of the bounding surfaces, since they are prevented from combining by the cause which produces the difference of potential (and which, without making a definite assumption, can be designated as a different attraction of the substances for the electricity). The result is the formation of an 'electric double layer,' which will exhibit a similar arrangement to the charge of a Franklin plate.

But such a double layer will have the property of tending to increase its surface as much as possible, since the similarly electrified particles present at each side repulse each other, and therefore tend to stretch the surface. Hence the development of such a double layer will act in opposition to the surface tension, which seeks to decrease the surface, and the actually observed surface tension is the difference between the real tension and the electric force.

When a surface so constituted is made larger, the electric layers are thereby extended, and their difference of potential decreases. But since, as is known from experience, a constant difference of potential is always formed at the boundary, which difference of potential does not depend on the size of the surface of contact, electricity will flow from the mercury as well as from the electrolyte to replace the loss, and in this way the current is produced.

If, on the other hand, the difference of potential of the electric double layer is changed, the surface tension must change also. It must get smaller when the difference of potential is made larger, and larger when it is made smaller.

By leading electric currents of varying electromotive force through a system consisting of two masses of mercury in sulphuric acid—one of which had a very small, the other a very large, surface of contact with the acid—Lippmann was able to follow the change of surface the sign at the small bounding surface which accom-

panied the change in the difference of potential at that surface. Because, since the change in the difference of potential between a metal and an electrolyte is proportional to the density of the current (current strength divided by the cross-section), the resulting difference of potential practically restricted itself to the small bounding surface, which was surpassed in extension some thousand times by the large one. It was found that when the mercury of the small surface was connected with the positive pole of the external cell, the surface tension decreased. On the other hand, when negative electromotive forces acted, the surface tension increased until the external force was 99 to 10 volt; beyond that it again decreased.

In accordance with Helmholtz's theory, we must infer from this that the difference of potential between mercury and sulphuric acid is of such a kind that the former becomes charged positively—i.e. that the positive electricity of the double layer is on the side of the mercury, and the negative electricity is on the side of the electrolyte. If the difference of po tential is increased by addition of positive electricity to the mercury, the electric repulsion increases, and therefore the surface tension decreases. If, however, negative electricity is added, the charge of the double layer decreases and the surface tension increases. On making the successive additions of negative electricity larger and larger, the difference of potential of the double layer eventually becomes zero; the surface tension has reached its greatest value, and, beyond this, a new double layer of opposite sign is produced. When this state is reached, the surface tension must again decrease.

According to the experiments of Lippmann, the maximum of surface tension is reached when the 'external electromotive force is 0.9 to 1.0 volt. Then no more double layer is present at the small surface of the mercury, and the metal and electrolyte have the same potential. Since this condition is separated from the ordinary one by about 0.9 volt, it follows that the usual difference of potential between dilute subphuric acid and mercury is 0.9 volt.

This result is confirmed by the following experiment of Pellat (C. R. 104, 1099). When the surface of contact between mercury and sulphuric acid is increased, a motion of electricity is produced, owing, as has been mentioned above, to the stretching of the double layer. But this must disappear when, by the use of a difference of potential of about 1.0 volt, the double layer has been made to disappear; and, in fact, under these conditions, Pellat, on changing the surface, could observe no current.

Another confirmation can be obtained in the following manner. When mercury is dropped very quickly out of a fine point into an electrolyte, it must, after a short time, as Helmholtz has shown, assume the potential of the latter (W. 16, 35), because if, for instance, the mercury were at the beginning positive, every falling drop would form a double layer at its surface, which would take positive electricity out of the mercury, and which would make its positive potential smaller and smaller till it became equal to that of the liquid.

But it is to be remembered that the mercury

in contact with sulphuric acid spontaneously becomes positively charged; everything will depend, therefore, on allowing the formation of drops to take place as quickly as possible, in order that the discharge may preponderate over the charge. Experiments by W. Ostwald (Z. P. C. 1, 583 [1887]) have shown that the discharge can be achieved to a great extent, but not completely; there still remain over, even with the best dropping electrodes which have yet been made, differences of some hundredths of a volt. But within these limits the experiment confirms the conclusion which Helmholtz had drawnthe difference of potential between the dropping electrode and the mercury at rest in sulphuric acid amounts in 'normal' sulphuric acid solution to 0.81 volt, while the maximum of surface tension (that is, the true difference of potential) lies at 0.86 volt.

Finally, another inference, which must be drawn from the theory of Helmholtz, has been confirmed by the same author. If the maximum of the surface tension of mercury, as obtainable by means of suitable electromotive forces, actually is the real surface tension of mercury in contact with aqueous liquids, free from auxiliary effects, then it must have the same value whatever be the nature of the electrolyte, while experience shows that the natural surface tension changes considerably with the nature of the electrolyte. This also was confirmed; while the natural surface tension in different solutions varied between 485 and 564. the maximum values were 610 to 611, and were, therefore, practically constant.

All these facts speak for the correctness of Helmholtz's theory of the electric double layers, and leave us, therefore, with the final conclusion that the electromotive force required for producing the maximum of surface tension of mercury in contact with an electrolyte is equal to the ordinary difference of potential at this bounding surface (but with inverted sign). But it must be again emphasised that this is the only group of phenomena from which the values considered can be deduced. An examination of the results by means of another entirely independent method has not yet been feasible.

If, now, the difference of potential between mercury and sulphuric acid is known, the difference of potential between all other metals and sulphuric acid can be measured by experiments which are easily carried out. For this purpose the electromotive force of the combination mercury, sulphuric acid, and metal alone need be measured: this is the sum of the differences of potential of mercury-sulphuric acid and sulphuric acid-metal, and since the first of these is known the other follows by difference. But here it is supposed that no appreciable difference of potential exists between the metals. Again, if the difference of potential between mercury and any other electrolyte is determined, either by the maximum surface tension or by means of the mercury-dropping electrode, the difference of potential of these electrolytes against any other metals can also be determined. In this manner, therefore, the whole subject of the differences of potential between metals and electrolytes has een made amenable to measurement.

kind have as yet been made; in the following table some numbers are given :---

			HOI	HBr	HI	H.SO.
Zn		•	-0.54	-0.46	-0.30	-0.62
Cd Sn	•	•	- 0·24 + 0·02	-0·18 + 0·12	-0.08 +0.28	-0.52 -0.03
Pb	:	:	+0.03	+ 0.10	+0.26	-0.04
Cu	•	•	+ 0.35	+ 0.35	+ 0.36	+0.46
Bi Sb	:	•	+0.41	+ 0·47 + 0·60	+ 0.60	+0.46
Ag	•		+0.57	+ 0.51	+0.15	+ 0.73
$_{ m Hg}$	٠	•	+0.57	+ 0.20	+ 0.44	+ 0.86

The values refer to 'normal' solutions of the electrolytes mentioned, and indicate the potential of the metal when that of the electrolyte is put equal to zero.

We see that those metals which dissolve in the acids become acgative; the others become positive. The values are also in very nearly the same order as the corresponding heats of reaction, but, as a calculation shows, they are not proportional. The nature of the electrolyte has generally a smaller influence than that of the metal, but there are cases where the reverse is

It should be mentioned that nearly the same numbers are obtained when salts of the acids. with metals which are not precipitated by the metal under examination, are used instead of the acids themselves. The difference of potential between the metal and the electrolyte depends, therefore, chiefly on the negative ion of the latter. From the numbers in our possession it is seen, for instance, that in the Daniell cell. whose difference of potential is 1.08 to 1.10 volt. the greater part of this (0.62 volt) is present at the bounding surface between zine and zine sulphate, and the smaller part at the surface (0.46 volt) between copper and copper sulphate.

No further conclusions of more general interest have as yet been drawn from these num-

Galvanic polarisation. When two metal plates are introduced into an electrolytic liquid and a galvanic current is made to pass through the electrolyte by means of the plates, these plates generally become the scat of a new electromotive force which acts in opposition to the current already active. This phenomenon is called galranic polarisation, and it may be perceived by connecting the plates with a galvanometer immediately after breaking the primary current.

The cause of this phenomenon is to be found in the change which is produced by the current at the boundary surface between the metal and the electrolyte. There the ions of the electrolyte separate out, and cause changes of the most manifold kind.

The simplest case occurs when the metal plates are surrounded by the solution of a salt which contains the same metal, for such a system scarcely exhibits the phenomenon of polarisation at all; such electrodes are 'un-polarisable.' The reason is that in this case the changes occurring at the electrodes do not change the condition of the bounding surfaces. But few trustworthy measurements of this If, for instance, we have zinc in zinc sulphate.

sine is separated out at the cathode, and this combines with the metal present without changing it, and at the anode SO, separates out, which then dissolves zine and forms zine sulphate. The only effect is that the zine sulphate solution becomes more concentrated at the anode, and accordingly a small concentration-current can be observed, whose electromotive force is, however, very inconsiderable.

Such a system of unpolarisable electrodes differs from all similar combinations in that it allows any, even the smallest, current to pass through. Polarisable electrodes do not behave thus. If, for instance, two platinum plates are placed in dilute sulphuric acid, and a current of small electromotive force - say, 0.1 volt-is allowed to pass, we observe by the galvanometer that at first a motion of electricity takes place, but that this ceases after a very short time. It is a phenomenon such as a condenser exhibits on being charged, with this difference, that the capacity of such electrolytic condensers appears to be very great. • On increasing the electromotive force, a corresponding quantity of electricity answering to a greater charge of the condenser always enters, but no permanent current is produced until the electromotive force is somewhat more than 2 volt; then a more copious passage of the current suddenly takes place, and simultaneously gaseous oxygen and hydrogen appear at the electrodes.

We must, therefore, represent the phenomenon to ourselves in the following way. Between the electrolyte and the platinum plates there exists originally some one difference of potential, and in consequence the double layers form there. Now, on allowing the electromotive force to act, on the one side the difference of potential of the double layer is increased, on the other it is diminished. The corresponding process to this is the condensing charge. On increasing the difference of potential, there is a moment at which the condenser no more isolates under the influence of the electro-static effects; a passage of electricity from the metal to the ions (or vice versa) occurs, corresponding to the disruptive discharge of the condenser, and the ions, deprived of their electric charges, separate out. When sulphuric acid is the electrolyte, the ions are H, and SO4; the latter substance is not stable, and reacts with the water present to form sulphuric acid and oxygen, the latter escaping in the gaseous state.

From this we see that a difference of potential of definite magnitude must exist when the electricity is to leave an ion in order to travel to a metal; until this difference of potential is reached, the system acts at the electrode like an isolator. But why does this not occur with unpolarisable electrodes? The answer to this question follows from the consideration of the processes occurring at these electrodes. Let us again take zinc plates in zinc sulphate, and let us lead positive electricity into one plate. This electricity can at once enter into the solution, by using as its vehicle a corresponding number of zinc atoms, which travel with it as positively charged zinc ions. At the other zinc plate an equal number of zinc ions can also deposit at once, and since there exists no difference of potential between zinc and zinc these can at once deliver up their electricity. Here, therefore, no cause exists for condensing effects. It is not, however, as if no difference of potential existed between the metals and their solutions; such differences, in fact, are present, and hence also corresponding double layers are formed, which at one side are made up of ions. But these do not act as condensers, free communication of their ions between the metal and the electrolyte being possible, and consequently the difference of potential, independent of the current, maintains itself at an unaltered value.

Beside the unpolarisable electrodes and those polarisable at both sides, there still exist combinations in which polarisation occurs only at one side, mostly at the cathode. This takes place, for instance, with copper plates in dilute sulphuric acid. At the cathode, when the electromotive force is sufficient, hydrogen separates out, just as it does at a platinum plate. But at the anode, on the other hand, copper sulphate is formed by the ion SO, acting on the copper—i.e. the ion SO, need not give up its negative electricity there, since in its stead positive electricity fixed to copper comes out of the plate. Hence, no polarisation occurs here.

From what has been said an explanation follows of the cause of the polarisation current, which occurs after breaking the primary current and connecting both plates in the opposite direction. It is, in brief, the discharge of the electrolytic condenser. Looking at the process more in detail, we see that when the charge in the double layers is formed, the electricity led in has remained in the electrodes, equal quantities of the opposite electricities having collected from the electrolyte on the electrodes -the electricity being, of course, bound to the ions. On the primary current being broken, and the electrodes being connected with each other, the electricities present in these neutralise each other, and the ions, which are no longer fixed, form the carriers of the current in the electrolyte. This lasts until the original condition of equilibrium has re-established itself.

In accordance with what has been said, the measurement of galvanic polarisation refers assume, or to the value of the difference of potential at which the double layer condenser no more isolates.1 The measurement of this quantity is somewhat difficult; because, when carrying out the simple experiment indicated above-i.e. when increasing the primary current up to decomposition, interrupting it, and afterwards connecting the electrodes with an electrometer-we observe that (in consequence of the secondary effects) the electromotive force of polarisation decreases very rapidly. We are, therefore, not sure whether a considerable portion of the polarisation has not already been lost in the time which elapses before the measurement. But there exists a means of obtaining information concerning the magnitude of the possible error. If the change of connections is carried out more and more quickly, increasing values at first are observed. But these approach

1 It must be observed that complete isolation does not occur; a small amount of percolation of electricity takes place when the maximum value is not reached. But, as Helmho's has shown, this phenomenou is a consequence of electrolytic convection, and is of a secondary character.

to a maximum, and when the number of current reversals reaches about 100 per second a further rise in the velocity no longer produces an increase, as was found by Raoult (A. Ch. [4] 2, 326), and the value observed under these conditions may be regarded as the correct one.

Other methods are based on making measurements of current strengths and resistances in the primary circuit, and on calculating from this the electromotive force of polarisation. These become uncertain by the fact that, owing to the processes occurring at the electrodes, the resistance of the cell undergoes variations during the passage of the current, which variations cannot be determined. Finally, we can use electrometric methods, by measuring the difference of potential between the electrode to be polarised and an auxiliary electrode through which no current passes, both before closing the circuit and while the current passes; the difference between the two magnitudes is the polarisation required. But difficulties, which have not yet been removed, appear in the practical application of this ingenious method, which was pointed out by Fuchs (P. 156, 158).

Because of these difficulties only a small number of trustworthy measurements of the electromotive force of the maximum polarisation have as yet been made. Consequently, no certain relations with chemical conditions have been discovered as yet. Though an attempt has been made to calculate the electromotive force of polarisation in a manner similar to that of the galvanic cell, from the thermal effects appertaining to it, the same objections can be raised against it as in the former case (p. 213): the observed electromotive force is generally different from that calculated.

It is especially remarkable that the maximum forces of polarisation corresponding to one and the same chemical process may be very different according to the nature of the metal. If we form galvanic cells of zinc, dilute sulphuric acid, and different metals - such as copper, silver, gold, platinum-or of charcoal, and if we close the circuit in the cells, the same process occurs in all . zinc sulphate is formed, and, to make up for it, hydrogen is expelled from the sulphuric acid. The latter appears at the metal, and polarises it. It is found that the electromotive forces of these cells, even after they have completely polarised themselves, are distinctly different; according to the nature of the second metal. a greater or less portion of the energy liberated by the reaction $Zn + H_2SO_4 = ZnSO_4 + H_2$ is transformed into electrical energy.

The cause of this can be understood after what has already been explained. The electricity must overcome unequal differences of potential in passing from the H ions to the different metals; hence different portions of the total available energy are used, and only the residue of this energy finds its expression in the electromotive force of the cells. We see, then, that the electromotive force cannot possibly bear the simple relation to the heat of reaction which was formerly supposed to be the case. But it is possible that the equation of Gibbs and Helmhoffz (p. 214) is applicable to galvanic

polarisation also; if this is so we shall be able, from a knowledge of the electromotive force and its changes with the temperature, to draw conclusions as to the thermal changes due to the processes which primarily participate in the polarisation.

W. O.

VI. FREEZING-POINTS OF SOLUTIONS, METHODS BASED ON; v. MOLECULAR WEIGHTS, vol. iii. p. 417; and ELECTRICAL METHODS, this vol. p. 186.
VII. QPTICAL METHODS.—Section 1;

VII. OPTICAL METHODS.—Section 1: REFRACTION AND DISPERSION. When a ray of light passes at an angle from a rarer into a denser medium, it is always reflected towards the perpendicular, the sine of the angle of incidence being in a constant ratio to the sine of the angle of refraction, namely the ratio of the velocities of wave propagation in the two media. This constant ratio is called the index of refraction, and is generally represented in England by the Greek letter μ , and on the Continent by n: $\mu = \frac{\sin i}{\sin i}$. The angle of incidence

being in such case greater than the angle of refraction, the index of refraction will be greater than 1. The reverse will be the case when the ray passes from a denser to a rarer medium.

The refraction of a ray of light is, however, always accompanied by another phenomenondispersion, as the ray is made up of a number of vibrations of different velocities which are affected diversely in passing from one medium to another. This causes the ray of common or white light to be spread out into a number of coloured rays corresponding to vibrations of different rapidity. In all precise determinations, therefore, a definite point of the spectrum thus formed must be measured for refraction, and two such points for dispersion. The work of early observers on the refraction of light is usually wanting in precision in this respect. the records being commonly described as having reference to the bright or yellow part of the spectrum, or to the extreme red; while they furnish no data at all for calculating the dispersion. Moreover, as each colour occupies a certain breadth in the spectrum, and the boundaries of the colours are not well defined, it is by no means certain that two observations made on the same colour will refer to exactly the same part of the spectrum. In more recent observations the most conspicuous lines of the solar spectrum, such as A, D, F, H, are adopted, or, if artificial light be used, the a, B, and y lines of the hydrogen spectrum; these are recorded as $\mu_{A_1} \mu_{D_2}$ &c.; $\mu_{\alpha} \mu_{\beta}$, μ_{γ} . The greater part of the English data of recent times are given for the solar lines, while foreign observers have generally adopted the hydrogen lines.

Refraction and dispersion equivalents. The index of refraction, minus unity, when divided by the relative density (d) and multiplied by the atomic weight if an element is examined, or by the molecular weight if a compound is examined (P), is usually represented by the for-

mula P
$$\frac{\mu-1}{d}$$
 in England and P $\frac{n-1}{d}$ on the

Continent, and is termed the refraction-equivalent. It will be expressed in this article by the simple letter B. When Lorenz's formula is used,

See, however, a recent investigation by M. Le Blanc (2 P. C. 8, 299).

 $\left(\frac{\mu^2-1}{\mu^2+2}\right)^{\mathbf{P}}_{\mathbf{d}}$, the refraction-equivalent so calculated will be distinguished as & The part of the spectrum to which the observation refers will be indicated by adding the sign for infinity, or the letters of the solar or other lines observed, as R_{∞} , R_{λ} , R_{α} , &c. The dispersion-equivalent represents the difference between the refraction-equivalents of two selected portions of the spectrum; thus the dispersion-equivalent for H-A will be expressed as

 $\frac{(\mu_{\rm H}-1)}{d} - \frac{(\mu_{\rm A}-1)}{d}$, or, more briefly $\frac{\mu_{\rm H}-\mu_{\rm A}}{d}$.

multiplied by P; or $R_H - R_A$.

The index of refraction of solids is generally ascertained by the method of total reflection, unless they are transparent, and can be cut into the form of a prism; that of gases is best determined by interference. The refraction of liquids is most conveniently arrived at by placing the substance in a hollow prism, with sides of plate glass; on the prism being so adjusted that the incident and emergent rays make equal angles with the refracting surfaces, the minimum deviation will be arrived at. Let D be the deviation, i and r the angles of incidence and refraction, and a the refracting angle of the prism; then

$$\frac{\sin e \, i}{\sin e \, r} = \frac{\sin e \, \frac{1}{2} (a + D)}{\sin e \, \frac{1}{2} a} = \mu.$$

Newton, acting upon the emission theory, proposed $\frac{\mu^2-1}{d}$ as representing the absolute refractive power of any substance, and this formula met with general adoption till recent times. Gladstone and Dale (T. 1863), as the result of a long series of experiments with different substances at various temperatures, found that the refractive index, minus unity, multiplied by the volume, gave nearly a constant. To $\mu-1$ they accordingly gave the name of 'refractive energy' as really representing the influence of the substance itself on the rays of light; and to $\frac{\mu-1}{d}$ that of 'specific refractive energy. This empirical formula has been adopted by most subsequent investigators; and Sutherland (P. M. [5] 27, 141) has lately advocated it on mathematical, as well as on physical, grounds. It holds its position side by side with the theoretical formula we have now to

Lorenz's formula. H. A. Lorentz, of Holland (W. 9, 641), and L. Lorenz, of Copenhagen (W. 11, 70), came almost simultaneously to the conclusion, from purely theoretical considerations, based, in the case of the former, on the electro-magnetic theory, that $\frac{\mu^2-1}{(\mu^2+2)d}$ must express the relation between the velocity of the transmission of light and the density of the medium through which it is propagated. Landolt (B. 15, 64) tested the comparative merits of this formula, and that which he had previously adopted—viz. $\frac{\mu-1}{d}$ —and found that so far as liquids were concerned there was nothing to choose between them, but that Lorens's formula showed much less difference between the specific refractive energy of a liquid

consider.

and that of its vapour. This is shown in the following table, in which it will be also noticed that the difference with the rise in temperature is uniformly plus in the one case, and minus in the other. Weegmann (Bonn. 1888) experi-menting at 10°, 20°, and 30°, noted the same rise in the one case and fall in the other.

Substance	State	Temp.	$\frac{\mu_{\rm D}-1}{(\mu_{\rm D}+2)d}$	$\frac{\mu_{\rm D}-1}{d}$
Water Ethyl alcohol Ethyl ether. Ethyl acetate Ethyl lodide Chloroform.	Liquid Vapour Liquid	10° 20° 100° 10° 20° 100° 100° 100° 20° 100° 20°	0-2062 0-000 0-2061 0-0007 0-2061 0-0007 0-2804 0-0007 0-2805 0-0018 0-3026 0-0007 0-3026 0-0007 0-3028 0-003 0-2547 0-0007 0-2683 0-1557 0-1557 0-0007 0-1557 0-0007 0-1571 0-0007	03101 0-0255 0-0255 0-0301 0-1011 0-1
Carbon di- sulphide .	Vapour Liquid "Vapour	100° 20° 100°	0·1796 0·2805 0·2809 0·008 0·2898	

In the case of liquid and solid phosphorus, as well as of other highly refractive bodies, the empirical formula appeared to give the best results. Landolt also found the simpler formula best adapted to his process of optical analysis subsequently described. But while he found that the refraction-equivalents (i.e. the specific refractive energy multiplied by the atomic weight in the case of elements, or by the molecular weight in the case of compounds) of substances calculated by Lorenz's formula are about onethird smaller than the numbers calculated by the formula previously adopted by him, the values which he obtained for the elements carbon, oxygen, hydrogen, and chlorine did not bear the same proportion. Adopting Brühl's figures for R_{α} (as described later on), the values according to Lorenz's formula vary from about 1 to 3 the values found by using the other formula. Thus :-

	Old Formula	Lorens's Formula
Carbon	5.0	2.48
Hydrogen	1.3	1.04
Oxygen, alcoholic	2.8	1.58
" aldehydic	3.4	2.34
Chlorine	9.8	6.02
Increase for double carbon bond	2.4	1.78

Brühl, however, in 1886 (A. 235, 1), maintained that the statement of Landolt, that the two formulæ lead practically to the same conclusions in respect to chemical constitution and the refraction of light, cannot any longer be accepted in its general sense. In this paper Brühl contended that the expression of the molecular refraction hitherto used—viz. $P = \frac{\mu - 1}{d}$ is generally adapted only to the paraffinoid series of carbon compounds, and for unsaturated compounds of

weak dispersive power; and that in these cases even the results are not altogether satisfactory. For the investigation of the relations between the refractive power and the constitution of bodies, Brühl claimed that in future Lorenz's formula must be used. The tables appended to the paper certainly show better proportionate results for Ra by this formula, especially in the case of the most dispersive substances; but in using these tables it must be borne in mind that the values assigned to the elements under the two formulæ are not strictly comparable. Nasini (Lincei, Rc. 3, 128) stated that he and Bernheimer did not consider that, from a chemical point of view, any great preference should be given to Lorenz's formula over the formula d, as the newer formula was insufficient to

represent every relation between the chemical constitutions of the substances and their refractive powers. Ketteler does not accept the Lorenz formula as altogether satisfactory; in place of it he has proposed $\frac{\mu^2-1}{(\mu^2+x)\cdot l}$, where x is

a variable quantity depending on the nature of the substance, but averaging about 3.5 instead of 2. Sutherland (P. M. [5] 27, 141) objects to Lorenz's formula on the ground that it assumes a mean wave length, whereas the wave length must vary in passing from ether to matter; and he maintains that while the formula holds good for both the liquid and gaseous states, it fails when change of density is produced by change of pressure. On the other hand, he thinks that Gladstone's formula meets the last requirement, but fails to bridge over the great gap in density between liquid and vapour. Ketteler (Z.P. C. 2, 905) suggests an equation of the form $(n^2-1)(v-\beta)$ M, where β is the volume actually occupied by the ponderable molecules, v that of the space in which they are contained, and M a molecular function depending on the constitution of the medium. M may have one of two values, both of which are definite constants, the one for the liquid and the other for the gaseous state. The value of β may be obtained by varying the temperature, the pressure, or the constitution of the media examined. Sutherland says that this formula gives for compressibility results less satisfactory than those given by that of Gladstone.

Zehnder (W. 34, 91) investigated the influence of pressure upon the index of refraction of water at different temperatures, and on comparing the results with the co-efficient of compressibility, he came to the conclusion that the formula $\frac{\mu-1}{d}$ was practically exact -much more so than that of Lorenz. Röntgen and Zehnder (W. 44) have since applied the same inquiry to CS2, and CaHe, ether, and a series of alcohols, with the result that in the cases of all these substances neither formula is sufficiently exact, the experimental figures occupying very nearly the mean place between those given by the two formulæ. Perkin (C. J. 61, 287) in studying magnetic

rotation at widely different temperatures, observed a slight reduction as the temperature was raised. Dale and Gladstone (as long ago as 1868) had observed that the specific refractive 1868) had observed that the specific refractive tains three unknown quantities, it requires for energy of substances was similarly affected; their determination three simultaneous equa-

Nasini and Bernheimer (G. 15, 59) in 1885, and Ketteler (W. 33, 506, 662) in 1888, also found small differences in the same direction. Perkin accordingly made a series of experiments to

see if the changes in $\frac{\mu-1}{d}$ due to temperature

vary with different classes of substances, as they do in the case of the magnetic rotation. The results seem to corroborate this, though not very definitely. On trying Lorenz's formula, he found the refraction rise with increase of temperature, and he came to the conclusion that this formula is not suitable when dealing with high tempera-

Guye (Ar. Sc. Genève, 23, 197, 204) pointed out a relation between the constants of the equation of Van der Waals and that of the formula of Lorenz for the refraction of light. He maintained that the relation of the absolute critical temperature to the critical pressure, which he termed the 'critical co-officient,' is proportional to the molecular refraction, and that it furnishes a valuable means of determining the molecular constitution of bodies at the critical point. By a comparison of the data given by a number of observers for forty different substances he obtained the result that the critical co-efficient (K) is in proportion to R as 1 to 1.8. The experimental difficulties connected with the determination of K, and the fact that Guye had not always the data for reducing R observed to Roo, rendered the final results less uniform than they might be otherwise; but the extreme range of his factor varied from 1.6 to 2.0, giving 1.8 as a mean. Guve found, however, certain classes of bodies which gave a different factor to that above mentioned. Such gases as O, N, and CO, gave a factor ranging from 1.1 to 1.4. Water gave 1.1, and methylic alcohol 1.1 to 1.2. He also recorded some which are exceptionally high, but in most of these cases the results of the experiments seem untrustworthy in consequence of chemical action having taken place. Having determined his factor, he was able to divide by it the recognised refractions of the elements according to Brühl, and so to get what he termed the 'atomic critical co-efficient,' from which he could build up the critical co-efficient of any substance of which the theoretical constitution was determined.

Dispersion formulæ. As the observations of Gladstone extended to the solar line A, his calculations were but slightly affected by dis-persion; whereas nearly all the Continental observers have used the hydrogen light, and have no actual measurements below the line a. They have, therefore, usually sought to get rid of the effect of dispersion by adopting one or other of the suggested formulæ for calculating the theoretical ray of infinite wave length, and have worked out their results both for the observed line a, and for the assumed limit. The simplest of these methods, and on that account the one most generally adopted, is that of Cauchy. It is usually expressed by the formula

$$\mu = \mathbf{A} + \frac{\mathbf{B}}{\lambda^2} + \frac{\mathbf{C}}{\lambda^4} + \dots$$

in which A represents the wave length of any given line of the spectrum. As this formula con-

tions: but the third term is often dispensed with ! to reduce the amount of calculation required. By the process of elimination, the values of A, B, and Care obtained, A being Cauchy's co-efficient of refraction, and B and C the co-efficients of dispersion. This theory accords fairly with the experimental data for substances of moderate dispersive power, though by no means well with the data for substances of high dispersive power, such as oil of cassia. Wüllner (A. 133) considered that this formula was sufficiently exact for bodies of low dispersive pover when two constants were used; but that for highly dispersive substances, such as carbon disulphide, it was necessary to go to the third term, as the difference between the observed value of us and that calculated from μ_a and μ_{γ} amounted to as much as 0.0022; while on using three terms the calculation was correct to the fourth decimal place. He also tried the formula of Christofle

$$n = \frac{n_0 \sqrt{2}}{\sqrt{1 + \frac{\lambda_0}{\lambda}} + \sqrt{1 - \frac{\lambda_0}{\lambda}}}$$

in which n_0 and λ_0 signify two selected constants, and n is the corresponding index of refraction of the wave length A; this also gave results which were not sufficiently accurate. Taking the observed indices for the lines a and y of carbon disulphide at 0° as 1.634066 and 1.692148, this formula gave 1.669397 for β , while the observed value was 1.669076. At 20° the calculated value for \$\beta\$ was as much as 000494 too high. Langley (P. M. [5] 17, 194) has discussed the relative merits of Biot's, Cauchy's, and Redtenbacher's formulæ, and has come to the conclusion that while each of them is sufficiently exact within the limits of the visible spectrum, they soon begin to give too small results for μ when that limit is passed. Biot's formula

$$\frac{1}{n^2} = a + b \binom{n^2}{\lambda^2} + c \binom{n^4}{\lambda^4} + k \binom{\frac{\lambda^2}{n^2}}{n^2}$$

gives more trustworthy results than either of the

Redtenbacher's formula $\frac{1}{n^2} = a + b\lambda^2 + \frac{c}{\lambda^2}$ has the serious objection that it reached a minimum at a point corresponding to n = 1.5647 in the prism which he employed, so that for every value of n greater than 1.5647 it gave two different values for λ . Langley has experimentally determined wave lengths in the invisible prismatic spectrum far beyond the extreme limit possible according to Cauchy's formula. Brühl, after working out his results for R_∞ as well as for R_a, has latterly (A. 235, 1; 236, 233) come to an adverse conclusion as to the utility of Cauchy's co-efficient of refraction for getting rid of the effect of dispersion, and he even asserts that when three terms are used the results are less to be relied upon for this purpose than when two terms only are employed. The following table shows the differences in Cauchy's A when calculated with two and Cauchy's A with calculated with two three terms respectively, from the observed indices μ_{α} and μ_{γ} in the former case, and from μ_{α} , μ_{β} , and μ_{γ} in the latter; and also μ_{α} as observed, compared with the same index of refraction as calculated by Cauchy's formula from μ and μ_{γ_i} showing in this case a difference

of from one to five units in the third place of decimals :--

	Cauch	y's A	μρ		
Substance	2 terms	3 terms	Ob- served	Cal- culated	
Benzoyl chloride Orthotoluidine Clinnamic alcohol Aniline Furfurol Cinnamic aldehyde	1:51:006 1:53715 1:54307 1:54741 1:48269 1:55:066	1 52700 1 54460 1 55253 1 55689 1 49816 1 58256	1.56964 1.58945 1.59993 1.60434 1.54566 1.65090	1 57097 1 59069 1 60151 1 60592 1 54824 1 65622	

In the case of substances of small dispersion, Brühl regards the use of Cauchy's formula as superfluous; with substances of medium dispersion, the results are generally preferable to those for the line a, though not to any great extent; but with substances of great dispersive power the differences are too great to be neglected in considering questions of chemical structure.

Nasini (Lincei, Atti, 18 [3]) comes to the same conclusion, that Cauchy's co-efficient of re-fraction ought to be rejected in studies of this nature, and that his co-efficient B is still more misleading if it be regarded as a measure of dispersion. N. (Lincei, Atti, 19 [3]) had already tested the merits of several formulæ, and given the preference to that of Lommel as affording better results than those arrived at by Cauchy's formula with two terms. The following table will show the differences between μ_{β} as observed, and as calculated by these two formula :-

Substance	μρου-	Calcu	lated	Difference		
Substance	served	Cauchy	Lommel	Cauchy	Lommel	
Benzene. Aniline. Methyl-a-	1·51339 1·60434			0.00065 0.00158	0.00088 0.00088	
naphthol .	1.64597	1.6477	1 64678	0.00173	0-00081	
naplithalene	1.63200	1.6330	1.6324	0.00100	0.00010	

Weegmann (Bonn., 1888) gives reasons why Cauchy's formula for the limit of the spectrum is not to be relied upon; and maintains that his B, or co-efficient of dispersion, must not be taken as a measure of dispersive power, but that it should in any case be divided by the relative density.

Helmholtz has proposed the formula
$$n^2 - 1 = Q_{\frac{\lambda^4}{\lambda^2 - \lambda^2 m}} - P\lambda^2$$

in which n and λ represent the index of refraction and the corresponding wave length, and Q, P and A2m are three constants dependent upon the nature of the medium. Ketteler has

$$n^2-1=\frac{A}{\lambda^2-B}+\frac{C}{\lambda^2-D}+\cdots$$

subsequently proposed another, viz. $n^2-1 = \frac{A}{\lambda^2-B} + \frac{C}{\lambda^2-D} + \cdots$ Brühl has tested the comparative merits of both these tested the comparative merits of both these formulæ, as well as that of Cauchy. Taking Gladstone and Dale's observations of a solution of phosphorus in carbon disulphide, he calculated the values of the lines B, D, F, and G from the observed values of A, E, and H, and again those of A, B, E, and G from those of D, F, and H. The following table above the differences in the two cases between the observed and calculated values (A. 286, 238):

Line	4	observed	Canchy	Helmbo:tz	Ketteler	Cauchy	Helmholts	Ketteler	
_	7.606	1.9209				+19	+48	+108	i
ABDE FGH	6.372	1.9314	-3	-5	+2	+ 9	+21	+ 47	ı
Ď	6.893	1.9527	-2	-4		,			i
E	5-271	1-9744		l	-4	5	-6	-9	i
F	4.862		+8	+9					l
G	4.304		+1	+2	-7	-7	-6		i
H	8.956	2-0746		۱ ۱					

The difference between Dispersive power. the indices of refraction of the rays of the spectrum of any refracting medium is termed the 'dispersion'; and by the dispersive power of a substance is expressed the ratio of the co-efficient of dispersion to the index of refraction of the mean ray minus unity. Thus taking the full length of the visible spectrum as extending from A to H, and F as the mean ray, the dispersive power would be represented by the formula, $\mu_{II} - \mu_{IA}$. $\mu_{IV} - 1$ Ketteler (Theoretische Optik, Braunschweig,

1885) has proposed two formulæ for dispersion based upon theoretical grounds:

$$\frac{\mu_n^2-1}{\mu_m^2-1}$$
 and $\frac{\mu_n^2-\mu_m^2}{\mu_n^2-1}$

 $\frac{\mu_n^2-1}{\mu_m^2-1} \text{ and } \frac{\mu_n^2-\mu_m^2}{\mu_n^2-1}$ when n is a ray more refractive than m. Costa (G. 19) regards these as having the advantage over the formula $\frac{\mu_n - \mu_m}{d}$ on account of their being independent of the density of the

medium. Early experiments. Newton, Herschel, Young, Wollaston, Browster, and others deter-mined the indices of refraction of a large number of solids and liquids, in most cases for the yellow or brightest part of the spectrum. The index for the solids ranged from 1:111 for tabasheer to 2.974 for chromate of lead, and for liquids and soft solids from 1.0570 for ether expanded by heat to thrice its volume, to 1.678 for disulphide of carbon, and about 1.8 for chloride of antimony (Encyc. Brit., 8th edit. Optics, 558).

Arago and Fresnel applied the method of interference to the comparison of the refractive indices of moist and dry air, with the result that moist air was found to be rather less refractive than dry air. Dulong determined the indices of refraction of a considerable number of gases and vapours.

Dulong, together with Arago, Biot, and others, adopted the formula of Newton $\frac{\mu^2-1}{d}$, and

came to the following conclusions; that the refractive power of a mixture of gases is equal to the mean of the refractive powers of the constituent gases calculated for the pressure to which each gas is actually subjected in the mixture, and that the refractive power of a compound gas is not equal to the mean of those of the component gases, but is sometimes greater and sometimes less.

Höck also found this formula to apply to some mixtures of liquids, and Schrauf (P. 133, 479) has more recently supported the same mode of calculating the refractive power; but Ketteler (P. 124, 890) found that liquid sul-Voz. IV.

phurous acid was not accordant with the known refraction of the gas as arrived at by the formula $\frac{\mu^2-1}{d}$, while the two came into agreement when he adopted the modern formula for the specific refractive energy $\frac{\mu-1}{d}$.

Jamin (A. Ch. [4] 3, 49) made careful experiments on the influence of the presence of aqueous vapour in the atmosphere upon the refractive index, and he found that the difference between the refractive indices of dry air and air saturated with aqueous vapour was only 000000726, a quantity so small that it may be safely neglected in the calculation of atmospheric refraction for astronomical purposes.

Ketteler (B. B. 1865) adopted Jamin's interference refractor for the measurement of the index of air, CO₂, CN, H, and SO₂, for the line D. He calculated the lithium and thallium lines from the wave length of the sodium line, according to the proportional number of rulings that coincide, it being found that this is independent of density and is a true function of the wave lengths.

RELATIONS BETWEEN PHYSICAL AND CHEMICAL PROPERTIES AND REFRACTION OF LIQUIDS.

Dale and Gladstone (T. 1858, 887) made an elaborate series of experiments on what they then termed the sensitiveness of liquids, or the effect of temperature on the refractive index. The principal conclusions they arrived at were that both the index of refraction and the length of the spectrum, $\mu_{\rm H} - \mu_{\rm A}$, diminish as the temperature rises, and that the sensitiveness of a substance is independent of its specific refractive or dispersive power. These conclusions were the result of observations on CS2, Et2O, H2O, P alcohols, &c. The following table and the table on p. 226 give the data for CS2 and H2O: -

Carbon disulphide (b.p. =43°)

Temp.	μ	μ _D	μ _{ιτ}	Sensi- tiveness	μ _Η μ _Α	Disper- sive power
0° 5° 10° 15° 20° 25° 30° 35° 40° 42.5°	1-6217 1-6180 1-6144 1-6114 1-6076 1-6036 1-5995 1-5956 1-5919 1-5900	1·6·442 1·6·397 1·6·346 1·6·303 1·6·261 1·6·290 1·6·182 1·6·140 1·6·103 1·6·082	1.7175 1.7119 1.7081 1.7085 1.6993 1.6942 1.6896 1.6850 1.6810 1.6778	0*0045 0*0051 0*0043 0*0042 0*0011 0*0038 0*0042 0*0042	0-0958 0-0939 0-0937 0-0921 0-0917 0-0906 0-0901 0-0891 0-0878	0-1489 0-1407 0-1477 0-1462 0-1463 0-1460 0-1457 0-1456 0-1459 0-1443

The sensitiveness is reckoned from the indices of the line D, and the dispersive power repre-

sents $\frac{\mu_{\rm H} - \mu_{\rm A}}{\mu_{\rm D} - 1}$. The sensitiveness indicates an anomaly in water, which has also been observed by others.

Gladstone and Dale (T. 1863. 317) extended the same inquiry to the following five points:— (1) the relation between sensitiveness and the change of volume by heat; (2) the refraction and dispersion of mixed liquids; (3) the refraction, dispersion, and sensitiveness of different members of homologous series; (4) the

	Water									
Temp.	μ	μ _D	μ _Π	Sensi- tiveness	μ _H - μ _A	Disper- sive power				
0° 5° 10° 15° 20° 25° 35° 40° 45° 50° 60° 65°	1·3291 1·3290 1·3288 1·3284 1·3279 1·8275 1·3270 1·8264 1·3257 1·3250 1·8241 1·8235 1·8233 1·3218	1.3330 1.3329 1.3324 1.3324 1.3320 1.3317 1.3309 1.3308 1.3297 1.8288 1.3280 1.3271 1.3259 1.3249	1.3438 1.3436 1.3131 1.3431 1.3427 1.3420 1.3416 1.3410 1.3405 1.3386 1.3388 1.3380	0-0001 0-0002 0-0003 0-0004 0-0006 0-0006 0-0006 0-0009 0-0008 0-0009 0-0012	0·0147 0·0146 0·0147 0·0147 0·0145 0·0145 0·0146 0·0146 0·0146 0·0147 0·0147	0-0429 0-0439 0-0445 0-0438 0-0449 0-0418				
70° 80°	1.3203 1.3178	1.3237	1·3344 1·3321	0.0012 0.0012v	0.0141 0.0143	0.0135				

refraction, dispersion, and sensitiveness of isomeric liquids; (5) the effect of chemical substitution on these optical properties. As to the first point of the inquiry, they came to the conclusion that the specific refractive energy

 $\left(\frac{\mu-1}{d}\right)$ is a constant not affected by temperature. They made the reservation, however, 'that there is some influence, arising wholly or partially from dispersion, which gives rise to the slight progression of most of the calculated products, and perhaps to the non-inversion of the sensitiveness of water at 4°, remarked on already by Jamin and ourselves.' As to the second point of inquiry, it was found 'that the specific refractive power of a mixture of liquids is the mean of the specific refractive powers of its constituents,' subject to some slight exceptions, as in the case of sulphuric acid and water. The inquiry into the refraction, dispersion, and sensitiveness of different members of homologous series showed a progressive increase in the specific refractive energy as the series advanced; but that the influence of each addition of CH., which is observable throughout the series of the methyl group, does not necessarily hold good with reference to substances of quite another type. The observations on isomeric bodies showed that some of them are widely different in their optical properties; but that those which have a close chemical relationship show an identity in their optical properties also. In the last branch of the inquiry it was sought 'to determine the amount of change in the optical properties which results-from a replacement of one element by another, the type remaining the same,' in order to 'attain to a knowledge of the influence of the individual elements on the rays of light transmitted by them.' The general conclusion of Gladstone and Dale was that every liquid has a specific refractive energy composed of the specific refractive energies of its compound elements, modified by the manner of combination, and which is unaffected by change of temperature, and accompanies it when

question which has since occupied the attention of many observers.

Landolt (P. 117, 122, 128) took up the inquiry, adopting the formula $\frac{\mu-1}{d}$ used by

mixed with other liquids.' This opened up a

Gladstone and Dale, and applied it in the first instance to an investigation of the values of C, H, and O. He simplified the investigation by multiplying the specific refractive energy by the molecular weight of the compound, which gave P $\frac{\mu-1}{d}$ as the molecular refractive power, or refraction equivalent, terms which had already been applied by Berthelot and Schrauf to the formula P $\frac{\mu^2-1}{d}$.

By comparing series of homologous compounds, acids of the series $C_nH_{2n}O_2$, alcohols of the series $C_nH_{2n}O_2$, and esters of the series $C_nH_{2n}O_2$, L. obtained the increment due to each addition of CH_2 as shown in the following selection from his data:—

selection	irom mis da	UR :				
	Substance	S.G.	μ	$\frac{\mu_a-1}{d}$	R.	Diff.
Acids C _n 11 _s nO _s	Formio Acetio Propionie Butyrio Valerianio Caproie (Enanthylie	1.0514 0.9963 0.9610 0.9313 0.9252	1·3693 1·3699 1·3846 1·3955 1·4022 1·4116 1·4192	0.3518 0.3860 0.4116 0.4319 0.4449	21·11 28·57 36·22 44·05 51·61	7:20 7:16 7:65 7:83 7:56 7:79
Alcohols OnH ₂ n+ ₂ O	Methyl	0.8011 0.8012 0.8074	1·3279 1·3605 1·3794 1·3940 1·1057	0.4501 0.4717 0.4879	20·70 28·30 36·11	7·53 7·60 7·81 7·78
Esters CnH _s nO _s	Mothyl acctate . Ethyl acctate . Methyl butyrate Ethyl butyrate	0.9015 0.8976	1·3592 1·3705 1·3869	0·4110 0·4311	36·17 43·97	6·81
ı.	Methyl valerate Ethyl valerate.	0.8800	1·3927 1·3950	0.4158	51.71	7·49
:	Ethyl formate . Ethyl acetate .	1	1·3580 1·3705			6-99
	Methyl butyrate Methyl valerate		1·3869 1·3927			7-74
	Ethyl butyrate Ethyl valerate.		1·3940 1·3950			7 -88
						<u></u>

The mean of Landolt's comparisons gave the value R=7:60 for CH₂. Dealing in the same manner with compounds differing by one atom of carbon, by two atoms of hydrogen, and by one atom of oxygen, respectively, he assigned to the several elements the following refraction-equivalents; C=5:00; H=1:30; O=8:00. Subsequent investigations would lead one to reject several of the substances which he brought into comparison.

Landoit also adopted a modification of Biot and Arago's formula for mixtures of gases, by substituting n for n² throughout, so that

$$\frac{N-1}{D}P = \frac{n-1}{d}p + \frac{n'-1}{d'}p' + \cdots$$

N, D and P representing the index of refraction, density, and 'molecular weight' of the mixture, and the small letters the same values of the several substances forming the compound. In this manner he calculated the value of n_c or n_c for mixtures of liquids as shown in the follow-

ing table. It will be seen that the calculated and observed values correspond very closely.

	-		,	Obse d	erved #•	Calcu- lated µe
Methyl alcoho Amyl	d Mixturo	:	96 88 184	0.7964 0.8135 0.8038	1·3279 1·4057 1·3640	1.3644
Ethyl alcohol Amyl "	Mixture	:	92 88 180	0-8011 0-8135 0-8065	1:3605 1:4057 1:3822	1.3821
Ethyl alcohol Amyl "	Mixture	:	46 176 222	0.8011 0.8135 0.8104	1:3605 1:4057 1:3961	1-3960
Acetic acid Butyric ,	Mixture	:	60 88 148	1-0518 0-9610 0-9930	1·3706 1·3953 1·3850	1.3847
Ethyl alcohol Formic acid	Mixture	:	46 46 92	0·8011 1·2211 0·9602	1:3605 1:3693 1:3610	1.3612
Oil of bitter a! Formic acid	monds. Mixture	:	106 46 152	1·0474 1·2211 1·0876	1:5391 1:3693 1:4900	1.4900

Landolt subsequently (A. 4, Suppl.) reversed the process, and applied it to the quantitative analysis of mixed liquids by means of their refractive indices and specific gravities. The following will serve as instances of the percentage results obtained:—

			μ1		entage
	μα	d	d	Calcu- lated	Actual
Amyl alcohol .	1.4057	0.8135	0.4987	47.4	47.8
Methyl " . Mixture .	1.3279 1.3640	0.7964 0.8038	0.4117 0.4529	52·6 100·0	52·2 100·0
Acetic acid . Butyric , . Mixture .	1:3706 1:3955 1:3850	1:0518 0:9610 0:9930	0:3523 0:4116 0:3877	40·3 59·7 100·0	40.5 59.5 100.0
Ethyl alcohol . Formic acid . Mixture .	1.3606 1.3693 1.3610	0.8011 1.2211 0.9602	0.4501 0.3024 0.3760	49·8 50·2	50.0
Oil of bitter al-					
monds	1.5391 1.3693 1.4900	1.0474 1.2211 1.0876	0.5147 0.3024 0.4505	89-8 30-2 100-0	69·7 30·3 100·0

Halogen compounds. Landolt's values for the refraction-equivalents of C, H, and O are:

Carbon . . R_{∞} 4.86 R_{\bullet} 5.00

Hydrogen . . , 1.29 , 1.30

Oxygen , 2.90 , 3.00 Adopting these values, Haagen (P. 131, 117) deduced values for Cl, Br, and I from some of their organic liquid compounds, and then deduced values for other elements from observations of R for their chlorine compounds. The following are the results he obtained for R_{∞} and R_{Σ} :—

R	emen	t	R _{so}	R.
Chlorine Bromine Iodine.	:	:	9·53 14·75 23·55	9·79 15·34 24·87
Sulphur Phosphoru	s.	•	14·74 14·60	16·03 14·93
Arsenic Antimony Silicon Tin Sodium	•	:	18·84 7·81 18·64 4·71	20·22 25·66 7·90 19·89 4·89

Refraction-equivalents of the elements. Gladstone (T. 159, 18; Pr. 18, 49) applied Landolt's P $\frac{\mu-1}{d}$ to inorganic compounds in order to arrive at the refractionequivalents of the several elements, and also to determine whether or not any of the elements had more than one definite refraction-equivalent. As most of his observations were made upon crystalline salts, many of which were doubly refracting, Gladstone adopted the plan of dissolving them in water, or alcohol, and deducting from the R of the solution the R due to the solvent. This mode of operation was supported by the consideration that in the cases of rocksalt and sugar, where the refraction equivalent of the substance has been obtained both in the solid and dissolved condition, it is found to be the same. Ca comparing a series of salts of K and Na, it was evident that, while the refractionequivalents of the compounds differed very widely, according to the nature of their negative constituents, the refraction-equivalents of the compounds of Na differed pari passu with those of the K compounds, and hence it was concluded that the negative constituent has the same effect on light, whichever metal it is united with. Values were arrived at for forty-six of the elements, a number which has been subsequently somewhat increased; and more recent investigations have led to slight modifications in the figures. The latest list is as follows: -

			
Element		At. ₩.	B _A
Aluminium .		27.5	7.7
Antimony .		120	24.5
Arsenic		75	15.4
Barium		137.2	15.8
Beryllium .		9.1	5.1
Bismuth		208	88.2
Boron, in borates		11	about 4
Bromine		80	15.3
Cadmium .		111.6	13.1
Casium		132	19.1
Calcium		40	10.0
Carbon		12	5.0
" doubly lin	ked .		6.1
Cerium		138.2	19.6?
Chlorine		35.2	9.9
Chromium .		52.4	15.4
" in chro	mates.	,,	about 22
Cobalt		58.7	10.4
Copper		63.4	11.5
Didymium .		145	28.3
Fluorine		19	1.6?
Gold		196.2	23.1
Hydrogen .		1	1.8
Iodine		,127	24.5
Iron, in ferrous	com-		
pounds .		56	11.6
Iron, in ferric	com-	1	
pounds .		"	19.4
Lanthanum .		138	22.9
Lead		207	24.3
Lithium		7	8.5
Magnesium .		24	6.7
Manganese .		55	11.7
nates	nanga-		about 25

Ele	ment			At. w.	R.
Mercury .			-	200	19.4?
Nickel .			.!	58· 7	10.0
Nitrogen			. !	14	4.1
" in	base	s, oxide	es,		
&c			•	,,	5.1
Oxygen, sing	gly li	nked	• :	16	2.8
" dou	bly l	inked		••	3.4
Palladium	:		. 1	106	21.6?
Phosphorus				* 31	18.3
Platinum				195	24.7
Potassium				39.1	7.85
Rhodium				103.4	23.4?
Rubidium			. 1	85.4	12.1
Selenion .			. !	78	30.1
Silicon .				28	7.4
	ilicio	acid		.,	about 6
Silver .			. 1	108	13.2
Sodium .			٠,١	23	4.4
Strontium			.	87.5	130
Sulphur .	•			32	16.0
	dy li	nked		,,	14.1
Thallium				203.6	20.4
Tin .	·		.	118	27.0?
				,,	18.6?
Titanium			:	48	24.6
Uranium				237.6	19.4
Vanadium		-	.	51.3	24.8?
Zine .	:			65.3	9.8
Zirconium	•	•	•	90	21.3

Anomalies were pointed out in the refractionequivalents of the hydracids, and of the benzenoid carbon compounds. With regard to the specific refractive energy it was remarked ;-First, hydrogen has more than double the energy of any other element, even in the lowest number that Second, phosphorus, can be assigned to it. vanadium, titanium, and sulphur have singularly high energies, and they are substances that present certain chemical analogies. Third, there are several pairs of analogous elements having nearly the same energy; thus bromine and iodine, arsenic and antimony, potassium and sodium, manganese and iron, nickel and cobalt. Fourth, an element in altering its valency alters its energy. Fifth, if the metals are arranged in the order of their energies, they are, with few exceptions, in the inverse order of their atomic weights.

Benzenoid hydrocarbons.—The anomalous refraction and dispersion of the hydrocarbons already referred to was treated in a paper by Gladstone (C. J. 23, 147), the tables in which indicated that the values for all these bodies and their derivatives were largely in excess of the normal, calculating R_A of carbon at 5·0. The refraction-equivalents of the typical hydrocarbons were expressed as in the following table; but while the physical fact indicated has been fully verified by subsequent research, the particular numbers in the third column have been modified, and a plue has been assigned to the olefines.

A similar table is given illustrating the inereased influence on light of carbon which is combined with two atoms of hydrogen or one of oxygen, in a series of oxidised bodies obtained from essential oils, differing from one another only in the quantity of hydrogen.

Hydrocarl	ons	Typical Formula	B
Paraffins . Olefines . Terpenes . Benzenes . Naphthalene Anthracene	:	C _n H _{2n+2} C _n H _{2n} C _n H _{2n-4} C _n H _{2n-6} C _n H _{2n-12} C _n H _{2n-8}	Normal ,, + 3 ,, + 6 ,, + 14 ,, + 17

Bedson and Williams (B. A. 1881, 155) tested the question whether the specific refraction of a solid body could be determined from the refractive power of its solution as stated by Dale and Gladstone, as this method had been called in question by Janovsky (Sitz. W. 82, 148). They found the specific refractive energy for the ray of infinite wave length, calculated from solutions of NaCl, Na₂B₂O₃, H₂BO₃, and NaPO₃ to be in substantial accord with the results derived from observations on the solids. They also found that the specific refraction of liquid phenol is practically identical with the value calculated from solutions in alcohol and in acetic acid.

In taking the index of refraction of solid NaPO₃, B. and W. immersed it in a liquid of greater refractive power, and then added a feebly refractive liquid until the refractive power of the mixture appeared to be the same as that of the solid suspended in it. The index of refraction of the mixture was then determined. The result being found satisfactory, the prisms of rocksalt and of fused borax were also tried by the same process, as well as in the ordinary way, and with similar results.

Double values of carbon and oxygen. Brühl, in 1879 and 1880 (A. 200, 139; 203, 1, 255), conducted a long investigation into the chemical constitution of carbon compounds in reference to their relative densities and their power to refract light. Taking up the observations of Gladstone, and also referring to some of the anomalous results in the tables issued by Landolt, whose mode of investigation suggested that the grouping of the atoms exercised a certain influence upon the refraction of light, Brühl set himself to inquire: What is the typical peculiarity which must be common to all the bodies that refract light in an abnormal manner? He usually determined the indices for the three H lines, μ_{β_1} and μ_{γ_1} and for the Na line μ_{D_1} and calculated the refraction-equivalents both for the line α , and for Cauchy's A, viz. R_{∞} . The following table is so arranged that between each horizontal line the first-named substance has the highest molecular weight, while those below differ only in having a smaller quantity of hydrogen, and, therefore, contain doubly-linked carbon atoms.

It will be observed that the density, the index of refraction, and the co-efficients of refraction and dispersion of Cauchy always increase with the diminution of H, and that the loss in specific refractive energy which is suffered by the disappearance of two atoms of H is at least fully made up by the consequent double linking of the carbon atoms. For the calculated values of the refraction-equivalents, Brühl has adopted the following values for the elements, vis.—for R. C=5-0, H=1-3, O=3-0, Cl=9-8, Br=15-3,

			T			1	1	R.	
Substance	Formula	s.G.	•	Cauchy's A	Cauchy's B	<u>µ. −1</u> d¥	Ob- served	Calcu- lated	
Propyl alcohol . Allyl alcohol .	C,H,O	0·8044 0·8540	1·38345 1·41051	1·37542 1·39881	0·34630 0·50453	0·4767 0·4807	28·60 27·88	28·4 25·8	
Propyl aldehyde. Acrolein	C,H,O	0.8066 0.8110	1·36157 1·39620	1·35344 1·38010	0·35065 0·69427	0·4483 0·4711	26·00 26·38	25·8 23·2	
Propyl ether . Allyl ether	C,H,(OC,H). C,H,(OC,H).	0·7386 0·7651	1·36758 1·38565	1·35975 1·37547	0·33758 0·43882	0·4977 0·5041	43·80 43·35	48·6 41·0	
Propyl acetate . Allyl acetate .	C ₂ H ₂ (C ₂ H ₂ O ₂) C ₃ H ₂ (C ₂ H ₂ O ₂)	0·8856 0 9276	1·38235 1·40205	1·37427 1·39151	0·34832 0·45458	0·4317 0·4334	44·04 43·34	44·0 41·4	
Propyl chloride . Allyl chloride .	C _a H,Cl C _a H,Cl	0.8898 0.9379	1·38659 1·41245	1·37813 1·40007	0·36174 0·53369	0·4345 0·4398	34·11 33·64	33·9 31·8	
Isobutyric acid . Methacrylic acid .	C ₄ H ₈ O ₂ C ₄ H ₆ O ₂	0·9490 1·0153	1·39093 1·42815	1·38259 1·41400	0·35971 0·61013	0·4119 0·4217•	36·25 36·27	36·4 33·8	
Amylene (34° to 35°) Valerylene	C ₅ H ₁₀ C ₅ H ₈	0·6476 0·6786	1·37330 1·39763	1·36352 1·38565	0·42173 0·51660	0·5764 0·5680	40·35 89·85	88·0 85·4	
Hexane Diallyl Benzene	C ₀ H ₁₄	0.6603 0.6880 0.8799	1·37337 1·39180 1·49668	1·36538 1·38589 1·47562	0·34462 0·52733 0·90816	0·5655 0·5787 0·5645	48·63 47·45 44·03	48·2 43·0 87·8	
Triethylamine .	C ₆ H ₁₅ N C ₆ H ₇ N	0·7277 1·0216	1·39801 1·57948	1·38803 1·54741	0·43179 1·38319	0·5470 0·5672	55·25 52·75	55·8 44·9	

N = 5.8; the first three being the values given by Landolt, the two halogens those by Haagen, and that for N being determined by Brühl himself. From the observations recorded in the foregoing table and others, Brühl has arrived at the following conclusions:—That the closing of the chain of atoms in the form of a ring, with which so marked an increase in the density and index of refraction is associated, exercises a very special influence on the power of the substances to disperse light; that the mol. refraction of the substances in which the existence of one or more pairs of doubly-linked carbon atoms is recognised is greater than the sum of the refractions of the constituent atoms by 2.0 in the case of Cauchy's limit, and 2.3 in the case of the line H. for each such pair. For combinations of the acetylene type, including the propargyl derivatives, he gives a rather lower value, viz.: 1.8 and 1.9 respectively. These data give the following atomic refractions for earbon, viz.—

Nasini and Bernheimer (Lincei, Atti, 18) do not, however, admit Brühl's views as to the constitution of the propargyl compounds, as well as some of the other conclusions at which he has arrived. They give tables of observations on naphthol compounds, styrol, cinnamic alcohol, anethol, anisol, thymol, and diamylene, and have worked out the results by the two

Ro and Ro, as well as showing the small differences both in specific refraction and specific disperson due to differences in temperature. The principal conclusions at which they arrive are as follows:-The statement that every double bond, and only every double bond, causes the mol. refraction to increase by a constant quantity is not confirmed by complete series of substances, because in compounds containing only four or five double bonds the increase in refraction indicates a much greater number. That the increase in mol. refraction grows step by step as the compounds become poorer in H; but no proportion exists between the increased values and the number of pairs of atoms of H that is lost; nevertheless, a simple relation exists with the other structural changes in the formula, expressed by double bonds, closed chains, &c. That the augmentation increases more or less rapidly from the paraffins to the olefines, and thence to the benzenes, and again to the naphthalenes, but by what law is not evident, and is not capable of expression by our structural formulæ. They consider it established, however, that the principle is approximately valid, that in every series of compounds each atom in the molecule furnishes its fixed contribution of refraction, and that in the paraffin series the mean values of the atomic refractions coincide with those derived directly from the elements them-selves. They remark that even in the paraffin series the constancy of the atomic refractions is not absolute; because the more the mol. w. increases the greater is the difference between ordinary formula for B. and B., and also for the calculated and experimental values. For

other series the same values no longer apply, being too low, and hence other constants are required.

Kanonnikoff (Bl. [2] 36, 557) has published observations confirming Brühl's calculation of the increase due to the double bond between carbon atoms, and of the loss in specific refractive energy due to the elimination of two atoms of hydrogen being counterbalanced by the increase due to the consequent double linking of the carbon atoms.

Landolt (P. 117, 122) had determined the refraction of oxygen from a comparison of the refraction-equivalents of various substances the empirical formulæ of which differed by one atom of oxygen; and from acids of the formula $C_nH_{nn}O_n$ by deducting the value of n times CH. The results were somewhat discordant, the first series giving a mean value for oxygen of 2.76, and the latter of 3.0. The former of these manifestly represented the atomic refraction of oxygen in hydroxyl; and if oxygen varied in its refraction according to its valency it is evident that a general average resulting from these two modes of determination could not be taken. Brühl shows that, adopting Landolt's second plan for arriving at the value of oxygen in the aldehydes and ketones of the formula C, H,,O, the R_a for oxygen will average 3.4; and that chloral, butyl-chloral, and the oxychlorides give substantially the same result. On the other hand, deducting the refraction-equivalents of the aldehydes from those of their corresponding acids, of the alcohols from the glycols, and of the acids from the oxyacids, he obtains 2.75 as the mean value for oxygen. An approximate result, 2.80, is obtained if, from the ethers, $C_nH_{2n}O_2$, the value of n times CH_2 + the higher value (3.4) for one atom of oxygen be deducted. For oxygen united to carbon by a double bond Brühl therefore assigns the refraction-equivalent 8.4 for the line a; and for oxygen in hydroxyl, or generally for oxygen united to two other atoms, he gives the value 2.8; he represents the former as O" and the latter as O'.

Hence C=0 = 5.0 + 3.4 = 8.4. C=0 = 5.0 + 2.8 = 7.8.

Whether, however, the increased result of the double linking of the carbon and the oxygen is due to one of the elements only, or whether both of them share in it, he leaves an open question, though he regards the latter as the more probable. If two atoms of H are removed from a substance without involving the double linking of carbon atoms, as in the case of an alcohol being converted into an aldehyde or ketone, there follows a very marked reduction of the specific refractive energy. This reduction, however, becomes less and less marked as the quantity of C increases in the higher members of the series. When the removal of two atoms of H involves the double linking of the C, the loss of refractive energy is more than compensated by the increase due to the doubly-linked C.

A comparison of a considerable number of isomeric bodies of the paralinoid series of acids ahows that the indices of refraction of the primary and normal compounds are a little greater than those of the secondary and iso-compounds, and that the densities are proportional in the case of unsaturated compounds of similar

empirical composition, however, the double linking of the carbon atoms increases the refractive power more than the density.

In a subsequent paper (A. 235, 1), Brühl treated of the molecular refraction of organic liquids of high dispersive power. He arrived at the conclusion that the dispersion of different substances stands in no clearly recognisable relation either to their refraction or chemical constitution; and that it cannot be numerically expressed. This, however, is contested by Gladstone (Pr. 42, 401), who, while admitting that there are difficulties in the investigation of dispersion which are not felt in dealing with refraction, still holds (1) 'that dispersion, like refraction, is primarily a question of the atomic constitution of the body: the general rule being that the dispersion-equivalent of a compound is the sum of the dispersion-equivalents of its constituents; (2) that the dispersion of a compound. like its refraction, is modified by profound differences of constitution, such as changes of atomic valency; (3) that the dispersion frequently reveals differences of constitution at present unrecognised by chemists, and not expressed by our formulæ.' Brühl held that the differences which still appear between the calculated and experimental values when Lorenz's formula is used, and which he showed to be less in proportion than when the old empirical formula is used, are principally due to the influence of dispersion, and that they would in great measure vanish if this disturbing cause could be overcome; that with substances with a dispersion equal to about that of cinnamic alcohol the molecular refraction for the line a would serve as a help to the determination of the chemical constitution, but beyond that limit the numerical results are too uncertain to be of use except as collateral evidence; that there is a direct and simple proportion between the number of unsaturated groups of atoms in any compound and the increase of the molecular re-

fraction $\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{p}{d}$ over the value derivable

from the empirical chemical formula; that the effect on refraction of the acetylene combination, which he represents by \equiv , is analogous to that of the ethylene, or doubly-linked carbon, \equiv , and that it is somewhat greater, but not twice as great, as the latter.

Gladstone questions Brühl's assumption that both cinnamic alcohol and cinnamic aldehyde have four pairs of doubly-linked carbon atoms, on the ground that they have widely-different dispersions; also that allyl paracresolate and anethol are similarly constituted, for the same reason. He also thinks that the evidence as to: the constitution of cymol and hexahydro-naphthalene from Brühl's observations is not conclusive as to the one having three pairs, and the other two pairs, of doubly-linked carbon atoms, seeing that they have nearly the same dispersion. Nasini (Lincei, Rc. 3, 164) in like manner holds. that these particular compounds do not justify the conclusions that Brühl has come to respecting them, and agrees with G. that the dispersion may be a constant, and a much more sensitive one than the specific refraction; and that as such it is affected more and varies more

by certain little differences of composition and constitution of which the specific refraction does not feel the influence.

Brühl (Z. P. C. 1, 6) maintains that Erlenmeyer's constitutional formula, with five ethylene combinations, correctly represents the structure of naphthalene, and those derivatives in which hydrogen is replaced by monovalent elements. But the results of the observations on which he bases this conclusion all show a larger increment than can be accounted for by this formula: the excess he attributes mainly to the influence of dispersion. In this and all the other inquiries he has adopted Lorenz's formula, and the solar line C, without attempting to get rid of the influence of dispersion by the use of Cauchy's co-efficient of refraction. In the same paper he formulates the following six propositions:-(1) Isomerides of similar atomic arrangement (Stellungsisomere) have similar specific and molecular refractive powers; on the other hand, those isomerides which show differences of saturation (Sättigungsisomere) have various specific and molecular refractive powers; (2) polymeric combinations never show similar specific refractive energy, or multiple molecular refraction corresponding to the molecular weights; (3) transformations of multiple linkings of atoms into simple ones have as their result a diminution of refraction, equally, whatever the kind of chemical change may be (polymeric or isomeric change); (4) the optical effect of the accumulation of multiple linkings is the same, whether it produces open chains (amylene-diamylene) or ring formations with one or more groups of rings (as in paraldehyde, cymhydrene, menthol, &c. in the one case, and in turpentine and cajeputol in the other); (5) the molecular refraction of a fully saturated body is very nearly that of the sum of the refractions of the atoms of the empirical chemical formula, each of these being reckoned as united by single bonds-all those are to be regarded as saturated bodies in which there is no multiple linking of the atoms, such as the true paraffins, or derivatives of the general formula $(C_nH_{2n+2})-xH_2$; (6) all unsaturated bodies show an increased refraction which is proportional to the number of ethylene, acetylene, or carbonyl combinations present; the proportion, as a rule, is the more exact the less the substances in question are distinguished by a specially great dispersion. While holding to the opinion that the monovalent elements have virtually each but one refraction equivalent, and that the change of valency in the others is the chief cause of their variable refraction, Brühl considers that exact values cannot be obtained, because the mode of the grouping of the atoms may not be altogether without influence.

In the meantime, Gladstone (C. J. 45, 241) had brought together a large number of observations on organic compounds, both liquids and solutions of solids, and placed against them the refraction-equivalents calculated on the basis of the following values for the elements:—

Carbon, saturated .			R	₄ 5·0
$_{n}$ in $C_{n}H_{n}$.				5 ·95
" doubly linked	• *	•	•	6·1
Hydrogen	•	•		1.8
Oxygen, singly linked	•		•	2 -8
n doubly n	•		•	8-4

Nitrogen				•		4.1
	in bases,	NO,	æc.	•	٠	5.1
Chlorine						9.9
Bromine.						15.3
Iodine .						24.5
Sulphur,	singly lin	iked				14.1
,, ,	doubly li	nked				16 ∙0

Gladstone's observations confirm Landolt's original determination for H, and also for C in saturated compounds. Gladstone points out that the hydrocarbons of the formula C.H. scarcely come up to Brithl's previous estimate of the higher value of C, so that in these cases he has adopted the figure 5.95 instead of 6.1, as the difference is more than he considers can be accounted for either by dispersion or by the distance from the boiling-points. In the case of those substances where the C atoms outnumber those of II, all of which show an inordinately high refraction and are at the same time enormously dispersive, Glaustone points out that Kanonnikoff's view that the increase is due to dispersion alone is not established by that observer's own figures for the theoretical limit of the spectrum according to Cauchy's formula. He admits, however, that if the limit were carried back considerably further, though still fairly within what Langley's observations would allow, the values would so far approximate as to render it not impossible that the refraction equivalent of C might prove to be the same in these compounds as in the benzenoid series, or wherever it is doubly linked. As to the halogens, the figures in the table are generally consistent with the values which were originally assigned by him to Cl, Br, and I, viz. 9.9, 15.8, and 24.5 respectively. These numbers are very nearly the same as those arrived at independently by Haagen, viz. 9.8, 15.3, and 24.8. The values for O are taken from Brühl's original determinations, though the evidence of the alcohols rather favours his old estimate of 2.9 for the line A.

With regard to the phenomena of dispersion, Gladstone points out 'that the double linking of carbon atoms, while it does not much affect the specific refraction, widens the spectrum greatly, to such an extent indeed that where there are three pairs of such carbon atoms the specific dispersion is about double that of a saturated compound; where, however, the carbon atoms are actually in excess the dispersion becomes far more rapid. This is evident throughout, but the following typical hydrocarbons may illustrate it:—

II		0.7000	a:	0.0040
	sp. rei.	0.5626, sp.	ausp.	
Amylene . C, II,	**	0.5708	91	0.0300
Benzene . C.H.	"	0.5595	.,	0.0486
NapthaleneC, H,	,,	0.5870	**	0.0782
Difluorene C26H18	,,	0.6057	**	0.1108

or the following alcohols: --

Isobutyl alcohol		sp. ref.		sp. disp.	
Allyl alcohol Phenol	C.H.O	**	0.1731	,,	0.0275
Naphthol	0,11,0	"	0 5487	11	0-0832

'The effect of the halogens in lowering both the specific refraction and dispersion is very marked, and that of NO₂ is still more remarkable.'

Gladstone (C. J. 59, 290, 589) has since published other long series of observations; including a record of experiments on the effect of changes of temperature on the refraction of

some highly-refractive substances, which seem to confirm the opinion previously expressed by Dale and himself. Among the substances contained in these tables the benzyl and benzal camphors of Haller call for special notice, as they have a very high refraction, and a dispersion which is altogether excessive. The latter compound has in like manner a very high rotatory power. The hydracids in aqueous solution are shown to have not only a higher value than the normal, a fact which has long been observed, but also that the value rises with dilution; and that in the dispersion the excess is still more striking. The same fact was observed by Perkin in regard to the molecular magnetic rotation of these acids dissolved in water, both as to the initial excess, and to its increase with the dilution up to a certain point where it remained nearly constant.

Other investigators have availed themselves of the optical proporties is order to determine the constitution of compound bodies, or to emfirm the views arrived at on other grounds. Knops (A. 248, 175) has determined the indices of refraction of the methyl, ethyl, and propyl salts of fumaric, malcic, mesaconic, citraconic and itaconic acids. A comparison of these acids with their ethereal salts leads to the conclusion that fumaric and maleic acids contain only one dopbly-linked carbon atom; and that fumaric acid stands in the same relation to malcic acid as mesaconic acid does to citraconic acid.

Kanonnikoff (J. pr. [2] 31, 321, 497) has made a long series of observations on solutions of solids, of which he tabulates seventy-nine different substances, using water, alcohol, benzene, and chloroform as the solvents. As a preliminary inquiry, he reviewed the work of former investigators, and in some cases added experiments of his own to confirm previous conclusions: that the refractive energy of a substance is not changed in passing from the state of a liquid to that of a gas or vapour; that the same applies to bodies in passing from the solid to the liquid condition; that the refraction-equivalent of a mixture of liquids is the sum of the refraction-equivalents of its constituents; and that if the refraction-equivalent of a mixture and that of one of the components, together with the proportion of the same, is known, the refraction-equivalent of the other component can be calculated; that the same law applies to solutions of solid bodies, and that like results will be obtained whatever the solvent may be; that a derivative will be comparable with the substance from which it is derived, though the one may be a liquid and the other a solid body, as in the case of mesaconic acid and ethyl mesaconate. From the results of the observations above referred to, K. has determined the refraction equivalents of fourteen of the elements, as follows :-

Element	Ro	R_{∞}	Element	R_{σ}	R _{so}
Lithium	3·16 4·22 7·75 12·04 13·05 19·55	8·00 4·00 7·40 11·30 11·60 12·53 18·70	Magnesium . Calcium . Zinc . Strontium . Cadmium . Barium . Moreury .	7.03 9.32 9.80 11.61 13.03 15.84 19.20	6:47 9:05 9:40 11:25 12:66 15:28 17:90

K.'s values for the solar line C will be found to be generally slightly lower than those determined by Gladstone for the line A. The refraction-equivalents for the theoretical limit of the spectrum were also calculated by Cauchy's formula from observations of the lines α and β of hydrogen. K. also gave determinations of refraction-equivalents of thirty organic liquids, showing the excess due to the double linking of the carbon atoms wherever this occurred.

Nasini (Lincei, Rc. 1, 1) points out that the suggestion thrown out by Gladstone that there may be a third and higher value of carbon when its four bonds are satisfied by other carbon atoms, is supported qualitatively by the researches of Bernheimer and himself, but not quantitatively, and that, therefore, this hypothesis is not a sufficient explanation of the facts. He argues as follows: naphthalene derivatives have two such atoms, while cinnamic alcohol has but one, whereas the values differ but very little. Anethol with one such carbon atom has a much greater excess than the naphthalene derivatives, while styrol shows so slight an excess, that on this hypothesis it could hardly be allowed to have any carbon atom in this condition. He compares two pairs of isomeric bodies, both as to refraction and dispersion

Substance		R _a	$\frac{\mu_{\beta}-\mu_{\alpha}}{d}$
Allyl phenylate. Cinnamic alcohol	:	70·45 73·83	0·0173 0·0220
Allyl paracresolate Anethol	:	78·79 82·95	0·018 0·0257

from which he infers that when the allyl group is directly united to the benzene nucleus the molecular refraction greatly increases, whereas when the union takes place through the intervention of oxygen no augmentation takes place; so far, therefore, while supporting the hypothesis of Gladstone, he does not find any proportionality between the number of such carbon atoms and the increase of refraction.

Nasini (Lincei, Rc. 3, 164) criticises some of the conclusions of Brühl in the paper on the molecular refraction of organic liquids of high dispersive power (A. 235, 1) already referred to; and in particular he points out that the elimination of dispersion, if that were possible, would not get rid of the discrepancies between the observed and calculated values for the refraction of substances of high refractive power, and he cites 'observations on a series of substances in which he finds the constant fact that on adding a saturated side chain to an aromatic nucleus the specific dispersion diminishes while the refractive power increases.

Costa (G. 19) has made observations with the special object of testing the effect on dispersion of adding saturated side chains to a benzene or naphthalene nucleus. For this purpose he used compounds of amyl with benzene, thymol, eugenol, resorcin, and naphthol, and found in each case a still further increase in the refraction-equivalent than could be accounted for by the nucleus itself, while at the same time the specific dispersion showed a decrease.

Dispersion equivalents. In the same way that Gladstone arrived at the refraction-equivalents of the elements, he has sought also to determine the dispersion-equivalents of several of them; and (Pr. 42, 401) he has given the results of his observations upon nine of them, together with the values for the combinations CH2 and NO. The values are as follows:-

Su	bstar	100		R_{\blacktriangle}	Disp. Eqt. II-A
Phosphor	rus			18.3	3.0
Sulphur,	doub	oly li	nked	16.0	2.6
-,,	sing	ly		14.0	1.2
Hydroger	ı. ´	٠.	¨ . I	1.3	0.04
Carbon				5.0	0.26
19				6.1 ?	0.51
,,			٠, ١	6.1	0.66
Oxygen,	doub	ly lit	iked	3.4	0.18
	sing	ly	,,	2.8	0.10
Chlorine		٠.	" . }	9.9	0.50
Bromine			. 1	15.3	1.22
Iodine			.	24.5	8.65
Nitrogen			.	4.1	0.10
CH, .				7.6	0.34
NO ₂ .		•		11.8	0.82

It will be observed that G. gives three dispersion equivalents for C, which he considers pretty well established, and he raises the question whether there may not be an intermediate refraction-equivalent corresponding to the dispersion-equivalent 0.51, which is found in such bodies as the allyl compounds and olefines. In his previous paper (Pr. 31, 327), G. suggested that there is a still higher refraction-equivalent of C in those cases in which it has four bonds satisfied by other C atoms, as in naphthalene and pyrene. Whatever may be the truth of this view, it appears that the dispersion-equivalents of these bodies are enormously high - much beyond what is recognised in the above table.

Brühl (Z. P. C. 7, 2, 140) has since modified his views upon the subject of dispersion; and has worked out carefully the atomic dispersions of some of the most important elements that enter into organic compounds. In the course of this investigation he has been led to revise his previous figures for the refraction as well as the dispersion. They now stand as follows: -

	Symbol	R.	R,-R.
Carbon, singly linked .	C'	2.365	0.039
Hydrogen	H	1.103	0.036
Oxygen (hydroxyl) .	0'	1.506	0.010
" (ether)	0; 0;;	1.655	0.012
" (carbonyl)	0"	2.328	0.086
Nitrogen, linked singly			
with C	N'	2.76	0.19
Chlorine	Cl	6.014	0.176
Bromine	Br	8.863	0.348
Iodine	I	13.808	0.774
Ethylene bond	-	1.836	0.23
Acetylene bond	=	2.22	0.19

It will be observed that B. retains Lorenz's formula; and that he takes the difference between the refraction of the hydrogen lines γ and α as his measure of dispersion. He now acknowledges that the molecular dispersion can be re-

garded and employed in like manner with the molecular refraction as a specific expression of the material composition of chemical bodies; and that the dispersion is decidedly more sensitive to structural influences than the refraction. His inquiries have convinced him that refraction and dispersion are in no general sense cor-relative properties; but that certain structural peculiarities that have much influence upon refraction have little upon dispersion, while others have the opposite effect, and, as a rule, exercise a much stronger Influence upon the dispersion. It is evident that this must be so, from the very high relative dispersion of O" as compared with that of O' or O<, and the large proportionate dispersion due to the ethylene bond. This figure, ·23, B. does not, however, recognise as a constant value. These revised values have since been used by him in his inquiries into the relations between the optical properties and chemical constitution of enchlorhydrin, the aldehydes and benzoyl (B. B. 24, 656), in which he draws attention to the concurrence of the evidence derived from chemical, calorimetrical, and optical investigations.

Essential oils. Gladstone (C. J. 17, 1; 25, 1) gave a long list of observations in which he recorded the circular polarisation as well as the index of refraction. The power of the oils in rotating the plane of polarisation appears to be very diverse, both in degree and direction; but he suggests that a comparison of the specific gravity and of the length of the spectrum may in some cases be of service in determining the genuineness or otherwise of the oils. The hydrocarbons obtained from these oils (of which a long table is given) divide themselves into two great groups, which are more fully investigated in the second paper.

Subsequently (C. J. 49, 609) the effect of the higher refraction and dispersion of C when united by double bonds was applied to the determination of the structure of the essential oils. Taking 2.2 as the increased refraction for the solar line A, and 0.8 as the increased dispersion, H-A, due to one pair of doubly-linked carbon atoms, the terpenes indicate, both by their refraction and dispersion, that they contain only one pair of carbon atoms doubly linked, thus corroborating the views of those who, on chemical grounds, have held that a terpene requires the addition of only two atoms of hydrogen, or their equivalent, to saturate it. The refraction and dispersion of solid inactive camphene also show that this substance does not contain more than one pair of doubly-linked carbon atoms, which is consistent with the fact that it combines with only one molecule of hydrochloric acid, and is directly converted by oxidation into camphor C₁₀H₁₅O, which is certainly a saturated compound both by c'emical and optical evidence. In the same way, the citrenes give a refraction and dispersion indicative of the presence of two pairs of doubly-linked carbon atoms. Allied to these are several hydrocarbons having different amounts of hydrogen, and the number of doubly-linked carbon atoms varying accordingly. Thus, while citrene C₁₀H₁₁ has two pairs, cymene O₁₄H₁₄, has three, while menthene C₁₀H₁₅ has but one pair of doubly-linked carbon atoms, and cymhydrene C₁₀H₂₀ has none, being

a saturated body. Pentene and isoprene C_sH_a are identical in their optical properties, and indicate that no less than four of the five carbon atoms are doubly linked, which accords with the fact that these compounds combine with four atoms of bromine or two molecules of hydrochloric acid. The following table will illustrate the foregoing conclusions:—

 μ_{L4} 2.408449 μ_{Na} 2.417024 and 2.417227 μ_{T1} 2.425487

These figures give R=4.8, a result slightly lower than his earlier observations on the diamond, in which the index for the red part of the spectrum is recorded as 2.434, and the S.G. 3.55. Selenion. Sirks (P, 143, 429) made

				Experi	mental .	Pairs of C	Theoretical		
Hydrocarbons			specific refrac- tive energy	Specific dis- persive energy	atoms doubly linked	Specific refrac- tive energy	Specific dis- persive energy		
Cymhydrene		•		0.543	0.0246	none	0.543	0.0243	
Menthene .				0.548	0.0313	one	0.547	0.0298	
The terpenes				0.537	0.0295	do.	0.537	0.0296	
Terebenthene				0.537	0.0294	do.	. ,,	,,	
Camphene .				0.528	0.0269	do.	,,	,,	
The cedrenes				0.438	0.0296	do.	,,	,,	
The citrenes			٠.	0.551	0.0334	two	0.553	0.0354	
Isoterebent hene				0.552	0 .0337	do.	١,,	.,	
Caoutchene	•			0.554	0.0366	do.	,,	,,	
Cymene .				0.560	0.0406	three	0.558	0.0113	
Isoprene .				0.592	0.0470	four	0.585	0.0472	

The advance in these experimental figures with the double linking is evident, though it is obscured in the first two cases by the larger amount of hydrogen contained in cymhydrene and menthene. The influence of the double linking upon the specific dispersive energy is apparent at a glance, and renders this property more valuable than the refractive energy in determining the rational constitution; though, of course, it is in the agreement of the two that the most conclusive evidence must be sought.

Kanonnikoff (Bl. [2] 36, 557) had already pointed out the differences between the calculated and observed refraction equivalents for the following substances:—

Substance	R_{∞}	Calcu- lated	Differ- ence
Peppermint camphor .	77.6	77:1	+ 0.5
Cajeputene hydrate .	74.8	74.5	+ 0.3
Terebenthene hydrate, lævogyrate	77.1	74.5	+ 2.6
French terebenthene, lævogyrate	71.7	69.2	+ 2.5
Hydrocarbon from oleum camillæ.	71.9	69.2	+ 2.7
Hydrocarbon from oleum thymiani .	71.4	69.2	+ 2.2
Isoterebenthene	73·6 74·8	69·2 69·4	+4·4 +5·4
Cymene from camphor .	72.0	66.6	+5.4

K. has drawn the conclusion that the first two contain no double bond, that the two terebenthenes and the two hydrocarbons contain one double bond, that isoterebenthene contains two, and that carvol and cymene contain three, double bonds.

Carbon. Schrauf (W. 22, 424) made observations on the refraction of a Brazilian diamond of the first water, the S.G. of which was 8.516, with the following results:

observations on the refraction and dispersion of solid Se. By pressing a small quantity of melted Se between two glass plates, he prepared a thin film of the substance, which exhibited Newton's interference bands. From these he was able to calculate the index of refraction for the solar lines A_a , B and C_a , with an estimated error not exceeding 0.003; and for D_a , with some difficulty and uncertainty, to the second place of decimals only. The values obtained were:— μ_A 2.654, μ_a 2.692, μ_a 2.730, μ_c 2.737, μ_D 2.98. From these S. calculated the dispersion as compared with water, calespar, and CS_a, the figures in each case being reduced to the standard of μ_0 — μ_A =100;—

Water 36 31	83	
		88
Calcspar 36 30 Disulphide of	34	90
carbon 34 31 Selenion 29 30	35 °	99 146

Comparing Se with CS, he found that while in the case of CS₂ $\mu_D - \mu_O$ differed very slightly from $\mu_O - \mu_A$, in the case of Se $\frac{\mu_D - \mu_O}{\mu_O} = 1.46$.

In testing Cauchy's and Christofle's formulæ for the index of the ray of infinite wave-length by the above observations, the former gave 2.733 and the latter 2.433. It will be observed that Cauchy's co-efficient of refraction is somewhat higher than the observed value for the solar line \mathbf{n} , which is 2.730, the co-efficient of dispersion in this particular case being a minus quantity.

Phosphorus. Gladstone and Dale (P. M. 1859) measured the index of refraction of both solid and liquid P. an elementremarkable not only for its very high refractive power, but for an unprecedented amount of dispersion. For solid Pat 25° they obtained for u. 2 1059, for u. 2 1442, and for the extreme limit visible in the violation.

fortion of the spectrum 2-3097. Assuming the latter to be equivalent to $\mu_{\rm H}$, the length of the spectrum $\mu_{\rm H}$ — $\mu_{\rm A}$ = 0-2038. For liquid P at 35° they obtained the following:—

μ	μ_{D} μ_{F} μ_{G}		μ _G	End of violet
2.0389	2.0746	2·1201	2.1710	2.2267

The change from the solid to the liquid state is attended with a considerable diminution of density, the ratio between the density and the refraction being about the same in the two conditions. The B_A of P is taken at 18:3 from the above observations on liquid P, but Gladstone points out (C. J. 23, 101) that when combined with O it seems to have a much smaller refraction, HPO_a giving a less value (18:0) than the P it contains, while H_APO₄ also has a refractionequivalent of only 23:6.

Sulphur. It was pointed out by Gladstone in 1869 (T. 159, 9) that while S, whether solid or liquid, has a refraction-equivalent of 160 or 163 for the solar line A, the equivalent for S deduced from CS_2 was 15.85; that the difference between KCN and KCNS gave a value of 16.24, and that S_2Cl_2 gave a similar figure. On the other hand, however, it was evident that in the two gases $H_2S = 14.28$, and $SO_2 = 14.91$, or in liquefied $SO_2 = 14.59$, the refraction-equivalent of S cannot amount to 160, nor yet in H_2SO_4 , which has a refraction-equivalent of only 21.9.

Wiedemann and Nasini have subsequently given considerable attention to the values of S in combination. Wiedemann (W. 17, 577) investigated the sulphur substitution products of the carbonic esters, and obtained the following results:—

influences, in a very distinct manner, the value of the index of refraction. From the refraction-equivalents given above W. obtains the value 14.04 for 8' in the compounds II. and III.; and for S'' 15.20, 16.31, and 17.45 respectively. Using Lorenz's formula he gets the value of 7.94 for 8', and 9.09, 9.44, and 9.38 for S''. Whichever formula be adopted, the figures show that the atomic refraction of S, like that of O, is greater when S is doubly linked to an atom of carbon. It should be observed that the above results are based upon the recognised values of O, H, O', and O'', which give

$$CO_{OC_2H_3}^{OC_2H_3} = R_{\infty}$$
 45.91, and R_{∞} 27.76;

and also that W. takes as the value of S' the mean derived from the observations II. and III. If Wiedemann had adopted a direct comparison of the actal observations, the values of S' would approximate more closely according to the old formula, and less closely according to Lorenz's formula.

Nasini (G. 13, 296; Lincei, Rc. 1, 1) has determined the value for S in various compounds. From sundry organic sulphides and mercaptans he obtained the atomic refraction of S corresponding to alcoholic oxygen. From CS₂, and from the compound CS(OC,II₂)₂, he deduced the refraction of S corresponding to aldehydic oxygen:—

Sulphur	Ra	R_{∞}	Ra	R _∞
	14-10	13.53	7.87	7.65
S" (doubly linked) .	16.05	15.09	9.02	8.84

		đ	μ1.1	μ _{Na}	μ	R_{∞}	R _∞
I.	COOC'H'	0.975	1.3837	1.3858	1.3876	45-66	27:80
II.	co ^{OC} ,H,	1.0285	1.4479	1.4515	1.4544	56-95	84-11
III.	COSC,H,	1.085	1.5168	1.5237	1.5287	69-15	40.57
IV.	CSOC,H,	1.0325 ?	1:4563	1.4601	1.4632	57.82	84.56
٧.	CS SC,H	1.085	1.5301	1.5370	1.5431	70-26	41.28
VI.	CS SC,H,	1.152	1.6105	1.6210	.—	82.73	47.56

From these figures it will be seen (1) that the index of refraction rises whenever an atom of O is replaced by an atom of S, and that so much the more, the more S there is already in the compound; (2) that the refractive indices of the combinations which contain the radicle CS are greater than those of their analogues containing OO; (3) that the refractive index likewise increases if, besides the radicle, first one and then a second atom of S replaces O, and in the latter case more than in the former; (4) the isomeric bodies II. and IV., as well as III. and V., have quite different indices of refraction, and in both cases the compound that has the S in the radicle has the higher index. This indicates that the mosition of the S in the compound

But when examining other compounds, such as H_xSO_t , SO_x , and SO_x . N. found that whatever hypothesis he adopted as to their constitution—or, in other terms, whatever value he took for the atomic refraction of O—he obtained values for S, not very discordant among themselves, but totally different from those given above. Treating the sulphur as divalent, R_∞ varied from 8:10 to 9:01; as tetravalent, from 6:94 to 6:43; as hexavalent, from 6:63 to 7:85. Calculating by Lorenz's formula, R_∞ ranged from 5:24 to 6:27 in the first case, from 4:51 to 4:91 in the second, and from 8:13 to 8:79 in the third. Some observations recorded by Kanonnikoff (J. R. 15, 434) substantially support these figures.

Nasini and Scala (Lincei, Rc. 1886. 617, 623) record observations on the sulphocyanides, which show that the mustard-oil compounds have refractive and dispersive powers in excess of those of their isomerides, while phenylic isosulphocyanide has a specific refraction and dispersion far above the calculated values-exceeding, in fact, oil of cassia or CS₂. In this combination the union of the group S=C=N, endowed with a high refractive power, with the phenylic group, also highly refractive, appears to produce a heightening of the refrangibility, a phenomenon which N. regards as analogous to the increase in refraction which he observed when in the benzene group an unsaturated side chain is ioined to an unsaturated carbon atom. In compounds containing four atoms of S there is an excess of refraction above what is estimated from the value of S in CS, the monothiocarbonates of Et and Pr giving a value of 17.4 and 17.5 for the refraction-equivalent of sulphur.

Nasini a. Costa (Ist. Ch. Rome, 1891) made

lished (Ar. N. 8) a long series of very careful determinations of the indices of refraction of mixtures of H.SO, and H.O, in various proportions for all the principal lines of the solar spectrum from A to H inclusive. These show a progressive increase in refraction and dispersion with every addition of H2SO4, until a maximum is reached at a point corresponding, apparently, with the monohydrate of the acid. after passing which the refraction and dispersion suddenly decline, while the density of the mixture continues to increase. Out of the seventeen series of determinations at different concentrations, the seven most conc. are given below, the central one of the series representing the nearest approach to the maximum. The indices are all reduced to a temperature of 18.3°. The specific gravity given in the line below is for 0°, water at the same temperature being taken as 1.0. In the cases of the two G's and the two II's, the higher one in each corresponds with the lines so designated by Fraunhofer.

μ.	63·69 p.c.	71.97 p.c.	81.41 p.c.	85.93 p.c.	88.97 p.c.	91.43 p.c.	04.72 p.c.
	SO _a	SO _s	SO ₃	SO.	SO _s	SO _a	SO,
A	1·40819	1·41930	1·43049	1·43279	1·43151	1·42918	1·4268 3
a	1·40928	1·42042	1·43168	1·43385	1·43270	1·43035	1·42781
B	1·41016	1·42133	1·43263	1·43476	1·43357	1·43114	1·42868
	1·41112	1·42227	1·43360	1·43579	1·43444	1·43198	1·42944
D	1.41342	1.42466	1.43596	1.43807	1.43669	1.43426	1.43163
E	1·41618 1·41669	1·42740 1·42793	1.43877 1.43928	1 44081 1 44130	1·43944 1·43996	1·43701 1·43749	1·43431 1·43484
F G	1.41838	1.42967	1.44103	1.44311	1.44168	1.43922	1.43649
G	1·42058	1·43186	1·44327	1·44534	1·44392	1·44144	1·43869
	1·42233	1·43364	1·44507	1·44706	1·44569	1·44316	1·44037
H	1·42421	1·43561	1·44703	1·44901	1·44759	1·44512	1·44229
	1·42567	1·43696	1·44841	1·45040	1·44883	1·44640	1·44347
S.G.	1.55438	1.64925	1.76066	1.80676	1.83123	1.84485	1.84994

further studies of S and its compounds. They conclude that the oxygen compounds, which are generally distinguished by a low refractive and dispersive power as compared with those not oxygenated, may be divided into two principal groups: those which may be regarded as derived from SO, have the higher, and those derived from SO, have the lower, refractive and dispersive powers. Kanonnikoff (S. Ph. Ch. Russ. 16, 129) assumed that the refraction of S varies with the change of valency, and assigned the following values for R_a:—

S divalent 14:10 S tetravalent 8:72 (in sulphones) S hexavalent 4:85 (in H₂SO₄)

but this is not accepted by N. and C. They find that the accumulation of S in the molecule is almost always accompanied by an increase in the refractive and dispersive power. In this respect, though not in others, S appears to have much analogy with carbon. Throughout this investigation N. and C. tested the dispersion formula of Ketteler, $\frac{\mu_a^*-1}{\mu_b^*-1}$, in which a and b represent rays of different wave-length, and found that it gave very uniform results; but from a physico-chemical point of view they do not regard this fact as an argument in favour of the formuls.

Sulphuric acid. Van der Willigen pub-

Van der Willigen pointed out that the formula $(100-p)\frac{n^2-1}{d}+p\frac{n'^2-1}{d'}=100\frac{n''^2-1}{d'}$ will not apply to mixtures of $H_2\mathrm{SO}_4$ and water, where 100-p and p are the respective weights of the two mixed liquids, n, n', and n'' the indices of refraction, and d, d', d'' the densities of the two liquids and the mixture respectively. Dale and Gladstone had formerly stated that the same was the ease in respect of their formula.

Nickel and iron carbonyls. Mond has prepared Ni(CO), and Fe(CO), both liquids of a highly-refractive character. former has been examined optically by Nasini (Lincei, Rc. 7, 411), and the latter by Gladstone. Ra for the nickel compound was found to be as high as 57.7, which, deducting 8.4 for the value of each CO, gives Ra = 24.1 for the metal itself, instead of about 10.0, as determined from the chloride, sulphate, and nitrate. This would seem to confirm the hypothesis that the refractive power varies with change of valency, increasing with the increased power of combination. In this compound the Ni is regarded by Mond a. Nasini as octovalent, and as justifying Men-deléeff in placing it in Group VIII. of his system of classification. Gladstone, on the other hand, is disposed to think that the metal in both compounds is, as usual, divalent, and that it is the

60 which has a greatly increased value. He obtained for Fe(CO), $R_{\rm h} = 67.33$, $R_{\rm p} = 69.40$. These figures show not only a very high refraction, but also very great dispersive power.

Silver iodide, bromide, and chloride.

Silver iodide, bromide, and chloride. Wernicke (A. 142. 560) measured the refraction and dispersion of light by these salts in two different ways: (1) by examining the light reflected from glass plates covered with a layer of these salts, by means of a spectroscope, and noting the position of the dark interference-bands; (2) by direct measurements of small prisms made of the fused salts. The portion of the spectrum observed ranged from the solar line C to G. The dispersion \(\mu_{\text{O}-\text{W}} - \mu_{\text{D}} \) was about twenty-seven times that of water in the case of the iodide; that of the other two salts is much less, though considerably greater than that of fint glass. AgI seems capable of existing in two conditions: at temperatures above 138° it gives a short spectrum limited to the red, yellow, and green, while below that temperature it gives a spectrum twice as long, showing all the colours. W. believes that AgI is partly dissociated at the higher temperatures.

ciated at the higher temperatures.

Bromino. Weegmann (Diss. Bonn, 1888) determined the refraction-equivalent of Br by Lornz's, as well as by the older, formula, for both the hydrogen lines, a, and Cauchy's limit, from a series of ethylene and acetylene compounds, adopting Brühl's values for C, II, and the ethylene linking. The following are his figures for Br compared with those arrived at by Brühl:—

Bromino	Rx	R.	R _∞	R.
Weegmann .	14·78	15·38	8·56	8·83
Brühl	14·81	15·39	8·70	8·95

Fluorine. The writer of this article has collated the observations made by various observers on bodies containing. F in order to arrive at the refraction-equivalent of this element (P. M. 1885, 481). Those of Brewster on cryolite, of Brewster, Wollaston, Fizeau, Stefan, and Kohlrausch on fluorspar, and of Gladstone on aqueous solutions of KF, give a refractionequivalent for F varying from 0.29 to 0.32. Those of Topsöe and Christiansen on crystalline silicofluorides of Cu, Ni, Zn, Mg, and Mn, of the formula RSiF, 6H,O, give a refractionequivalent for F varying from 0.62 to 0.84; while (NH.), SiF. gives 0.59 for F. The latter figures must be accepted with caution, as a very slight difference in the values ascribed to the other elements will account for the whole of the discrepancy. It is evident, however, that in any case the refraction-equivalent is of exceedingly small amount, and that the specific refraction, even if the highest value be taken, can scarcely be the half of that of any other element known.

J. H. and G. Gladstone (P. M. 1891. 1) have investigated the optical properties of fluorbenzene and allied compounds. The molecular refraction for C_bH_cF, for six lines of the solar spectrum, is given in the following table; from this is deducted the value for benzene less one atom of H, leaving a small balance as the atomic refraction of fluorine.

These figures are remarkable as giving a negative value for the dispersion R_B-B_A namely the

	R	R _a	R	R	Ro	RH
C.H.F C.H.	42·92 42·29	43·33 42·70	43·70 43·17	44.68 44.20	45·61 45·17	46·40 46·05
F	0.63	0.63	0.53	0.48	0.44	0.85

quantity, -0.28. According to Lorenz's formula $\mathbf{R}'_{\mathbf{A}} = 0.92$ and $\mathbf{R}'_{\mathbf{R}} = 0.84$, showing in like manner a negative dispersion. The observations of Baille, Stefan, and Sarasin on fluorspar, and those of the authors on solutions of KF and NII, F, all distinctly confirm the foregoing evidence as to the anomalous dispersion; while a comparison of the refraction of the three lines C, D, and F of the solid silicofluorides measured by Topsöe and Christiansen, and the author's observations on aqueous solutions of $\mathbf{H}_{\mathbf{Z}}\mathbf{SIF}_{\mathbf{z}}$, seem to point in the same direction.

Liquefied gases. Bleckrode (Pr. 87, 889) adopted a special apparatus for measuring the indices of refraction of liquefied gases, consisting of a modification of a Faraday tube, forming a vessel having two parallel side plates, free from leakage even at high pressures. By observing, through a microscope provided with a graduated scale and a micrometer screw, test objects, such as lepidoptera scales, attached to the inner surface of the glass plates of the cell, the variation in the focus between the direct observation and that through the cell and liquid was found, and, with a correction for the effect of the glass, he obtained the data from which to calculate the index of refraction according to D

the equation $\frac{D}{D-d} = \mu$, in which D represents the thickness of the layer of liquid and d the apparent displacement of the test object. The observations were taken both with a sodium flame and with daylight, and the calculated probable error of the result amounted to \pm 0-003. The first table on p. 218 gives the results of B.'s observations compared with those of Dulong, Ketteler, Croullebois, and Lorenz on the same substances in the gaseous state; the specific refraction is calculated by both the formulæ in common use.

B. drew attention to the remarkably low S.G. of cthylene, as the lightest fluid substance known; his determinations gave 0.335 at 8°, 0.361 at 6°, and 0.386 at 3°. B. also gave determinations of the indices of refraction of the following substances taken by the same process; and commented on the high indices of the organo-metallic compounds as inconsistent with the opinion expressed by early observers that a high index of refraction is indicative of a body being combustible.

Substance	Temp.	μ_{D}		
Hydrobromic acid Do. Hydriodic acid Bromine Methylamine Dimethylamine Trimethylamine Zinc ethyl Aluminium ethyl Aluminium methyl	•		10° 15° 16·5° 13° 17·5° 17° 16° 12·5° 14° 6·5° 12°	1.825 1.830 1.466 1.571 1.842 1.850 1.853 1.485 1.474 1.480 1.482

Substance			Liquid		<u>µ−1</u> gl		$\frac{\mu^3-1}{\mu^3+2}\times\frac{1}{d}$			
					s.G.	μ _D	Liquid	Gas	Liquid	Gas
Sulphurous anhydride		•			1.359	1.851	0.252	0.236	0.153	0.157
Cyanogen			•	•	0.866	1.327	0.378	0.350	0.284	0.233
Hydrocyanic acid .					0.697	1.264	0.379	0.368	0.238	0.246
Nitrous oxide					0.870	1.204	0.235	0.255	0.150	0.170
Carbonic anhydride .					0.863	1.196	0.227	0.221	0.145	0.147
Hydrochloric acid .					0.854	1.257	0.300	0.277	0.190	0.185
Chlorine					1.33	1.367	0.270	0.240	0.169	0.160
Ammonia		•			0.616	1.325	0.528	0.490	0.327	0.327
Ethylene					0.361	1.180	0.498	0.526	0.321	0.350
Hydrogen phosphide .					0.622	1.323	0.519	0.500	0.322	0.333
Hydrogen sulphide					0.91	1.390	0.429	0.413	0.262	0.275

Liveing and Dewar (P. M. 1892. 205) have determined the refractions of three liquefied gases, at their respective boiling-points, by direct observation through a hollow prism. They obtained the following results for the sodium line D:—

		μ _D	n _d	R _D
Oxygen	•	1·2236	3·182	2·024
Nitrous oxide		1·3345	11·587	7·163
Ethylene .		1·3632	17·556	10·752

Alums. The indices of refraction of some of the alums have been measured by several observers, amongst them Grailich, Fock, Kohlrausch, Stefan, Topsöe, and Christiansen. The most complete series of observations on inorganic sulphuric alums is that of Soret (Ar. Sc. Geneve, 12, 553; 14, 96; 20, 517), including those containing Rb, Cs, In and Ga. His mode of determination was by total reflection, which he considered the best adapted for the purpose; he gave indices which he calculated to be correct to two units in the fourth place of decimals. His observations were given for eight rays of the solar spectrum, viz. the lines a, B, C, D, E, b, F and G. He remarked on the very low value of the index of refraction of the Na-Al alum. He gave the following comparative table for $\mu_{\rm D}$, showing that the different series of alums vary in general with much regularity. The horizontal lines contain the same metal, and the vertical lines the same metal or alkaline radicle.

	NH.	K	Rb	Cs	Ti
Aluminium Indium Gallium Chromium	1:4594 1:4664 1:4683 1:4842 1:4848	1.4564 1.4658 1.4814 1.4817	1·4566 1·4638 1·4658 1·4815 1·4823	1:4586 1:4652 1:4649 1:4810 1:4838	1·4975 1·5066 1·5228 1·5236

Calculating for each salt the difference between its $\mu_{\rm D}$ and that of the ammoniacal alum on the same horizontal line, Soret obtained:—

	NH ₄ -K.	NH ₄ -Rb	NH ₄ -Cs	NH ₄ -Tl
Aluminium Indium Gallium Chromium Iron	+0.0080 0.0080 0.0028 0.0081	+0.0028 0.0026 0.0025 0.0027 0.0025	+0.0008 0.0012 0.0034 0.0082 0.0010	-0.0381 0.0383 0.0386 0.0388

These figures show a close accord, except in the case of Cs, in which the Gs and Cr compounds

appear to be too low. Soret did not consider that the impurity in the specimens, if any existed, could be due to the Ca.

could be due to the Cs.

Gladstone (P. M. 1885. 162) worked out the refraction-equivalents from the data given in the first named of Soret's papers, and also from those by Topsõe and Christiansen, in order to test his former conclusions that a salt has the same specific refraction whether it is in a solid form or in solution, and that the refraction-equivalent of a compound body is the sum of the refraction-equivalents of its constituents. As to the first point, in the case of the two alums given below he found the specific refractions, after deducting the amount due to the solvent, to be in substantial accord:

Dissolved Crystallised Ammonium-aluminium alum 0.2780 Sodium-aluminium alum . 0.2613 To test the second point, the alums were regarded as compounds of the sulphates of two metals of different kinds with twenty-four molecules of water. Taking the RA of water in the uncombined state at 5.926—and taking the observations of Kanonnikoff, Topsöe, and Christiansen, as well as his own, of the several sulphates-Gladstone arrived at the results given in the following table. The other observers did not take the A line, but their observations have been reduced to A for purposes of comparison. The agreement between the calculated and observed refraction-equivalents is as near as might be expected, except in the case of Cs.

		RA observed and reduced		
Substan ce	R _A calcu- lated	Boret	Topsöe and Christiansen	
Ammonium-aluminium alum Sodium " " " " " " " " " " " " " " " " " " "	252-0 239-8 267-2 345-1 254-0 268-0 257-1 266-0 280-0 370-6 263-7 273-6 286-6	252·2 238·5 267·7 246·8 253·7 265·9 261·2 266·7 275·5 269·1 265·0 278·2 278·0	268-6	

Gladstone also sought, by means of Soret's observations, to determine the refraction-equivalents of In and Ga, and (B. A. 1892) he gave the following constants:—

				At. W.	RA
Indium Gallium	:	:	:	113·4 69·9	13·7 11·6

These figures, however, can only be looked upon as approximate, as all experimental errors are accumulated on these residual numbers.

Perrot (Ar. Sc. Genève, 1880) has made a series of observations on the refraction and dispersion of an isomorphous series of biaxial orystals -the double sulphates of Zn with K., Rb₂, (NH₄)₂, Cs₂, K₂, and of Mg with Rb₂, and in each case 6H₂O. He has followed the plan adopted by Soret in his observations on the alums. The results conform satisfactorily to the values computed on the same principle as that adopted by Gladstone with respect to the alums, except in the case of casium and rubidium, in both of which, especially the former, the observed values are lower than the theoretical. The mean ray adopted for this calculation is, however, the arithmetical mean of the three indices observed for each of the lines of the spectrum, and has, therefore, no real physical significance. A glance at the tables of observations will show at once what a wide scope for error there is in arriving at a mean value by this process.

Analogy between refraction and dispersion and magnetic rotation. Gladstone and Perkin have recently observed an analogy between the magnetic rotation and the refraction and dis-persion of light. They have tested this in the case of organic compounds containing nitrogen (C. J. 55, 750), with the result that they have found a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance. These three properties are really comparable with one another, for in each case the observed value is divided by the density of the substance, and it is determined, not for equal weights, but for an equal number of molecules. It has been found that each property is determined in the first instance by the atomic composition of the substance, so that it may be laid down as a primary law that the molecular magnetic rotation, like the molecular refraction or dispersion. of a compound is the sum of the molecular magnetic rotation, refraction, or dispersion of its constituents. The values are, however, subject to large modifications dependent upon differences in the structures of the compounds. Thus a change of valency-is attended by a marked change of value in these optical properties, and they are apparently affected by some circum-stances which are not as yet recognised in structural formulæ.

The following values have been deduced by Perkin for the molecular magnetic rotations of certain elements in the paraffin group of carbon compounds; and against them are placed the recognised values for their molecular refraction and dispersion:—

	Molecular mag- netic rotation	R_{A}	R _{H-A}		
CH	1.023	7.6	0.34		
c	0.515	5.0	0.26		
H	0.254	1.3	0.04		
O, alcoholic .	0.194	2.8	0.10		
O, aldehydic.	0.261	3.4	0.18		
ci	• 1.733	9.9	0.50		
Br	3.562	15.3	1.22		
Ι	7.757	24.5	2.62		
N, in amines	0.717	5.1	0.88		
· .					

These figures show a certain analogy; and when modifications are introduced by changes in the mode of combination, the change that occurs in the one property is noticeable also in the other two, and that in the same direction, though not necessarily to the same extent. Thus there are in all cases two different values for oxygen in alcohol and aldehydes, and a very great increase of the values in the case of unsaturated carbon compounds. The values also of CH, in the first and second members of homologous series (such as the alcohols, parallinoid acids, &c.) are different from its value in the higher members of the same series, and always in the same direction.

P. also applied the same inquiry to solutions of HCl, HBr, and HI, which when dissolved in water were known to give higher values for refraction and dispersion than the normal. The same was found to be the case in the magnetic rotations. When HCl was dissolved in isoamyloxide, however, all three values were found closely approximating to the normal, as will be seen in the following table:—

Hydrochloric acid	Molecular magnetic rotation	$\mathbf{R}_{\blacktriangle}$	R _{H-A}
In water , isoamyloxide .	4·412 2·238	14·45 11·36	1·12 0·51
By calculation for free acid	2·187	11.20	0.54

It is, therefore, laid down as generally, if not always, true, that where there is a departure from the normal values in regard to one or other two. The different properties are evidently similarly affected by change in chemical constitution. The investigation seems to indicate another close relationship between electro-magnetism and the velocity of light. G. G.

OPTICAL METHODS.—Section 2: SPEC. TROSCOPIC METHODS.

Historical notes.—Spectrum analysis is an optical method of making a diagnosis of the chemical composition, and in certain cases the chemical constitution, of either (a) a self-luminous body, or (b) an absorbing medium, whether self-luminous or not. Newton first discovered that light could be analysed when passed through a prism, and, in 1752, Thomas Melvill made an optical analysis of alcohol fiames coloured with

salt and with nitre. Wollaston, in 1802, observed with the prism certain obscure bands in the solar light which had traversed a narrow slit in his window shutter. Fraunhofer, in 1814-15, was the first to employ a very narrow and accuratelyformed aperture with a prism, telescope, and divided circles, and he not only observed the dark lines in the solar spectrum, but measured their indices of refraction or refrangibilities. He examined, subsequently, the spectra of the stars, of electric light, and of the exterior envelope of the flame of a wax candle. 'The latter spectrum he discovered to consist of homogeneous yellow light, composed of two distinct rays very close together, and coincident with the two dark lines in the solar light which he had termed D. Brewster floted the presence of this yellow light in the combustion of many substances, but it was Box Talbot who, in 1826, clearly proved that the source of this light was sodium. He likewise connected a red ray with the presence of potassium and an orange ray with strontium, and concluded that a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to detect. Herschel had previously described the spectra of a few of the metals and of boracic acid. In 1834 Fox Talbot described the strontia and lithia spectra, and stated that optical analysis could distinguish the most minute portions of these two substances with as much, if not greater, certainty than was afforded by any other known method.

Wheatstone, nearly at the same time, published some experiments similar to those of Fox Talbot, and Swan first estimated the amount of sodium which can produce the D lines. At the Manchester meeting of the British Association in 1842, Brewster read a paper On Luminous Lines in Certain Flames corresponding to the defective Lines in the Sun's Light. He discovered the dark lines of absorption in nitrogen peroxide gas when white light is directed through it, and he observed and mapped a number of atmospheric lines in the solar spectrum. In 1849 Foucault obtained a reversal of the D lines in the electric arc. Stokes, about 1850, gave in his lectures the true explanation of the coincidence of sodium lines with the dark lines D. Angström in 1853 stated that an incandescent gas emits luminous rays of the same refrangibility as those which it absorbs, and Balfour Stewart, 1858-9, based the following statement on experimental data: The radiating power of a body for any ray is equal to its absorbing power for the same ray.
In 1859, Kirchhoff and Bunsen gave a great

In 1859, Kirchhoff and Bunsen gave a great impetus to spectrum analysis by publishing their researches on the constitution of the sun, and also by designing an extremely simple spectroscope and describing its use. Chemists were further made aware of the new power placed in their hands by Bunsen's discovery of two new metals, rubidium and cessium, in 1860, by the discovery of thallium by Crookes and by Lamy in 1862, of indium by Reich and Richter in 1863, and of gallium by Lecoca de Boisbaudran in 1875.

and of gallium by Lecocq de Boisbaudran in 1875.

Fundamental laws. Spectrum analysis primarily depends on the following two laws:

1. Every solid and liquid when heated begins by emitting rays of longest wave-length, which are

the result of comparatively slow vibrations, but as the temperature rises the vibrations become more rapid, and shorter waves are emitted, so that at the highest temperatures the sum of the radiations is white light, consisting of waves of all possible lengths, the effect of which is a continuous spectrum. A mass of iron gradually raised to its melting-point would be an example of this. 2. Every substance vapourised by heat emits rays of definite wave-lengths, and these rays are characteristic of each substance, because it alone can emit them. In other words, every substance vapourised by heat has its own definite periods of vibration, by which it can be absolutely identified, because no other substance can vibrate in the same manner and with the same periods. All flame and spark spectra furnish examples. From this second law it follows that the spectrum of an element is a constant of very great importance. The determinations of the spectra and of the atomic weights present similar diffi-culties, which arise from the necessity for obtaining the elements or their compounds in the highest possible degree of purity, and also in many cases from the complexity of the spectra, and the careful observations which are necessary in identifying and measuring the wave-lengths of the rays.

Determinations of the absolute wave lengths of the bright lines in any spectrum are now usually made either with a plane or a concave diffraction grating ruled on speculum metal. When a sufficient number of accurately-measured lines is known for any region of the spectrum, determinations of the wave-lengths of lines in new spectra may be made by observing with a prism-spectroscope, and by the use of an interpolation curve the wave-lengths corresponding to the positions of the lines measured may be found. From time to time the curve will require verifying and correcting.

There are two classes of spectra, emission and absorption spectra.

Emission spectra consist of: (1) Continuous spectra and (2) Interrupted spectra. 1. Continuous spectra are characteristic of most incandescent solids, liquids, and gases at great pressures, or of a cloud consisting of solid glowing particles. 2. Interrupted spectra consist of: (a) Bands of light or 'fluted band' spectra, characteristic of certain vapours, especially the vapours of compound substances rendered glowing at comparatively low temperatures; (b) bright line spectra, characteristic ohiefly of transparent vapours at high temperatures or at low pressures; (c) reversed line spectra, which are dark lines segn on a brilliantly-illuminated ground. When a bright line spectrum is observed in front of a more brilliant continuous spectrum, the lines appear dark on a bright ground of colour, instead of bright and coloured on a dark ground, and they are then said to be reversed.

Absorption spectra. When rays capable of giving a continuous spectrum are made to traverse (ag transparent solids, (b) transparent liquids, (c) transparent gases at ordinary temperatures, it is frequently observed that a definite band of rays is absorbed at either end of the spectrum. This is called a continuous absorption. Quite as frequently a band of rays is out out of the middle of the spectrum; this is called a

selective absorption, and the region of the rays absorbed is said to be occupied by an absorption band.

The production of emission spectra. Emission spectra may be produced in the following ways (a) By flames of low temperature, e.g. by a spirit lamp or Bunsen burner, acting on solids, or the spray of solutions. The flame may be fed with chlorine, bromine, or iodine, or with hydroshlorine acid when salts of the halogens are examined. (b) By flames of high temperature: blow-pipe, and oxyhydrogen flame. (c) By sparks in vacuum tubes containing residual gases or vapours. (d) By sparks of low tension acting on solids or solutions. (e) By sparks of high tension. (f) By solids in the electric arc. (g) By electric discharge on solids in vacuo; these are phosphorescence spectra.

As a rule, line spectra are the spectra of elements, band spectra are the spectra of compounds.

Salts of the alkali metals in the Bunsen flame emit line spectra characteristic of the metals, while the alkaline earth salts emit lines and bands which are characteristic of the metallic oxides. On the other hand, the burning of hydrogen and of hydrogen compounds causes the emission of more than 160 lines in the ultraviolet region, which can only be assigned to the vapour of water at a high temperature. Carbon is an element which emits bands in the coloured region, in hydrocarbon flames. A list of compounds which emit characteristic banded flamespectra is given on p. 246. Erbia and erbium phosphate emit luminous bands when the solid substances are heated in a Bunsen or blow-pipe flame. Discharges in vacuum tubes sometimes emit a continuous spectrum; oxygen does so at the lowest temperature at which it is luminous. Most gases emit a banded spectrum with low tension sparks at ordinary pressures; The spectrum alters with diminution of pressure until finally nothing but a line spectrum is visible - for example, this is the case with air in the ultraviolet region. Sparks of low tension from solids, such as metallic electrodes, and from solutions, emit lines chiefly in the visible region, while those of high tension are generally richest in radiations of high refrangibility, chiefly in the ultra-violet region.

Low-tension sparks may be produced in two ways from solutions, first by wires of platinum moistened by the liquid, secondly by pieces of charcoal giving the flaming spark used by Bunsen. Many elements have been shown to emit a few bands or lines in the infra-red. The difference in action of high- and low- tension sparks is chiefly, if not entirely, due to temperature; the highest temperatures cause the emission of rays of the highest refrangibility. Solid elements, with few exceptions, yield spectra in the electric arc. The lines exhibited by some of the metals are exceedingly numerous. Reversed line spectra are common in the sun, and afford evidence of the presence of metals whose bright line spectra are coincident therewith. number of bright lines seen reversed in the sun's spectrum indicates the strength of the evidence of the existence in the sun of certain elements.

As to the distribution of known kinds of Vol. IV.

matter in space, the following list shows the elements observed in the sun with the numbers of their reversed lines seen in the solar spec trum: Fe 730, Ti 230, Ca 94, Mn 85, Ni 102, Co 91, Cr 71, Ba 26, Na 11, Mg 17, Cu 7, H 5, Pd 5, V 4, Mo 4, Sr 4, Pb 3, U 3, Al 18, Ce 2, Cd 2, Be 2, Sn 1.

Methods of spectrum analysis. For efficient work with the spectroscope an instrument is to be preferred which admits plenty of light, has a rigid collimator, and immovable prism. Compound prisms of Grubb's and of Thollon's construction are among the best. The arc should be divided on the vertical edge of the prismtable or on an edge inclined at an angle of 45%. A vernier travelling over the are and a mounted lens, for convenience in reading the scale and vernier, should be fitted ficar the telescope. A beautiful instrument made by the Societé Génevoise pour la Construction des Instruments de Physique has a circle completely divided, and titings for investigating ultra-violet spectra, either by photography or with a fluorescent eyepiece of Soret's design. It is provided with two verniers, and an automatic arrangement admitting of the prism being placed at the minimum angle of deviation for each ray under examination. This is necessary in order to secure the best definition. The instrument, of whatever form. should be capable of dividing and measuring the lines D1 and D2 of sodium, the first, second, and third lines of the yellow band; and in the carbon spectrum the first, second, third, and fourth lines of the green band, and the first, second, and third lines of the blue band, which are seen in the green inner cone of a powerful Bunsen burner. An instrument with a photographic scale, if it is sufficiently delicate, which is seldom the case, is of great use. One of these, constructed by Duboscq, was employed by Lecocq de Boisbaudran. A lens of short focus should be used to concentrate the light, from whatever source, upon the slit of the instrument. A test tube about 12 mm. diam., supported vertically, if filled with water and placed close to the slit of the instrument. answers this purpose. The telescope should be capable of easy movement without vibration, and be supported for two-thirds of its length from the object glass; neither clamping nor the use of the focussing screw should be capable of displacing its position. The rays should pass straight down the collimator and completely fill the lens. Before commencing any serious work. the capabilities of the instrument and its use for obtaining measurements should be carefully studied.

Supports of platinum wire fused into glass tubes are used for examining concentrated solutions and fused beads of salts in ordinary flames. Bunsen burners with steatite tops are particularly useful. Blow-pipe flames with a vertical direction, urged by bellows worked by the food are useful for examining the alkaline earths. Hydrogen gas from a constant generator made of lead and of large size is better than coal-gas or hydrogen be used, it is advantageous in examining salts of the alkaline earths, particularly chlorides, to pass the gas through a litre of strongest hydrochloric acid into a Bunsen burner, which is made of hard glass tube tipped

with platinum. The flame is thus supplied with hydrochloric scid, and the chlorides are volatilised apparently without decomposition, so that they emit rays of great brilliancy which yield simple line spectra. For high temperatures a very small gas blowpipe may be supplied with oxy-In this case the supports of platinum would be fused, and it has therefore been found convenient to use a wire of iridium, twisted into a loop, the compound being placed in the loop. In this manner manganese dioxide yields the bands of the dioxide, the spectrum of which is observed in the Bessemer flame. Calcium fluoride and copper oxide readily yield characteristic spectra. The alkaline earths yield very brilliant spectra, which are due to the metallic oxide in each case. When volatile substances, such as salts of lithium and the other alkalis, are under observation, it frequently happens that a difficulty in measuring their lines occurs owing to the evanescent appearance of their spectra; more lasting spectra may be produced by converting the volatile salts into silicates or borates by heating in a platinum spoon, or even in a porcelain crucible, with crystals of boracic acid. Beads of the borates will continue to illumine a flame for a lengthened period; with lithium and thallium, measurements have been made for as long as twenty minutes without renewing the material. Should the alkalis be accompanied by lime, strontia, or baryta, the spectra of these earths are suppressed, but towards the end of the observation sometimes the green colour of boric oxide appears. Sparks, both of low and high tension, may be used with Delachanel and Mormet's fulgurator. This instrument has the advantage of using very little solution, and losing none. Some solutions, such as salts of yttria, do not yield their characteristic spectrum to lowtension sparks, and it is necessary to strengthen the current by interposing a Leyden jar in the circuit, or, what is better, a pane of glass coated on either side with 930 square centims. of tinfoil. The spark should be 3 to 6 mm. in length. The lines of platinum, hydrogen, sodium, and a few of chlorine are visible, but these are known and are measurable. When the solution becomes contaminated with platinum, it may be removed and purified to be used over again if necessary. For such work it is best to use a coil which can yield sparks 170-180 mm. long in air.

For observations on ultra-violet spectra the arrangements described by Soret and by Cornu consist of an optical train of quartz and a prism of 60°, which is composed of two halves each of 30°; one of the two lenses and one half of the prism are out from a right-handed crystal, the other corresponding parts from a left-handed crystal, so that the double refraction of one is corrected by that of the other. One half of the prism may be fixed on the collimator close to the lens, the other in front of the object-glass. For ordinary observations a fluorescent eye-piece is necessary, but generally photography is more convenient. Cornu has used lenses achromatised with colourless fluorspar, but this is not necessary, because the peculiarity of the camera employed by Hartley enables whole spectra to be accurately focussed on one plate if only one prism of 60 degrees be used. The camera back is sloped at an angle of about 22° to the normal,

which brings one end of the plate nearest to the rays of shortest wave-length, and the locus of the foci of all the rays, from the least to the most refrangible, lies upon the plate. There is thus a saving of time in the observation of complicated spectra, with the additional advantage that angular measurements are abolished and linear measurements substituted. Moreover, an increased dispersion and separation of the rays is obtained. This arrangement is most suitable for use with two half-prisms of quartz of 30°. Six hundred lines in the spectrum of iron have thus been photographed with such excellent definition that a magnifying power of 25 diameters was used in their measurement. A quartz lens 75 mm. in diameter and of 75 mm. focus is placed in front of the slit. The camera back is so constructed that by a rack and pinion motion a succession of twelve or fifteen spectra may be taken on one plate. The lenses, which are not achromatised, are of 425 mm. focus for vellow light, and 50 mm. in diameter, the prisms being of corresponding dimensions.

Sparks of high tension obtained in the manner already described are necessary. They may be passed between metallic electrodes 3 to 6 mm. apart.

For photographing spectra yielded by solutions electrodes of graphite are used, or wicks of fine wire drawn from pure gold. The solution is placed in a small I tube; in the shorter limb the electrode is placed, and a platinum wire passes down the longer limb to make connection with the coil. By means of a pipette the tube is easily charged. The graphite electrodes are cut from good sound pieces of Ceylon or Siberian graphite, and are chisel-shaped, with grooves scored along them with the point of a pin. The opposite electrode may be of graphite or of any suitable metal. In order that the strongest discharges may pass from below upwards the lower should be the negative electrode. The admirable work of Lecocq de Boisbaudran on flame and spark spectra (Spectres Lumineux, 1874) not only gives the practical details, but maps of prismatic spectra, and the same applied to a scale of wave-lengths, as well as a complete description of the spectra and a description of each line. The publication proves to be all that a guide to the use of the spect oscope should be, but it deals only with the visible region. In photographing spark spectra the trouble of making drawings is unnecessary, since the photographs themselves are better than any reproduction; all that is required is a description and a map of the principal lines on the scale of wave-lengths. In photographing the spectra of solutions by means of graphite electrodes it is, of course, necessary to ascertain that the material does not yield any of the numerous lines in the spectrum of iron, generally speaking four lines of magnesium with wave-lengths 2801-1 to 2789-6 are visible. Although photography has been applied almost exclusively to the ultra-violet rays and to the infra-red, there is no reason why it should not be used for visible rays, since gelatin plates stained with cyanine, eosine, erythrosine, and some other dyes, render the plates sensitive to the orange, red, and yellow rays. Cyanine is a dve which is sensitive to most of the spectrum as far as the rays of very long wave-lengths.

On the sensitiveness of emission spectra.

The following table gives the sensitiveness of the emission spectra of various elements in fractions of a milligram. It will be observed that radiations in different regions, and excited by different means, greatly vary in emissive power even with the same element.

•	Visible fla	me spectra.	
	Mgr.		
Ba	2,000	Kirchhoff	a. Bunsen
Ca	50. VOU	**	*
Cs	25,000	,,	91
Cu	1 285	Simmler	
ľ n	2,000	Cappel	
Li	1 600,000	Kirchhoff	a. Bunsen
Mn	83 83	Simmler.	
K	1 8,000	Kirchhoff	a. Bunsen
Rb	7,000	,,	**
Na	14,000,000	**	19
Sr	30,900	**	"
Tl	50,000	Lamy	

Visible spark spectra (Cappel).

-	T / / /	- /-
Mgr.	1	Mgr.
900,00 0	Li	1 40,000,000
70,00 0	Mg	1 500,000
18,000	Mn	200,000
10,000,000	Hg	10,000
1 4,000,000	Ni	1 600
4,000	K	1 400
1 20,000	Rb	1,000
15,000	Sr	100,000,000
1 4,000	Tl	1 80,000,000
1 90,000	Sn	1 17,000
26,000	Zn	1 600,0 00
20,000	-	,
	1 900,000 1 70,000 1 18,000 1 10,000,7700 1 4,000 1 20,000 1 15,000 1 90,000 1 20,000 20,000	Mgr. 1 900,000 1 70,000 18,000 Mg 18,000 Mn 10,000,000 11 4,000,000 R 1 20,000 T1 15,000 T1 15,000 T1 15,000 T1 10,000 T1 10 00,000 T1 10

Photographed ultra-violet spark spectra (Hartley).

Mgr. 1 100,000,000

On ultra-violet spectra. The conditions necessary in photographing ultra-violet spectra, are: 1st, a sensitive salt exerting an equality of action throughout the whole range of the spectrum; 2nd, a perfectly diactinic vehicle to hold the salt; 3rd, a process of development which will not exert a preferential action on any portion of the spectrum. These conditions are fulfilled tain the lines of calcium, with wave-lengths

by the use of silver bromide emulsion, the gelatin being of the purest description, and the image being developed by pyrogallol, hydroquinol, or hydroxylamine hydrochloride and caustic sods. The new developer eikonogen is suitable. Ferrous oxalate, as usually employed, is not to be recommended, because strong lines become developed much more strongly than weak lines. The exposure varies slightly with the sensitive nature of the plates, the width of the slit, the conducting power of the electrodes, the emissive power of the rays to be observed, and lastly with the excellence of the developer. Having once ascertained by comparative exposures how to obtain the best effect, there is very seldom any necessity for altering the exposure.

The following facts have been established regarding ultra-violet spark spectra: 1. When carbon or metallic electrodes, which emit short lines, are moistened or partially immersed in water, the short lines are lengthened. 2. The impurities in a metal, or the minute constituents of an alloy, generally appear as spectra com-posed of short lines. When both electrodes are of the same material, the impurities in minute proportion appear at the negative pole only, but when the proportion of the impurity or alloy is increased, the long lines are seen as short lines at both poles; a further increase in proportion brings them out as long lines. 3. Of the nonmetallic elements, boron, carbon, and silicon exhibit line spectra. The line spectra of the elements are seen in spectra of borates and silicates, and in boracic and hydrofluosilicie acids. 4. The spectra of carbon and silicon may nearly always be detected in photographs taken from electrodes of metallic iron. 5. Insoluble compounds which are not volatile, such as ferrous sulphide, ferric oxide, and ferrous phosphate, do Insoluble, though not yield spark spectra. somewhat volatile, compounds, such as thallium chloride, yield a feeble spectrum of metallic lines. 6. With the exception of boron and silicon, the non metallic constituents of a salt do not affect the spark spectra of solutions. 7. The spectrum of a metallic chloride, nitrate, or sulphate yields spectral lines identical in number and position with the principal lines of the metal itself. Some of the short lines become long lines, but whether the spectra are produced by metallic electrodes or solutions their character is identical. 8. The effect of diluting solutions of metallic salts is first to weaken and attenuate the metallic lines, then, with a more extensive dilution, to shorten them, the length of the longest and strongest lines generally decreas. ing until they finally disappear. There are two lines in the spectrum of copper which disappear by attenuation only, and a similar pair of lines in the spectrum of silver behaves in like manner. Both pairs of lines have been observed as short lines in alloys containing very small quantities of these metals. 9. Accidental differences in the passage of the spark, or in the time of exposure of the photographic plate, when the normal period varies from half-a-minute to five minutes, do not cause sensible variations in spectra obtained from the same substances, under any ordinary circumstances. 10. Spectra of metallic

2967.3 and 8933, also occasionally those with wave-lengths 3736.5 and 3705.3. These calcium lines are due to dust when the electrodes are dry, and to impurity in the acids when solutions are prepared therewith and examined. 11. Five modified spectra have been observed in photographs taken from graphite electrodes. which apparently belong to no other element but carbon. The first and second were produced under identical circumstances, and were taken from dry points in air. The first contains 20 lines, the second only 12. The third was taken from wet electrodes in air, and consists of 20 lines, some of which are lengthened. The fourth was taken from dry electrodes in oxygen, and consists of 17 lines, some being much lengthened. The fifth was taken from dry electrodes in carbon dioxide, and consists of 18 lines, all much lengthened and strengthened

(T. pt. i. 1884).
The examination of metals and altoys. When a metal is to be examined it may be filed or hammered into electrodes of a convenient shape, and held between screw clips or between the points of cheap drawing pens. According to circumstances, both electrodes need not be of the same metal, but one may be of gold, platinum, or a tin-cadmium or lead-cadmium alloy containing in either case 20 p.c. of cadmium. Such an alloy gives convenient reference lines. If it be required to bring out the lines of the constituent of an alloy present in the metal in minute proportion, or present as an impurity in the metal, it is best to partially immerse the lower electrode in water contained in a small glass J tube, as if a solution were being photographed. Under these circumstances the short lines become much lengthened and consequently more prominent. The best form for electrodes is flat with curved edges, or even somewhat rounded discs, such as blow-pipe globules flattened.

The identification of lines in photographed pectra. When the spectrum of an alloy, metallic precipitate, or solution has been photographed, it is seldom easy to determine what substances are present or absent, partly on account of the complexity of the spectra and partly from the absence of colour. It is necessary in such cases to have recourse to one or both of the following methods of identification. (a) Method of identifying the elements by lines photographed from a known specimen. A series of photographs taken from metallic_electrodes and from solutions should always be kept for reference. A substance may then be readily identified even when the wave-lengths of its lines are unknown, by superposing one photograph on the other, film to film, since there are but very few cases of actual coincidences of lines of similar character belonging to different elements. If this examination does not account for all the lines, it is necessary to proceed according to the next method. (b) Method of identifying lines when comparison-spectra are not available. By chemical processes of separation it is easy to ascertain what metals may be looked for. The wave-lengths of the unrecog-· nised lines may then be ascertained by measurements and reference to an interpolation curve. The measurements need not be made with a

micrometer unless great accuracy is required. It suffices generally to measure the spectra by means of an ivory scale with bevelled edges, the divisions on the scale being hundredths of an inch. With a strong magnifier we may read by judgment to tenths of a division or thousandths of an inch. The best form of magnifier is made like the compound eyepiece, of a microscope with cross hairs or fibres of cocoon silk in the field. The lens is placed very close to the surface of the scale and photograph, so that false readings caused by parallax are avoided. When all the lines in a photograph which have been recognised, or vice versa, have been pricked off, the scale is very carefully adjusted so that it gives correct readings with lines of known wavelengths at different parts of the spectrum, such for instance, with Nos. 9, 10, 11, 12, 17, and 25 of cadmium. In order to adjust the scale accurately, it is advisable to rule a line along the whole of the spectrum, which may be done when photographing by placing a wire at right angles to the slit, and one-third or one-fourth the length of the spark, above the lower electrode. The edge of the scale is applied to this line, and held in position by spring clips or screws. The scale numbers of the unrecognised lines are then read off, and by reference to the interpolation curve their oscillation-frequencies or their wavelengths are obtained. From maps, or descriptions of spectra, accompanying a list of wavelengths, the corresponding lines are selected and identified.

Descriptions of the spectra of the elements. Emission spectra. The spectra of non-metallic elements, particularly those which are gaseous, have been found to vary in character with the conditions under which they have been obtained. Thus N, O, C, Br, I, S, Se, Te, and P yield band spectra or, line spectra, according to variations in temperature or pressure. The chlorides of B and Si likewise give line spectra due to Band Si; under certain conditions they emit spectra of their own. The fluted spectrum of carbon has given rise to great discussion. Swan, and later Angström, attributed the bands to a hydrocarbon, so also did Morren, and Liveing a. Dewar, but they finally arrived at the conclusion first enunciated by Attfield, that the bands were caused by the element carbon. Van der Willingen, Plücker and Hittorf, Marshall Watts, Wüllner, Lockyer, and Fievez, have all adduced evidence of this. It appears, however, that a banded spectrum of cyanogen can be obtained which is distinct from that of carbon. Certain bands in the ultra-violet spark spectrum, which have been considered by Liveing and Dewar to be caused by cyanogen, have been observed by Hartley, and he is led to the conclusion that they are in reality carbon bands intensified by the presence of an atmosphere of nitrogen, but not cyanogen bands, for the reason that they cannot be obtained from various cyanogen compounds, such as soluble cyanides. They are always. present when graphite electrodes are used in air, they are intensified when the electrodes are moistened, and they become particularly strong when concentrated solutions of chlorides, such as zine chloride or calcium chloride, surround the electrodes; moreover, the strength of the bands increases with the strength of the solutions.

A review of the facts shows that large mole-

cules give banded spectra, as is evident from the spectra of compounds, and various other considerations lead to the conclusion that the elements which give such are capable of existence in different molecular conditions, the most complex molecules emitting bands of rays, the simpler molecules emitting line spectra.

Hydrogen. When sparks are passed through hydrogen, four very well known lines appear. Huggins has observed the same in some stars, together with a remarkable series of lines in the ultra-violet, and it has been surmised that the whole series, visible and invisible, belong to the one element. Cornu has recently proved this to be the case. Fifteen lines in the visible and ultra-violet constitute the only true line spec-

trum of hydrogen.

The alkali metals, Li, Na, K, Rb, Cs. These metals are distinguished by the fact that most of their salts are decomposed in the flame, and the metal set free, or the metallic oxide formed from it, is sufficient to colour the flame intensely. The spectra are very simple, and all the principal lines are in the visible region. Their ultra-violet spark spectra are insignificant.

The alkaline earth metals, Ca, Sr, Ba. The spectra of these elements are obtainable by flames. When the chlorides are fused and heated in a flame supplied with hydrochloric acid, lines due to the metallic chlorides are visible. Without hydrochloric acid, the spectrum is at first a simple line spectrum, but subsequently bands, shown by Mitscherlich to be due to the oxides, take their place. Feeble sparks give line spectra with solutions of salts. In the ultraviolet, a series of well-marked groups of doublets and triplets is seen.

The magnesium group, Be, Mg, Zn, Cd. The element beryllium stands at the head of two families, that of the alkaline earths and the magnesium family. It occupies a position similar to that of lithium with regard to the alkali metals and the copper and silver family. Its spectrum is similar in many respects to that of lithium, being very simple and composed of iso-lated lines. There are two in the blue and five in the ultra-violet not visible in the flame, but obtainable by the action of condensed sparks. Magnesium and the compounds of the other metals of this group do not easily yield flame spectra, but give characteristic groups of lines when solutions are submitted to feeble or condensed sparks. In the ultra-violet these consist of well-marked groups of isolated lines, pairs, triplets, and groups of four and of five lines.

The aluminium elements, B, Al, Ga, In, Tl. Boron, which stands at the head of this group, gives a flame-spectrum only of its oxide, but the boron compounds, such as borates, emit three lines in the ultra-violet due to this element. Aluminium gives no flame spectrum, but gallium, indium, and thallium emit rays in the violet and green. Sparks taken from solutions of indium and thallium yield characteristic spectra in the ultra-violet consisting of many isolated lines and pairs of lines.

The tin elements, C, Sn, Ge, Pb. Carbon presents a very simple spectrum when condensed sparks are used; most of the lines are in the ultra-violet. It is a remarkable fact that under the same conditions the number of lines some-

times varies, and no satisfactory reason for this can be assigned. Four spectra of graphite have been mapped from photographs described as follows: 1. Dry electrodes in air. 2. Wet electrodes in air. 8. Dry electrodes in oxygen. 4. Dry electrodes in carbon dioxide. The strength and length of the lines vary under certain circumstances; in 1 the lines are all short, in 2 some lines are lengthened, in 3 some lines are much lengthened, and in 4 all the lines are lengthened and strengthened.

The spark spectra of tin, germanium, and lead contain numerous lines which are not characterised by any evident special grouping. The ultra-violet spectrum of germanium has yet

to be photographed.

The group of rare earths, Ce, La, Di, Sm, Yt, Sc, Er, Tr. These elements give no flame spectra, and but weak spectra with feeble sparks. Ce, Di, Yt Sm, Sc, Tr yield very complicated spectra to powerful sparks, the spectrum of cerium in the ultra-violet being remarkable for the immense crowd of lines. Attrium and scandium chlorides give spectra composed of bands which are very characteristic in the visible region. Didymium, samarium, erbium, and thallium will be dealt with under the head of Absorption spectra. Lanthanum gives a large number of lines in the visible region, but very few in the ultra-violet.

The nitrogen elements, N, P, As, Sb, Bi, V. Nitrogen gives a large number of lines under the action of condensed sparks. The ultra-violet portion of the spectrum has been photographed. Nothing of the same kind is known of phosphorus. Phosphorus in a current of hydrogen gives a beautiful banded flame spectrum, especially when the flame is cooled. This reaction is exceedingly sensitive. The spectra of arsenic, antimony, and bismuth in the ultra-violet are very well marked, and they each contain a large number of lines, some of which are nebulous, others are mere dots, and there is a characteristic background of continuous rays. Vanadium yields spark spectra, with a large number of lines.

The chromium elements, Te, Cr, Mn. The line spectrum of tellurium obtained from the element is very complex, and by far the greater number of lines are in the ultra-violet; the character of the spectrum resembles those of arsenic, antimony, and bismuth. The chromium and manganese spectra are very complex and similar to those of the iron group.

The iron, nickel, and cobalt group. These metals present very complicated spectra when condensed sparks are employed in the visible, and more particularly the ultra-violet, regions. The grouping of the lines in the dif-

ferent spectra is similar.

The palladium, gold, and platinum These elements present complicated spectra, though less so than the foregoing. The strong lines of gold are few in number. These metals do not excel in emissive power. Feeble sparks with them give feeble spectra. Iridium gives a spectrum only with condensed sparks, which in the ultra-violet consists of a great crowd of lines.

The spectra of many elements, such as tungsten and uranium, have yet to be examined

thoroughly. It may here be remarked that elements usually associated by their natural occurrence, or by classification according to their chemical properties, exhibit spectra with characters in common.

A very important paper by Mitscherlich (A. 121, 459) first drew attention to the fact that a number of compounds emit distinct spectra, for the most part band spectra. A list of such compounds here follows, most of the gpetra of which were originally described by Mitscherlich. Diacon also (Thèses de Physique et de Chemie, Montpelier, 1864), using a flame the interior of which was fed with chlorine, obtained distinct spectra of chlorides, such as those of the alkaline earths, gold, lead, iron, cobalt, and nickel; the alkalis gave no spectra excepting where they became converted into oxides or metal, as in the mantle of the flame.

Compounds emitting distinct spectra (Mitscherlich). 'Venetian blind' or degraded band spectra. Flame. BaO; BiCl₃, BiBr₃, BiJ₃; Badi, Gudi, GuBr, Cu,I., Gud; Audl; Fe₂O;
MgO; MnO₂; PhUl, PhO; MgCl,
Plain band spectra. BaF, BaCl, BaBr;

Bil,; CaF, CaO; CuF,; SrO.

Line spectra, or lines with bands. BaCl₂, BaBr₂, BaI₂; CaCl₂, CaBr₂, CaI₂; SrF₂, SrCl₂,

SrBr, SrI,

Other observers have discovered and described specific spectra emitted by the following compounds:—Al₂O₃; feeble sparks (Wüllner and others). NH₃; flame (Dibbits). CO; spark others). NH₃; name (Dibbits). CO; spark (Plücker and others). CN; flame (For Talbot, Draper, Dibbits, and others). Er₂O₃ and ErPO₄; flame (Bunsen a. Bahr). MgO and hydride of Mg; flame and spark (Liveing a. Dewar). PH₃; flame cooled (Christofle a. Beilstein). SiCl. SiBr, SiI, spark (Plücker, also Salet). H.O.

flame (Liveing a. Dewar; Huggins).

Harmonic relations between the lines of a spectrum. The self-luminous nature of a molecule is connected with the vibrations of those The number of vibrations is indicated by the inparts of the molecule which are called atoms. verse wave-lengths of the lines in the spectra. The spectrum of iron contains more than 1,200 distinct lines, and it follows, therefore, that the molecule or its atoms must simultaneously excite as many different vibrations. We are acquainted with similar relations in acoustics. For instance, it has been observed by Hipkins that the simplest vibration of a pianoforte string will cause it to emit its own proper note, and as many as twenty-four overtones or harmonics. Johnstone Stoney first discovered such harmonics in spectra. The visible spectrum of hydrogen contains the three lines Ha wavelength 6563.9, $H\beta = 4862.1$, $H\delta = 4102.4$, these are the 20th, 27th and 32nd overtones of a vibration. of which the wave-length = 0 013127714 mm. But the fourth line $H\gamma = 4341$, and the lines in the ultra-violet do not fall in with this system. Soret has calculated the harmonics of the three groups of triplets in the magnesium spectrum to be the 20th, 27th, and 31st harmonics of the fundamental vibration. Similar groups occur in the cadmium spectrum, which are the 20th, 23rd, 27th, and 31st of a fundamental vibration. Schuster has observed several harmonics in the

bismuth, calcium, thallium, and gold. According to Mascart, sodium has five series of doublets which are the 132nd, 138th, 143rd, 158th, and 163rd harmonics. One of the most remarkable spectra is the absorption caused by chromyl chloride. Johnstone Stoney and Emerson Reynolds have shown that under great dispersion and lime-light illumination it gives a series of harmonics which are similar to those of a violin string, and of which the order lies between 628 and 733. Liveing and Dewar have observed that many ultra-violet spectra contain lines which are harmonically related, not so simply related perhaps as the harmonics of a uniform stretched string, but like the overtones of a string which is not of uniform thickness, or is loaded at different points, similarly related in origin though not exact harmonics. Lithium, potassium, calcium, magnesium, and zinc are such elements. The alkali metals have each one series in the visible spectrum, and another in the ultra-violet. It may happen in other cases that two or more such series overlap, and it may be very difficult to distinguish and separate them. There is a remarkable fact to be noted with regard to ultraviolet spectra, namely, that similar groups of lines, evidently harmonically related, are alternately sharp and nebulous in character.

Huggins discovered that the four hydrogen lines in the solar spectrum are part of a much longer series of lines which occur in the spectra of white stars. Cornu discovered the whole series in the spectrum of pure hydrogen, and Balmer showed that the whole series of lines can be expressed by the following formula:

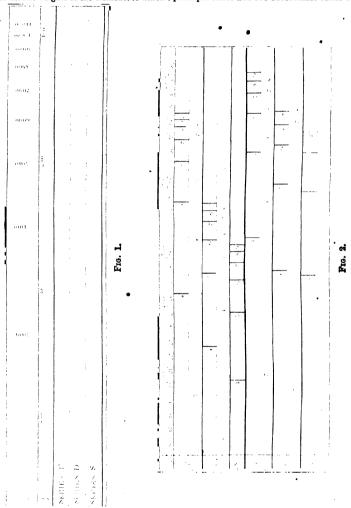
$$N_{m-2} = k\left(1 - \frac{4}{m^2}\right)$$
, in which k is a constant

for the whole series, and by substituting the whole numbers 3, 4, 5, 6, &c., for m, we obtain values for N which are the oscillation-frequencies of the successive lines.

Relations between the spectra of different elements. Lecocq de Boisbaudran has observed such a relationship between the lines in the different spectra of the alkali metals and their atomic weights, that he has been able to calculate the atomic weight of gallium from its spectrum. It may be stated that the atoms of greater mass vibrate more slowly, and therefore emit rays of proportionally greater wave-lengths. Ciamician made an extended series of observations on the spectra of elements usually classed together on account of their chemical properties. and he described several of these spectra as being homologous, that is to say, similarly constituted. A. Grünwald observed mathematical relations between the spectrum of water vapour and the line spectra of H and O, which led him to predict the existence of many lines in the spectrum of water vapour which had not been photo-graphed. By prolonged exposures, Liveing and Dewar obtained photographs of a number of lines approximating very closely to those calculated by Grünwald.

Hartley, in 1883, observed the law of homology in the visible and ultra-violet spectra of the magnesium, zinc, and cadmium group. Elements with properties in common exhibit spectra with Schuster has observed several harmonics in the similar groupings of lines, but the dispersion of spectrum of strontium; also in the spectra of the lines and the refrangibility of the strong lines in each group vary with the atomic weights of ; the elements. In each spectrum the differences between the oscillation-frequencies of the individual lines of each triplet is a constant quantity. The law also applies to the series of doublets. The differences between the oscillation-frequencies of individual rays in the series of triplets increases with the atomic weights of the elements to which

who it appears recognised it independently in 1885. J. S. Ames, in 1890, proved the perfect homology, line for line, of the arc spectra of zinc and cadmium. Kayser and Runge have shown that the series of triplets referred to in the magnesium, zinc, and cadmium spectra are in reality three series of harmonic vibrations, a principal series and two subordinate series over-



the triplets belong. A survey of these facts led to the conclusion that as the molecules of these elements contain but one atom, the atoms have a complex constitution, and that those elements the spectra of which are homologous are composed of the same kind of matter in different states of condensation, the molecules having similar modes, but different rates, of vibration. The law

lying each other. The magnesium series they place along with those belonging to the calcium, strontium, and barium family, but according to the periodic law, the magnesium spectrum might be expected also to stand at the head of the spectra of the family which includes zinc and cadmium. The series of lines in the alkali and alkaline earth metals do not fall in with Balmer's law for the of homology has been studied by J. R. Rydberg, hydrogen lines. Homology has been observed in the spectra of the following groups: lithium, sodium, potassium, rubidium, exsium, also in aluminium, indium, thallium. Runge announces that doublets and triplets existing in the spectrum of an element can be arranged in series which show an appearance of great regularity, and are seemingly analogous to the overtones of a vibrating body (see figs. 1, 2, and 3). In fig. 1 the spectrum of sodium is shown with a scale of unequal parts, A corresponding to wave-lengths,

and a scale of equal parts 1 corresponding to

oscillation-frequencies. The lines forming the entire spectrum are arranged in three series. Each line in the maps indicates a closely-placed pair of lines. Series P is the principal series, series D is the subordinate series of diffuse lines, series S the subordinate series of sharp lines. The three series are regular, the intervals between the lines decrease as the wave-lengths of the lines diminish from right to left. In fig. 2 we have similar maps, but the scales run the reverse way, from left to right. The principal and subordinate series of lines are shown in the spectra of Mg, Ca, Zn, Cd, and Hg. Corresponding lines in two different series of the same spectrum are numbered alike. The homology of the spectra is evidenced, and also variations following increase of atomic mass in elements of the same group. In fig. 3 the homology of

determined the composition of some homogeneous alloys of gold and silver, also of lead and cadmium, by comparison of their spectra with check pieces of known composition. Sir J. G. Alleyne estimated phosphorus in iron and steel, and Ballman attempted the estimation of lithium by the spectroscope. Liveing and Dewar made observations on a spectroscopic method of estimating sodium by measuring the width of the sodium lines. Hartley determined the different spectra emitted by solutions of different strengths, and found these constant when the ultra-violet lines were photographed. Accordingly, by comparison, the metals may be determined in solutions made from determinate weights of material, diluted to a definite volume. Quantitative determinations of the basic constituents of limestones, of copper in pyrites cinder, and of lead, silver, and copper in zinc blende, have been made with quantities of matter so small that no other method could have dealt with them. It will be seen later on, that absorption spectra are serviceable in quanti tative analysis.

Spectra of the infra-red region and spectra of solids in vacuo. There are three methods of spectroscopy which have not yet been much employed. 1. The method of E. Becquerel for observing the infra-red rays. This is accomplished by the use of an eyepiece covered with Balmain's phosphorescent paint. When it is excited by exposure to a brilliant

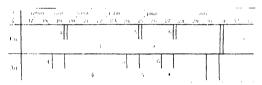


Fig. 3.

the spectra of copper and silver is well shown. The difference of two consecutive oscillationfrequencies decreases as these values increase, and there seems to be a finite limit to the oscillation-frequencies of a series. If n represent whole numbers, the oscillation-frequencies of a series may, with great accuracy, be represented by the formula $A - Bn^{-2} - Cn^{-4}$, where A, B, C, are positive constants. B has nearly the same value for all the series of the different spectra.' A is the limit towards which the oscillation-frequency tends when n increases. For elements that are chemically related the series are distinctly homologous, both in appearance of the lines and the values of A, B, C, and with increasing atomic weight they shift towards the less refrangible end of the spectrum. The spectra show relationships between the elements similar to those between their chemical proper-

Quantitative analysis by the spectroscope. In 1862 W. A. Miller first attempted to apply the spectroscope to the quantitative estimation of the constituents of an alloy. Jansen, in 1870, proposed two methods of quantitative analysis. Champion, Pellet, and Grenier successfully applied a spectro-photometrical method to the estimation of alkalis. Lockyer and Roberts-Austen

light, it glows, but as soon as any radiation of very low refrangibility falls upon it the phosphorescence is destroyed. 2. Abney observes the same rays by means of specially-prepared photographic plates, sensitive to exceedingly slow vibrations. Even the radiations from a kettle of boiling water can impress themselves permanently on his preparation of silver bromide. V. Schumann and also Waterhouse have used photographic plates prepared with cyanine, erythrosine, and other dyes for the same purpose with some success. 3. Crookes has made much use of the phosphorescent spectrum obtained by the action of an electric discharge in high vacua, and has made a most interesting series of observations on the rare earths by this means. Among other results he has proved the wide distribution of yttria, its occurrence in strontianite, coral, oyster shells, and limestones. He considers that there are several kinds of yttria with different phosphorescent spectra, but as they all give the same spectrum when excited by the spark in the usual manner, they must be considered as being derived from the same elementary yttrium.

Absorption spectra. In dealing with absorp-

Absorption spectra. In dealing with absorption spectra, we may observe the effect on a continuous spectrum of (a) gases, (b) liquids, (c)

solids. When rays enter a transparent medium—either gaseous, liquid, or solid—they do not leave it in a condition identical with that in which they entered it. They may be either partially absorbed or altered in refrangibility. No known substance is capable of transmitting radiations of all known wave-lengths; those media which do not absorb appreciably any of the coloured rays, or any of the rays in the ultra-violet which are capable of being photographed, absorb a portion of the infra-red spectrum. It may be remarked that substances like air and water which in thin layers do not appear to absorb the rays in the visible spectrum, in thicker layers are seen to absorb the rays of a limited region. The A and B groups of lines in the solar spectrum have been shown to be due to oxygen in the atmosphere, while nine lines lying between the two D lines in the solar spectrum were observed, and proved by Josiah P. Cooke, in 1866, to be caused by water vapour in the atmosphere amounting to not more than 1.5 g. in 100 litres of air. With 0.18 g. only one line was visible, and with 0.55 g. two lines. The successful application by Piazzi Smyth of the spectroscope to weather forecasts is based upon such facts.

Many cases of absorption are known in the. infra-red and in the ultra-violet, when no visible rays are absorbed. Colours may be either visible or invisible; since we must regard every substance which absorbs rays as coloured. The eye cannot always distinguish colour, because the most sensitive eve cannot observe the rays which are absorbed by its own aqueous humour, and are thus prevented from affecting the optic nerve. Hence the infra-red rays have no effect upon the retina, and most of the ultra-violet cannot affect it. The colour of a substance is determined by the combined effect of the rays which are not absorbed. Cobalt glass, which absorbs the yellow and green rays, transmits the red, blue, and violet, but as it transmits comparatively little of the red its colour appears blue. The purity of the light by which the substance is examined is of importance. Chromium solutions which are green by daylight are red by gaslight, because the yellow and red rays are predominant in gaslight, and as the red rays and the green are transmitted by pure white light, the dominant colour is red by light of less purity. There is but little importance to be attached to the general absorption of rays, but well-defined absorption bands afford evidence both of the composition and the constitution of substances.

The theory of absorption spectra. It is a well-known fact in acoustics that a vibrating musical instrument, a tuning-fork, or a stretched string, will communicate its vibrations to any similar instrument near to it which is capable of similar vibrations, and a sufficient number of strings or tuning-forks can entirely absorb the vibrations of a similar string or fork. In like manner when a molecule of a substance is capable of vibrating synchronously with a radiation, the rays received on the substance are absorbed by reason of the molecules being put in motion by the waves which strike them. The absorption is complete if the direction of vibration of the rays and of the molecule is the same, but the phase is opposite. A general absorption appears fin the ultra-violet at any rate) to be due

to the vibration of the molecule, while selective absorption appears to be caused by the vibrations of atoms within the molecule. When a substance in solution absorbs all the rays of a certain region of the spectrum which fall upon it, it is because the molecules are vibrating synchronously with these rays, and the number of molecules present is sufficient to damp all the vibrations. When the rays traverse a smaller quantity of substance—as, for instance, when a solution is diluted - the number of molecules present is not sufficient to damp all the vibrations, and some rays pass through. If, however, certain atoms within the molecule are vibrating synchronously with certain rays, we shall have a selective absorption of these rays after the general absorption has been so weakened by dilution as to allow them to pass. It has been shown by Hartley that the vibrations of the atoms depend upon the rate of vibration of the molecule, or in other words, the rate of vibration of the molecule determines the rate of vibration of its parts. Four absorption bands in the three hydrocarbons benzene, naphthalene, and anthracene are evidence of this. The mean rate of vibration of the rays absorbed by naph-The mean thalene and anthracene is less than that of the rays absorbed by benzene, and the vibrations of the carbon atoms within the molecule are not independent of, but are a consequence of, the molecular vibrations; they must, in fact, be regarded as overtones or harmonics of the fundamental or molecular vibrations. When the rate of the fundamental vibration is reduced by an increase in the mass of the molecule, the rate of vibration of the carbon atoms is reduced in a similar ratio. Greater amplitude of vibration means a louder note, or in the case of luminous radiations a brighter light. Consequently the converse of this may be considered to hold good, that a greater intensity of absorption is caused by a greater amplitude of vibration in the molecules of the absorbing medium, the number of atoms or molecules remaining constant.

An examination of the three hydrocarbons benzene, naphthalene, and anthracene shows that the mean rate of vibration of the rays absorbed by benzene is greatest, naphthalene comes next, and anthracene is least; but the absorptive power is in the reverse order, that of anthracene being greatest. Hence we conclude that the amplitude of vibration is greater as the rate of vibration is slower (C. J. 1881). The approximate rates of vibrations of the three hydrocarbons are given as follows:—

	ave-length absorbed.		lar vibra- r second.	Molecular weights.
Benzene	2526	1,248	billions	78
Naphthalene	2687	1,177	***	128
Anthracene	8489	910	**	178

The various absorption spectra may be referred to in no better order than that of the refrangibility of the rays absorbed.

tion, the rays received on the substance are absorbed by reason of the molecules being put in motion by the waves which strike them. The absorption is complete if the direction of vibration of the rays and of the molecule is the same, but the phase is opposite. A general absorption acid, chloroform, carbon tetraphate is opposite. A general absorption acid, chloroform, carbon tetraphate is opposite. A general absorption acid, chloroform, carbon tetraphate is opposite. A general absorption acid, chloroform, appears (in the ultra-violet at any rate) to be due

lines, which, however, do not appear in carbon compounds containing no hydrogen; they do not all appear in some hydrogen compounds. The inference is that they belong to hydrogen. When oxygen is present as a part of hydroxyl it obliterates the rays between two of those lines which are due to hydrogen. When it forms part of the carbon nucleus of a compound, as it does in aldehyde, the spectrum is inclined to be linear, or the bands are bounded by well-defined lines. There appear to be characteristic bands which indicate the carbon nucleus of a series of substances. Certain radicles have a distinctive absorption lying near \$\lambda 7000 and others about λ 9000; thus in the three compounds C₆H₈, C₈H₅,H₂N, C₆H₄(C₂H₅).H₂N we have the following coincident bands probably due to the benzene nucleus; the line \(\lambda \) 8670 is the principal one; λ 8670, λ 8670 to 8720, λ 8720 to 8850, a fourth band about λ 9300, a fifth about λ 10400-10660. In benzene and ethyl-aniline there occurs a band also at \$10970 to 11050. If the line \$8670 is associated with a band, it is almost certain to be caused by the benzene nucleus. Ethyl compounds are indicated by absorption at \(\lambda \) 7410, λ 8950 to 9030, 9040 to 9070, 9130 to 9180, 9270 to 9300.5, 9320 to 9420. The solar spectrum shows an absorption at A 8660, and, with the excention of the line at 7410, the absorptions noted above have been observed to be coincident with bands or lines in the solar spectrum.

Visible and ultra-violet absorption spectra. The absorption spectra of the coloured region were long since carefully studied by Gladstone. These spectra pass gradually into the extreme violet and ultra-violet. In dealing with the subject it will be convenient first to consider the absorption caused by gases and vapours, elementary or compound, then the absorption by inorganic salts, and lastly the spectra of organic substances.

Elements which exhibit absorption spectra.

Gases and vapours.

Metals, the salts of which show banded spectra.

Br, Cl, I, O, ozone, K,
Na.

Cr, Er, Sm, U, dysprosium, holmium, neodymium, praseodymium, thulium.

Compounds which exhibit absorption spectra.

Gases and vapours.

Salts the acids of which show banded spectra. Chromates 1 Ultra-

ICl, IBr, NO₂, H₂O vapour, oxides of Cl.

Chromates \ UltraNitrates \ violet.
Nitrites (some); permanganates.
high exhibit absorption
hydrocarbons and ter-

Organic suostances which exhibit absorption spectra. All benzenoid hydrocarbons and tentary bases derived from the same. All haloid, hydroxyl, carboxyl, and amide, derivatives of benzenoid hydrocarbons. Cyanuric and uric acids, with colouring matters derived therefrom. Albumens and allied substances. Organic colouring matters of unknown constitution, such as chlorophyll and hæmoglobin. Many alkaloids and their derivatives, e.g.: Aconitine, pseudaconitine, japaconitine, morphine, narcotine, codeline, papaverine, oxynarcotine, apomorphine hydrochloride, tetracetylmorphine, diacetyl-

containing hydrogen show the same group of codeline, quinine, quinine sulphate, cinchonine sulphate, which, however, do not appear in carbon sulphate, quinidine sulphate, cinchonidine sulcompounds containing no hydrogen; they do phate, veratrine, piperine, brucine, strychnine.

The relation of absorption spectra to the chemical constitution of carbon compounds.

1. Substances with a nucleus consisting of an open chain of carbon atoms transmit continuous spectra and are highly diactinic. Examples: the alcohols, acids, ethereal salts, haloid ethers, and the carbohydrates. 2. In homologous series the greater the number of carbon atoms the shorter the transmitted spectrum. 3. In substances with the same carbon nucleus that containing the most oxygen transmits the shortest spectrum, as, for instance, in acids the spectrum is shorter than in alcohols, and in dibasic shorter than in monobasic acids. 4. Substances with a closed chain nucleus when not more than two atoms of carbon are doubly linked transmit continuous spectra, but their absorptive power is much greater than that of open chain compounds; e.g. camphor, benzene hexachleride, and the terpenes, also hexahydropyridine. 5. The more closely the carbons in a closed chain are linked, the greater is the absorptive power of the molecule; e.g. the terpenes withstand dilution more strongly than benzene hexachloride, and camphor. 6. The carbon nuclei of benzenoid hydrocarbons possess strong absorptive power, and after great dilution exhibit absorption bands; e.g. four bands are seen in the spectrum transmitted by benzene when 1 part is diluted with 2,400 parts of alcohol, three bands in naphthalene with a dilution of 1 in 100,000 parts, one band in phenanthrene with 1 in 500,000 parts, and one band in anthracene with 1 in 5,000,000 parts of alcohol. 7. The introduction of radicles in place of hydrogen and of side-chains into the benzenoid nuclei diminishes the number of absorption bands, but increases their width and intensity. 8. The simple union of carbon to nitrogon does not cause selective absorption ; e.g. in hydrocyanic acid and cyanides. 9. When a benzenoid nucleus contains an atom of nitrogen in place of an atom of carbon, the molecule exhibits absorption bands, and its absorptive power is generally not impaired, but is sometimes increased, e.g. picoline, pyridine, quinoline, and their derivatives. 10. Isomerides exhibit different spectra, e.g. the terpenes and isomeric benzene derivatives. 11. When the condensation of the carbon atoms in the quinoline nucleus is modified by the combination therewith of four atoms of hydrogen, the intensity of the absorption bands is reduced but is not de-12. Nitrogen combined with oxygenas in nitroxyl, nitrites, and nitrates—exhibits absorption bands. 13. When several carbon atoms are united by oxygen and nitrogen atoms, the resulting compounds exhibit intense absorption bands, e.g. cyanuric acid, uric acid, and derivatives, including murexide. 14. Molecules of compounds—that is to say, molecules composed of dissimilar atoms-vibrate as wholes or units, and the fundamental vibrations give rise to secondary vibrations which stand in no visible relation to the chemical constituents of the molecule, whether these be atoms or groups of atoms. Hence it appears that a molecule is a distinct and individual particle which is not fully represented by our usual chemical formula.

since these only symbolise certain chemical reactions and fail to express any relation between physical and chemical properties. As certain molecular groupings are characterised by the absorption of rays of particular wave-lengths (absorption bands), it is evidently possible to draw conclusions as to the constitution of substances from their absorption spectra. Many of the foregoing statements may be usefully and clearly summarised by means of formulæ. These render evident how the optical properties of a compound are determined by the skeleton of carbon atoms.

compounds which exhibit selective absorption of the ultra-violet rays are coloured. The subtlety of the colour, however, is such that the eye cannot perceive it without the aid of photography or a fluorescent screen.

That which in the ordinary acceptation of the term is a coloured substance is merely one in which the absorption of rays extends into a region limited by the red and violet ends of the spectrum, or between wave-lengths 7000 and 4000. According to this view, the colour of a substance may be fivisible to the unaided eye. As bands of selective absorption appear to be the

Typical carbon nuclei, transmitting continuous spectra.

Typical carbon nuclei, exhibiting absorption bands.

Nuclei containing oxygen and nitrogen, exhibiting absorption bands. R representing any radicle.

On the cause of colcur in organic compounds. According to 0. With, the tinctorial character of aromatic compounds is conditional upon the simultaneous presence of a colour-producing group and a salt-forming group in the molecule. A group of atoms of the former kind he terms a chromogen, and of the latter a chromophor. He says: 'For instance, NO₂ is the chromophor of nitraniline and nitrophenol, but nitrobenzene is the chromogen of these bodies. The different nitrodiphenylamines are all acids and dye-stuffs, and their tinctorial power increases with the number of nitroxyls.' In this connexion it is of interest to study the relation of the hydrocarbons to the more complex compounds which are colouring matters derived from them.

If a source of light emits all luminous and invisible vibrations capable of being transmitted through 8 feet of air, a perfectly colourless substance will transmit these rays without impairing their intensity. A coloured substance is one which absorbs rays at either end of the spectrum, or selects rays of a definite wave-length from the middle of the spectrum. Every fluorescent substance is therefore coloured, and benzene, benzenold hydrocarbons, phenois, and other derived

effect of vibrations taking place within the molecules of a substance, and these are dependent upon the rate of vibration of the molecules themselves, they are called in general 'molecular vibrations.' If, then, it be desired to convert a substance such as benzene, the colour of which is invisible, into a compound with a visible colour, it is necessary to slacken its rate of vibration so that the molecule will absorb rays with oscillation-frequencies (inverse lengths) occurring within the limits of visibility. That which is called a chromogen is an invisibly coloured substance, and that termed a chromophor is an atom or group of atoms capable of so affecting the molecule as to reduce its rate of vibration, so that it absorbs rays within the limits of visibility. Under certain conditions of combination, nitrogen and oxygen are chromophors, hence also nitroxyl and hydroxyl; that is to say, they are themselves coloured either visibly or invisibly. When two benzene mole-cules are doubly linked by two nitrogen atoms, as in azobenzene, their mode of vibration is profoundly modified, and a brilliant colour as low down in the scale as the yellow rays is the result.

A similar modification takes place when two

atoms of oxygen replace two of hydrogen, as in quinone, which is of a golden-yellow colour. The effect of linking two or more benzene nuclei by carbon atoms has been already dealt with; the colours are not rendered visible, but the molecular vibrations are greatly reduced in rapidity. and the amplitude of the vibrations is much increased. That is to say, the absorption bands are transferred to less refrangible rays, and withstand a much larger amount of dilution. These modifications are both observed in the curve of benzene as modified in trip! envlmethane. The vibrations of this radicle are reduced in rapidity in rosaniline hydrochloride, Hofmann's violet, iodine green, and other such derivatives in which the carbon nucleus remains intact.

There is a family likeness in the curves of azo-benzene, azo-naphthalene, chrysoïdine, and other derivatives of these substances, which is quite in accordance with these observations. In short, in a general way, the change of colour effected by any given series of reactions may be predicted from an inspection of the curve of molecular vibrations of any benzenoid hydrocarbon. Ŵ. Ν. H.

BIBLIOGRAPHY.

ABNEY AND FESTING. 'On the Influence of the Molecular Grouping in Organic Bodies on their Absorption in the Infra-red Region of the

Spectrum, T. 172, 887 (1881).

Ames, J. S. 'On Relations between the Lines of various Spectra,' P. M. [5] 30, 33 (1890).

Connu, A. 'Hydrogène,' J. de Ph. [10] 5, 341

CROOKES, W. 'Absorption Spectra of Rare Earths and Phosphorescence Spectra,' C. J. 55, 250

Deslandres, H. 'Spectre du pôle négatif de l'azote. Loi générale de répartition des raies dans les Spectres de bandes,' C. R. 103, 375 (1886). 'Sur le spectre de bandes de l'azote, et sur les trois groupes distingués au pôle positif,' C. R. 101, 1256. 'Loi de répartition des raies et des bandes commune à plusieurs spectres de bandes. Analogie avec la loi de succession des sons d'un corps solide, C. R. 104, 972 (1887). 'Spectres de bandes ultraviolet des composés hydrogénés et oxygénés du carbone, A. Ch. [6] 14, 5 (1888). Spec-tres de l'oxygène, A. Ch. [6] 14, 257.

Fox-Talbor, H. 'Note on the Early History of Spectrum Analysis,' Pr. E. 7, 461 (1870-71). GRÜNWALD, A. 'Mathematical Spectral Analysis,' P. M. [5] 24, 354; 25, 343 (1887-8).

HARTLEY AND HUNTINGTON. 'Researches on the Action of Organic Substances on the Ultra-

Violet Rays, T. 170, 257 (1879). 'An Examination of Essential Oils,' Pr. 29, 290.

HARTLEY AND ADENEY. 'Measurements of Wave-

lengths, T. 175, 63 (1884).

Harrier, W. N. 'Researches on Spectrum Photography, T. 175, 49, 325 (1884). (Ab.) sorption Spectra of the Alkaloids, T. 176, 471 (1885). On Homologous Spectra, C. J. 43, 890 (1883). 'Researches on the Relations between the Molecular Structure of Carbon Compounds and their Absorption Spectra, C. J. 89, 153 (1881-2); 41, 45; 47, 685 (1885); 51, 152; 53, 641 (1888). 'On the Physical Character of the Lines in the Spark Spectra of the Elements,' Pr. 49, 448 (1891). HASSELBEEG, B. 'Untersuchungen über das zweite Spectrum des Wasserstoffs,' Mémoires de l'Académie Impériale des Sciences de St. Petersbourg [7] 25, No. 7 (1882); also 31, No. 14 (1883). 'Zur Spectroscopie des Stickstoffs,' ibid. 32, No. 15 (1885).

HASSELBERG. 'Untersuchungen über das Absorptions-Spectrum des Broms.' Kongl. Svenska Vetenskaps Akademiens Handlingar, 24, No. 3. 'Ueber das Absorptions-Spectrum des Iodgases,' Mémoires de l'Académie des Sciences

de St.-Pétersbourg [7] 36 (1889). YSER AND RUNGE. 'Lehrbuch der Spektral-KAYSER AND RUNGE. analyse,' Berlin (1883). 'Ueber die Spectren der Elemente.' Abhandl. der Kön. Preuss. Akad. der Wiss. zu Berlin, 1888; 1890-1.

LECOCO DE BOISBAUDRAN. 'Spectres Lumineux,' Paris (1874).

LIVEING AND DEWAR. 'Spectrum of the Oxyhydrogen Flame,' T. 179, 27 (1888). 'Absorption-Spectrum of Oxygen.' P. M. [5] 26. 286 (1888). 'Spectra of the Elements.' 174, 210 (1883); 179, 231 (1888). LOVE, E. F. J. 'On a Method of Discrimina-

ting Coincidences between the Lines of different Spectra.' P. M. [5] 25, 1 (1888).

митесивыси, А. Р. 116, 499; 121, 459 (1864). Nordenskiöld, A. E. 'Sur un Rapport Simple entre les Longueurs d'Onde des Spectres, C. R. 105, 989 (1887).

Runge, C. 'On the Line Spectra of the Elements,' N. 55, 607 (1892).
Rydberg, J. R. 'Recherches sur la Constitution

des Spectres d'Émission des Éléments Chimiques, Kongl. Svenska Vetenskaps Akademiens Handlingar, Stockholm, 23, No. 4 (1890).

STONEY, G. JOHNSTONE. Trans. Roy. Dub. Soc.

4 (1891). Soler, G. 'Traité Elémentaire de Spectroscopie.' Paris (1888).

WATTS, W. MARSHALL. 'Index of Spectra.' Manchester, Abel Heywood & Son (1889).

OPTICAL METHODS .- Section 3: ROTA-TION OF THE PLANE OF POLARISATION OF LIGHT.—When a ray of plane polarised light is passed through a plate of quartz cut at right angles to its optical axis, it is found that the plane of polarisation of the emergent ray is not coincident with that of the incident ray; the angle through which the plane has been rotated is called the angle of rotation. If the rotation takes place in the same direction as that in which the hands of a watch move when the face of the watch is looked at, the quartz is said to show dextrorotatory power; if the rotation is in the opposite direction, the quartz is said to show levorolatory power. The symbol + is used to express dextrorotation, and the symbol - to express levorotation. Substances which rotate the plane of polarisation of a ray of light passed through them are said to be optically active.

The polarimeter is an instrument wherein a ray of light can be polarised, the position of the plane determined, the ray passed through a determinate quantity of an optically active substance, and the position of the plane of the

The angle of rotation depends upon (1) the nature of the active substance, (2) the thickness of the layer of the substance through which the

fight passes. (8) the wave-length of the light !

used, and in most cases (4) the temperature.

The composition of the substance examined must then be known; the length of the column of liquid used if the substance be liquid, or the thickness of the layer if the substance be a solid, must be measured; the temperature must be noted-observations ought to be made at a common temperature; and monochromatic light should be employed.

Suppose we are dealing with a liquid carbon compound. Let l = length of column of liquid in decimetres, d = sp.gr. of liquid (referred to water), and a = angle of rotation of the plane of polarisation of light of stated wave-length; then

$$[a] = \frac{a}{l \cdot d}$$

The value of [a] is usually called the specific rotatory power of the substance. It is customary to indicate the light employed by placing a letter to express the wave-length below the bracket: thus [a], means spec. rot. power for light of wave-length D. The spec. rot. power of a liquid as thus defined is the angle through which the plane of polarisation of a ray of light of stated wave-length is rotated by passing through a column one decimetre long of the liquid containing one g. of the substance in 1 c.c.

If a solid compound is to be examined, it must be dissolved in an optically inactive solvent. In this case l = length of column of solution in decimetres, d = sp. gr. of solution, p = g, of optically active substance in 100 g, of solution; then, assuming that the solvent is without influence on the rotatory power of the 100a

dissolved substance, $[a] = \lim_{t \to 0} \frac{1}{t} \cdot p \cdot d$ The question as to the effect of an inactive solvent on the rotatory power of an active substance in solution will be examined later (p. 257).

Connections between optical activity and constitution. Landolt (Handbook of the Polariscope, English trans.) has divided substances which rotate the plane of polarisation of a ray of light into three classes: (1) those which are active only when in the form of crystals; (2) those which are active only when liquid or in solution; (3) those which are active both as crystals and also in solution or in the liquid state. The only substance at present known to belong to the third class is strychnine sulphate. The liquid crystals examined by Lehmann (Z. P. C. 4, 462; 5, 427) probably belong to the first class.

The optical activity of carbon compounds. All compounds which exhibit optical activity unconnected with crystalline form-in other words, all compounds which are optically active when liquid or in solution - are compounds of carbon. Le Bel (Bl. [2] 22, 337) was the first (1874) to trace a definite connection between the optical activity and the constitution of carbon compounds. He was followed by van't Hoff (Bl. [2] 23, 295 [1875]). The subject has been much advanced by van't Hoff in his pamphlet, La Chimis dans l'Espace, and more especially by a small book published in 1887, Dix Années dans l'Histoire d'une Théorie (translated into English by Marsh, and published in 1891, entitled Chemistry in Space).

The hypothesis of Le Bel and van't Hoff

connects optical activity with the presence of one or more asymmetric atoms of carbon in the molecule of the active compound. An asymmetric atom of carbon is one which is in direct combination with four different atoms or radicles. these atoms or radicles being arranged so that any three are similarly situated with regard to the fourth. The conception of the asymmetric atom carries with it the conception of the arrangement in space of the parts of the molecule. The asymmetric atom of carbon is supposed by van't Hoff to be placed in the centre of regular tetrahedron, and a different radiole is supposed to be held by the carbon atom at each summit of the tetrahedron. Two forms of this arrangement may exist, and these forms are geometrically different. Neither is superposable on the other. They bear to one another the relation of an object to its image, or of the right hand to the left, as shown in the figure.





This arrangement corresponds to the enantiomorphous (non-superposable) form of crystals. Ammonium malate, for instance, crystallises in two non-superposable forms, which differ in exactly the same way as the molecules of two geometrical isomerides, each containing an asymmetric carbon atom and both having the composition CR₁R₂R₃R₄, are supposed to differ. If one of the isomerides CR₁R₂R₄, rotates the plane of polarisation to the right, the other rotates to the left. If this hypothesis is to be accepted, every compound of carbon which is optically active must contain at least one asymmetric carbon atom. So far as investigation has gone, this deduction from the hypothesis has been confirmed (v. van't Hoff, Dix Années &c., 31; Landolt, Handbook, 25 et seg.). Further, it has been found that compounds which do not themselves contain asymmetric carbon atoms are inactive, although they are derived from optically active compounds.

There is no doubt that compounds exist which contain asymmetric carbon atoms but do not affect the plane of polarisation of a ray of light. At first sight this fact might be supposed to be irreconcileable with the hypothesis; but the recognition of the existence of inactive compounds containing asymmetric carbon atoms has led to a most ingenious and interesting development of the hypothesis.

Some inactive compounds containing asymmetric carbon atoms can be separated each into two optically active isomerides, one of which is dextrorotatory and the other is isovorotatory. Some inactive compounds which contain asymmetric carbon atoms cannot be separated into active isomerides. Racemic acid, which can be resolved into dextrorotatory and laworotatory tartaric acid, is an example of the first of these classes, called inactive resolvable compounds; mesotartaric acid, which cannot be resolved into active isomerides, is an example of the second class, called inactive non-resolvable compounds.

Inactive resolvable compounds are said, in the language of van't Hoff's hypothesis, to be inactive by external compensation; inactive nonresolvable compounds are said to be inactive by internal compensation.

To understand these expressions consider

the formulæ $(R_2R_2R_1)C.C(R_1R_2R_3)$ and $(R_2R_2R_1)C.C(R_1R_2R_2)$; an italicised C represents an asymmetrical atom of carbon. Each formula contains two asymmetric carbon atoms, and both carbon atoms in either formula are united to the same radicles; in the first formula each C is united to the radicles R_1 , R_2 , R_3 , and $C(R_1R_2R_3)$; in the second formula each C is united to the radicles R_1 , R_2 , R_2 , and $C(R_1R_2R_2)$. The structure represented by one of these formulæ is the reflected image of that represented by the other: hence if one of these geometrically isomeric compounds is dextrorotatory, the other will be laworotatory, and both will rotate the plane of polarisation to the same degree. But if a compound were formed by the combination of equal numbers of molecules of these two geometrical isomerides, that compound would be inactive, for the tendency to righthanded rotation of one part of the compound molecule would be exactly neutralised by the equal tendency to left-handed rotation of the other part. Moreover, if the inactive compound were split into two compounds, one consisting of molecules of the form represented by the first of the above formulæ, and the other of molecules of the form represented by the second formula, then each of these compounds would be optically active, and the compounds would be active in opposite directions. The hypothetical inactive compound $(R_2R_2R_1)C.C(R_1R_2R_3) \times (R_2R_3R_1)C.C(R_1R_2R_2)$ would be said to be inactive by external compensation.

Racemic acid, which is optically inactive, can be resolved into dextrorotatory and hevorotatory tartaric acids. Both tartaric acids have the formula C₂H₂(OH)₂(CO₂H)₂; the hypothesis we are considering represents one of these acids as (H.OH.HOOC) C.C(COOH.OH.H); and the other acid as (H.COOH.OH)C.C(OH.COOH.H); and the hypothesis represents racemic acid as made up of an equal number of molecules of the two active acids, and therefore as a substance which

is inactive by external compensation.

But suppose the molecule of a compound contained two asymmetric carbon atoms, both united to the same radicles but having one half of the molecule the reflected image of the other. then the tendency to right-handed rotation belonging to one part of this molecule would be neutralised by the tendency to left-handed rotation belonging to the other part of the molecule; the molecule as a whole would be incapable of rotating the plane of polarised light, and the compound would be inactive by internal compensation. The general formula of such an in**set**ive compound is $(R_2R_3R_1)C.C(R_1R_2R_3)$.

A compound of this type cannot be resolved into active isomerides, because a resolution into parts is only possible by splitting the molecule, removing one of the radicles, and so destroying the asymmetry of one, or both, of the atoms of

carbon. Mesotartaric acid, which is non-resolv. able, probably belongs to this class of com. pounds; it may have the formula

'H.COOH.OH)*C.C*(COOH.OH.H).

The hypothesis therefore provides for the exis. tence of two classes of optically inactive compounds, both containing asymmetric carbon atoms; the members of one class are resolvable into active isomerides, the members of the other class cannot be so resolved.

Those compounds which contain in their molecules more than one asymmetric carbon atom, each of which atoms is united to the same radicles, whether these radicles are arranged in space in exactly the same way, relatively to each carbon atom, or not, are called by van't Hoff symmetrical compounds; and the term unaummetrical compounds is used to designate those which contain more than one asymmetric carbon atom each of which is united to different radicles. The typical formulæ for symmetrical compounds containing two asymmetric carbon atoms are

 $(R_1R_2R_3)C.C(R_3R_2R_1), (R_1R_3R_2)C.C(R_3R_2R_1), \&c.$ The typical formula for an unsymmetrical compound containing two asymmetric carbon

atoms is (R₁R₂R₃)C.C(R₄R₅R₆).

Unsymmetrical compounds may be either active or inactive; if inactive, they must be inactive by external compensation, and therefore they must be resolvable into pairs of active isomerides. Symmetrical compounds may be active or inactive; if inactive, they may be inactive by external, or by internal, compensation, and therefore they may be either resolvable or not resolvable.

An unsymmetrical compound containing n asymmetric carbon atoms may exist in 2" isomeric forms, which will always be grouped in pairs, one being dextrorotatory and the other lævorotatory. A symmetrical compound containing n asymmetric carbon atoms may exhibit \$2ⁿ active isomeric forms, grouped in pairs of opposite rotatory power, and may also exist in

 $\frac{1}{2}$ non-resolvable inactive modifications (van't Hoff; Dix Années &c., 54-5).

There are three general methods for separating inactive resolvable bodies into their dextrorotatory and lavorotatory isomerides.

In the first method advantage is taken of the differences between the actions of certain minute organisms on the two active isomerides. The second method proceeds by treating the inactive compound with an active body with which one of the isomeric constituents of the inactive compound combines more readily than the other. The third method consists in separating the inactive body into two active isomerides by crystallisation at a definite temperature (van't Hoff. l.c. 63-69).

Racemic acid, which is an inactive compound, can be resolved into equal quantities of rightand left-handed tartaric acid by each of the three methods. When penicillium is allowed to act on a dilute solution of ammonium racemate, lævorotatory ammonium tartrate is found in the solution after a time, the dextrorotatory tartrate having been destroyed by the action of the or-ganism. When a quantity of active cinchonine sufficient to neutralise half of a determinate quantity of racemis acid- is added to a solution of the racemic acid, crystals of levorotatory cinchonine tartrate are obtained, and dextrorotatory tartaric acid remains in solution. When a solution of racemic acid is neutralised by soda, and another equal quantity is neutralised by ammonia, and the solutions are mixed, and evaporated at a temperature slightly below 28°, crystals of two forms are obtained; one set of crystals is dextrorotatory, and the other is levorotatory, sodium-ammonium tartrate. Hoff (l.c. 69) has shown that sodium-ammonium racemate is changed to a mixture of the active isomeric tartrates by heating the dry salt with water, in the ratio NaNH, H, C,O6, H,O:3H,O (the salt crystallises with H2O), to a little under 27°, and that the reverse change is effected by heating the mixed tartrates to a little above 27°. The changes may be represented thus-

centre of figure of the tetrahedron. When the molecule is asymmetric, the centre of gravity will not be situated on any one of the six planes of symmetry of the tetrahedron. So long as the substitution of one radicle by another does not move the centre of gravity of the molecule to the other side of one of the planes of symmetry of the tetrahedron, Guye supposes that the rotatory power is increased or diminished, but is not changed in sign, by such substitution; but that a change of sign of the rotatory power accompanies a substitution which results in moving the centre of gravity of the molecule from one side to the other side of one of the planes of symmetry of the tetrahedron. Guve gives about fifty cases to which he has applied his hypothesis successfully. The derivatives of tartaric acid afford the most complete example.

Replacement of the acidic hydrogen of tar-

$$2(\mathrm{NaNH_4.H_4C_4O_6.4H_2O}) \underset{\leftarrow}{\longrightarrow} 2(\mathrm{NaNH_4.H_4C_4O_6.H_2O}) + 6\mathrm{H_2O}.$$

The racemate crystallises with H₂O, and the tartrates with 4H₂O. Slight variations of temperature above or below 27° determine the direction in which the change shall occur.

The change of inactive sodium-ammonium racemate to a mixture of the active tartrates, and vice versa, is very similar to some changes which occur among inorganic compounds; for instance, when a mixture of MgSO.7H₂O and Na.SO.10H₂O is heated to a little above 21°, it is changed to the double sulphate MgNa₂(SO₄).4H₂O, and water, and this double sulphate is resolved into the two single sulphates at a little under 21°; these changes may be represented thus:—

tario acid by alcoholic radicles is accompanied by increase of rotatory power, and the greater the molecular weight of the replacing alkyl the greater is the increase of rotatory power; thus—

Methyl tartrate
$$[\alpha]_D = +2.14$$

Ethyl , 7.66
Propyl , 12.44
Isobutyl , 19.87

Replacement of the hydroxylic hydrogen of the acid by benzoyl moves the centre of gravity to the other side of the plane of symmetry which is situated between the COOH and OH groups; this replacement is accompanied by a change of sign of the rotatory power. But if the H of the COOH group is now replaced by one alkyl group,

$$MgSO_4.7H_2O + Na_2SO_4.10H_2O \longrightarrow MgNa_2(SO_4)_2.4H_2O + 13H_2O$$
.

Van't Hoff calls the temperature at which such a chemico-physical change as this occurs the transition-point of the system (v. Z. P. C. 1, 165, 227).

Extension of the hypothesis of van't Hoff and Le Bel. The hypothesis of van't Hoff and Le Bel connects the power of rotating the plane of polarisation of a ray of light primarily with the configuration of the parts of molecules, but it points to the formation of molecular aggregates, without change of molecular structure, as a cause of the disappearance of optical activity. Although optical activity is primarily dependent on the arrangement of the parts of certain molecules, and although we cannot assign a definite part of the total rotatory power of a molecule to each atom, or to each group of atoms which together form the molecule, nevertheless a consideration of the constitution of optically active compounds shows that the amount of the activity of any compound is dependent on the greater or less differences between the four radicles which are in direct union with the asymmetric carbon atom or atoms in the molecule of that compound. The greater the differences between the radicles the greater will be the asymmetry of the molecule, and, therefore, the greater will be the rotatory power. An attempt has been made by P. A. Guye (C. R. 110, 714) to connect the degree of asymmetry of the molecule of an optically active compound with the mass of each radicle, and the distance of its centre of gravity from the

the centre of gravity is moved back towards the plane of symmetry already mentioned, and the rotatory power is diminished. Thus—

Dibenzoyl tartaric acid $[a]_D = -117.7$ Methyl salt of , 88.8 Ethyl , , 60.0 Isobutyl , , , 42.0

If acetyl is used in place of benzoyl the rotatory power changes its sign, but the value of the leworotation of diacetyl tartaric acid is less than that of dibenzoyl tartaric acid; the replacement of acidic hydrogen in the diacetyl acid by alkyl radicles decreases the rotatory power, and, as the alkyl radicles of large molecular weight exert a greater effect than the acetyl group, and an effect in the opposite direction, the rotatory power again changes its sign. Thus—

Diacetyl tartaric acid $[a]_{b} = -23\cdot 1$ Methyl salt of , 14·3 Ethyl , , , +1·0 Fropyl , , 6·5 Isobutyl , , , 10·3

Crum Brown (Pr. L. 17, 181) has tried to connect the greater or less rotatory powers of different active compounds with differences between the constitutions of the substituting radicles. Crum Brown admits the influence of the masses of the radicles, but he tries to show that their constitution must also be taken into account. If two methyl groups are introduced into destrorotatory tartaric acid, the salt thus obtained is still dextrorotatory; in this change

two CO.OH radicles have been changed into two radicles CO.O.CH_a. If now this dimethyl tar-trate is treated with acetyl chloride, a strongly isvorotatory dimethyl diacetyl-tartrate is obtained; in this change the CO.O.CH, groups remain, and two OH groups have been changed to two groups O.CO.CH. In the first change, the introduction of the group CO.O.CH, for H altered the rotatory power but did not change its sign, in the second change the introduction of the group O.CO.CH, changed the sign of the rotatory power; therefore, Crum Brown argues, the effect of the radicle O.CO.CH, on the rotatory power is greater than the effect of the isomeric radicle CO.O.CH₃. As the masses of these two radicles are the same, it is evident that the constitution of the substituting radicle affects the rotatory power of the compound.

The specific rotatory powers of compounds often change more or less with small changes in certain physical conditions. Some active Lodies become inactive by heating, and at another temperature the change is sometimes reversed. The values of the rotatory powers of active bodies dissolved in inactive solvents are dependent on the nature and the quantity of the solvent used (v. post, p. 257); the rotatory power of a solution sometimes changes on keeping until a constant value is attained (v. Landolt's Handbook of the Polari-scope, 62). This readiness to change shown by the rotatory powers of carbon compounds finds some explanation in van't Hoff's hypothesis, and especially in the development of it made by Wislicenus. According to Wislicenus (Kön. Sächsischen Ges. der Wiss. 14, 1) the arrangement of the four radicles attached to an asymmetric carbon atom is conditioned chiefly by the affinities of these radicles for one another in the sense that those radicles which have the greatest mutual affinity will tend to get as near as possible to one another; but besides those configurations which are conditioned by the affinities of the radicles, and which will be comparatively stable, other configurations will probably exist con-ditioned by the temperature and by the collisions of other molecules—for instance, the molecules
of the solvent—and these arrangements will be
relatively unstable. These unstable forms may be optically active, as they are only geometrically different from the stable forms, but their rotatory powers will probably differ from those of the stable forms. This way of looking at the question of optical activity enables us to connect the fact that active compounds easily undergo changes in the values of their rotatory powers with the conception which the hypothesis of van't Hoff and Le Bel furnishes of the cause of optical activity.

Molecular rotatory power. The notion of molecular rotation, as the product of the specific rotation into the molecular weight of a substance, was introduced by Wilhelmy (P. 81, 527). Krecke (J. pr. [2] 5, 12) proposed to define molecular

rotatory power as $[m] = \frac{m}{100} \times \frac{a}{l \cdot d}$, where m =

molecular weight of compound, and a, l, and d have the same meaning as before (p. 253); m is divided by 100 to obviate the use of inconveniently large numbers.

Krecke endeavoured to generalise the rela-

tions between the values of [m] for certain com-pounds and bodies derived from, or closely connected with, these compounds. Some years before Krecke's attempt, Mulder (Z. 1868. 58) put forward a statement to the effect that optically active compounds contain certain active radicles, which may be transferred to other active atomic aggregations, and the rotatory powers of the new bodies bear a simple relation to those of the original radicles. Krecke, on the basis of further experimental results, modified and extended Mulder's statement. Krecke announced two generalisations:

(i.) 'When an optically active body forms a compound with an inactive body, or when it is altered by the action of chemical reagents, either the molecular rotatory power of the body is unchanged, or the molecular rotatory power of the new substance is a simple multiple of that of the parent substance.

'(ii.) 'The molecular rotatory powers of iso-merides are multiples of one and the same value.'

Most of Krecke's values were obtained from measurements of substances in solution, and, as we shall see in another paragraph, the results of such measurements are trustworthy only in a few cases. Landolt (B. 6, 1073) made a careful examination of the rotatory powers of tartrates in solution; he came to the conclusion that the value of [m] for tartrates containing a single atom of a monovalent metal is double the value of [m] for free tartaric acid, and that [m] for tartrates containing two atoms of a monovalent metal is three times [m] for the free acid. In this case, Krecke's first statement was confirmed.

In 1885, Oudemans (v. P. B. 9, 635) arrived at the conclusion that the compounds of active bases with inactive acids, and also the compounds of active acids with inactive bases, follow the simple law that 'the molecular rotatory power of a salt, in fairly dilute solution, is independent of the nature of the inactive part of the salt.' This result has been confirmed by the measurements of camphorates and tartrates made by Landolt, of salts of cholic acid by Hoppe-Seyler, of malates by Schneider (A. 207, 286), and of camphorates by Hartmann (B. 21.

221).
This result indicates that the rotatory powers like the extent that the rotatory powers of liquid compounds are affected, by the nature of the radicles which compose them. The rotatory power of a salt in solution approaches to being an additive property, whereas the rotatory power of a liquid compound is a constitutive property (cf. Ostwald, Lehrbuch, 1, 499 [2nd ed.]).
Optical activities of bodies in solution. The

specific rotatory power of an active substance in an inactive solvent has been defined (p. 253) as [a] = $\frac{100a}{l \cdot p \cdot d}$, where l = length of column of solution in decimetres, d = spec. grav. of the solution, and p = g. of active substance in 100 g. of the solution. This formula is expressed in more general terms as $[a] = \frac{n \cdot a}{l \cdot g \cdot d}$, where n = g. of solution containing g g, of the substance; in this case, 1 c.c. of the solution weighs d g. and contains $\frac{g.d.}{n}$ g. of the active substance.

This formula assumes that the rotatory power of the dissolved active substance is not affected by the inactive solvent. In 1838 Biot (A. Ch. [3] 36, 257; cf. 59, 206) found that the rotatory power of tartaric acid in aqueous solution increased with increasing dilution; that solutions of equal concentration, of the same active substance in different inactive solvents had different rotatory powers; and that the same inactive solvent raised the rotatory powers of some active substances, and decreased the rotatory powers of others. Results similar to those of Biot were obtained by Oudemans (A. 166, 65; 182, 33), Hoorweg (Maanblad voor Naturwet, 3, 12 [1873]), and Hesse (A. 176, 89, 189).

Landolt (A. 189, 241; B. 21, 191; Handbook of the Polariscope, 80-94) made many observations on the effect of inactive solvents on the rotatory powers of active substances; he came to the conclusion that the specific rotatory powers of such solutions are expressed by equations of the following forms: [a]=A+Bq, or

$$[\alpha] = A + Bq + Cq^2$$
, or $[\alpha] = A + \frac{Bq}{C+q}$, where A, B,

and C are constants, and q is weight of active substance in 100 pts. of the solution. Which formula must be employed is discovered from the results of several observations made with solutions of different concentrations in different solvents. In some cases the observed values of [a] for liquid compounds agree with the values calculated from series of observations of a for solutions of the same compounds. Thus Landolt got the following results:—

on the solubility in water of the salt used; the greater the atomic weight of the metal, the greater was the concentration whereat the change began, and the greater was the difference from the normal state of the salt. Schneider (A. 207, 257) found that the rotation of an aqueous solution of malic acid was right-handed in concentrated solutions, left-handed in dilute solutions, and at 34 p.c. was equal to zero. These observations, and others of a similar character, seem to me to show that observations of the rotatory powers of solutions of solid compounds cannot be applied, at least not in all cases, to draw conclusions concerning the connections between the rotatory powers and the chemical constitutions of the compounds themselves. There is undoubtedly an action of some kind between the molecules of the active dissolved substance and the molecules of the inactive solvent. Molecular aggregates of the solid substance may be broken down by the solvent, or the solvent may form a series of unstable compounds with the dissolved substance, or the solvent may bring about changes in the configuration of the atoms which form the molecule of the dissolved body, or the dissolved compound may be electrolytically dissociated into ions by the solvent. Some of these actions may occur in certain cases, and others in other cases. The action of much water on active salts dissolved therein seems to consist in the electrolytic dissociation of the salts into their ions.

Magnetic rotatory power. Following observations made in 1871 by A. de la Rive (A. Ch. [4] 15, 57), Becquerel in 1877 (A. Ch. [4] 22, 5) made a number of measurements of the rotations.

[a]	[a] _D calculated from observations on solutions in					
observed	(1) EtOH	(2) McOH	11,0	(4) C _a H _a	AcOH	Max, diff.
8·31 14·15	8·27 14·87	8.42	8.09	_	_	-·22 +·72
37·01 161·55	36·97 109·83	_	161.29	86.97	36.89	-·12 -·72
	8·31 14·15 37·01	Calp Calp	Calp Calp	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

It is not possible to determine with certainty whether the true values of [a] for solid compounds can be determined from observations on solutions of such compounds. In some cases the values obtained seem to approach constancy when the solutions become very dilute; but according to Pribram (B. B. 1887, 505; B. 20, 1840), who used a very delicate method of measuring, [a] does not certainly attain final constant values in aqueous solutions of tartaric acid, nicotin, and cane sugar, even with very great dilution. R. von Sonnenthal (Z. P. C. 9, 656) determined [a] for dilute aqueous solutions of normal and acid tartrates of K, Na, Li, and NH,; he found that [a] decreased as dilution increased, but that when the solutions became very dilute (c. '4 to '2 p.c. salt in solution) [a] began to increase as dilution still further increased. conclusion come to by von Sonnenthal was, that a change in the state of the dissolved tartrates occurred when more water was added to the very dilute solutions; this change was supposed to be of the nature of dissociation. The dilution whereat the change occurred was found to depend on the nature of the metal of the tartrate, and

Vor. IV

tory powers of liquid substances, and of salts in solution. The subject was taken up by Perkin in 1882, since which time a series of memoirs by this investigator has appeared (C. J. 45, 421; 49, 777; 51, 808; 53, 561; 55, 680; 59, 981; 61, 800). The methods employed in the measurements are based on the discovery which Faraday made in 1846 (T. 1846. 1), that most transparent bodies acquire the power of rotating the plane of polarisation of a ray of light when they are brought within the action of a magnet, or of an electric current which is made to pass round the body so that its plane is at right angles to the direction of the ray of light. Faraday showed that the amount of rotation is proportional to the strength of the current, or the intensity of the magnetic action, and to the length of the laver through which the light passes, and that it is dependent on the temperature and on the nature of the substance examined. Perkin has worked with liquid compounds and with solutions. The fluid to be examined was placed in a glass tube about 103 mm. long. and 9 mm. diameter, the ends of which were closed by circles of glass cemented on; the ends of the tube were let into

the pole-pieces of a large electro-magnet. Sodium light was employed by Perkin. (For a description of the apparatus, and the various precautions and corrections, v. Perkin, C. J. 45, 421-445.) Perkin calculates his results so that the observed rotations of liquid compounds are referred to lengths of the liquids related to one another in the same proportion as the molecular weights of the gaseous compounds obtained by vapourising the liquids; the results when thus calculated represent the magnetic rotatory powers of quantities of the various-compounds proportional to the weights of the gaseous molecules of these compounds.

The molecular rotation of water is taken as unity. If r is the rotation of unit-length of liquid, and r' is the rotation of the same length of

water under the same conditions, then γ is the specific rotation of the liquid; and

sp. rot. $\times \frac{\mathbf{M}}{\mathbf{M'} \cdot \mathbf{d}}$ is the molecular rotation, where $\begin{vmatrix} \text{series.} & \text{Per} \\ 45, 574 \end{vmatrix} : -$

is not constant; the change from a normal paraffin, CH_nCH_CH_, to the next higher isoparaffin, CH(CH_), nCH_nCH_, CH_n, raises Mol. R. by 1.023 + .105; in the change from a normal acid to the next higher iso-acid of the same series, CH_has a different value; and so on. When Cl is substituted for H in a hydrocarbon the mol. rotatory power increases, but each Cl atom has a different value from the others. So with the replacement of H in a hydrocarbon by OH; each OH group has its own value, the effect on Mol. R. of the second OH being less than that of the first. So again with the group NO₃; the second NO₃ does not increase Mol. R. so much as the first.

The molecular rotatory powers of various homologous series of carbon compounds may be expressed by the general formula

(Mol. R.) = $c + nI \cdot 023$, where n = number of atoms of C in the molecule of any stated compound in the series, and c is a constant for each series. Perkin gives the following table (C. J. 45, 574):—

Mol. R. of members of homologous series.

Paraffins .					C_nH_{2n+2}	$\cdot 508 + n1 \cdot 023$
" iso-			•	•	• ,,	·621 "
Alcohols .			•		$\mathbf{C}_{n}\Pi_{2n+2}\mathbf{O}$	·699 "
,, iso- ar	nd sec				• "	·844 ,,
Oxides .					• "	·642
., iso-					• ",	.932
Aldehydes.	-				$\mathbf{C}_{n}\mathbf{H}_{2n}\mathbf{O}$	261 "
	and l	ketones				.978
Acids .			•	•	. C,H,,,O,	*303
iso	•		•	•		•500
Formic etherea		. /151	and his	hor)	• "	-405
Acetic	Sait	5 (130,	min me	ner)	• "	370
Acetic "			"		• "	
35 41 1 - 11 - 9			11	18	io- ,,	•485 "
Methyl salts	:	٠ ;	. •	•	• ,,	.273
Ethyl ,, an	d higi	ner sai		•	•' "	337
	,	,	130-	•	•,,	•449 ,,
Succinic methy	l salts			•	$\mathbf{C}_{n}\mathbf{H}_{2^{n}\cdot 2}\mathbf{O}_{1}$.093
" ethyl	,,		•	•	• ,,	·196 "
19 29	,,	iso-		•	• ,,	.422
Chlorides .				•	$\mathbf{C}_{n}\mathbf{H}_{2n+1}\mathbf{C}\mathbf{I}$	1.988 ,,
., iso- a	nd sec				• "	2.068
Bromides .					$\mathbf{C}_{n}\mathbf{H}_{2n+1}\mathbf{Br}$	
" iso- a	nd sec					3.924
Iodides .				-	. C, H,,,,I	0.011
iso- and	Bec.		•	-		
Ethyl salts, uns			•	•	$C_nH_{2n-2}O_2$	1.451
winding and	avuiu	iou .	•	•	0_{n+1}	1.401 19

M = molecular weight of substance, M' = molecular weight of water, and d = relative density of substance. The calculation may be expressed by

one equation, thus: (Mol. R.) =
$$\frac{r \cdot M}{r' \cdot M' \cdot d}$$

About 200 compounds have been examined by Perkin, the observation of r being repeated five to ten times for each compound, and the specific gravity of each being determined with great care

Magnetic molecular rotatory powers of liquid carbon compounds. In strictly homologous normal series of carbon compounds, each increment of CH, produces a constant increase in molecular rotatory power, amounting to 1023. But when the addition of CH, is accompanied by a change in the distribution of the atomic interactions the change of Mol. R.

These results indicate that the molecular rotatory power of a liquid carbon compound is not the sum of certain constant values belonging to each atom or atomic group, but that it depends, to some extent, on the arrangement of the atoms which form the molecule. This result is confirmed by the outcome of attempts to assign values to the atomic rotatory powers of oxygen and carbon. The following data are given as examples of such attempts.

The atomic rotatory power of hydrogen may be deduced thus:

- 1. Mol. R. $C_nH_{2n+2} = Mol.$ R. $nCH_2 + H_2$; but Mol. R. $nCH_2 = n1.023$.
- The value thus deduced for At. B. of H = 254.
- 2. Mol. R. C_nH_{2n+2} minus Mol. R. $C_nH_{2n+3} = At$. R. of H.

Thus, Mol. R. C.H. = 8.577

Mol. R. C.H. = 3.323 = Mol. R. C.H. At. R. of H = .254

Now, At. R. of C = Mol. R. CH, minus At. R. of $H \times 2 = 1.023 - .508 = .515$.

By applying similar methods to the data for compounds of O, the following results are obtained:

The At. R. of Cl varies according to the series of compounds considered, and also as one or two atoms of II are replaced by one or two atoms of Cl, according as the H replaced is in one part of the molecule or in another part, and so on. Two values are obtained for At. R. of N, according as the atom of N is directly connected with 3 or 5 other atoms or groups. The general conclusion is that changes in the magnetic molecular rotatory powers of liquid carbon compounds are intimately connected with changes in molecular structure, so that any cause which alters this structure also alters the rotatory power.

In C. J. 61, 800, Perkin gives an elaborate study of the constitution of ethyl acetoacetate and allied compounds, which elucidates very clearly the connections between the constitution and the magnetic rotatory powers of carbon compounds.

Mol. R. of compounds in presence of water. Perkin has used determinations of Mol. R. of certain compounds before and after addition of water, to throw light on the question whether hydrates are formed by the action of water on these compounds (C. J. 49,777; 51,808; 55,680). In all measurements of Mol. R. the molecular rotatory power of water is taken as unity; if therefore a compound is formed by the Addition of water to another compound, the Mol. R. of the new compound might be expected to be nearly equal to that of the original compound, plus one unit for each molecule of water added; if the observed Mol. R. is distinctly less than that calculated in this way, the difference may be explained by supposing that the formation of the new compound has been accompanied by a rearrangement of the atoms of the reacting moleoules.

The following are examples of the application of this method. In each case the compound and

formic, acetic, and propionic acids in the ratio of equal molecules of water and acid, either a hydrate or a mixture is formed in each case; but that when H.,SO, and H.O react in about the ratio H.,SO,:H.O (or a little more H.O than this), a rearrangement of atoms occurs with formation of a new compound of S, O, and H (perhaps SO(OH),); and that reactions of this nature, involving rearrangements of atoms, also occur between HNO, and H2O, and CCl2.CHO and H.O.

The following data are interpreted by Perkin to mean that a solution of NH, in water, or in alcohol, 'simply consists of the solvent and ammonia':

$$\begin{array}{ccccc} \text{Mol. R. NII}_{J} + 2 \cdot 11\text{H}_{2}\text{O} = 3 \cdot 91 \\ & 2 \cdot 11\text{H}_{2}\text{O} = 2 \cdot 1 \\ & \text{NII}_{2} & 1 \cdot 81 \\ \\ \text{Mol. R. NII}_{J} + 2 \cdot 18\text{C}_{2}\text{H}_{4}\text{O} = 7 \cdot 886 \\ & 2 \cdot 18\text{C}_{2}\text{H}_{4}\text{O} - 6 \cdot 06 \\ & \cdot & 1 \cdot 826 \end{array}$$

Mol. R. of acids and salts in aqueous solu-tions. Perkin (C. J. 55, 680; 59, 981) gives Mol. R. for HCl as 2:187. This is arrived at by finding values for At. R. of H and Cl from observations of Mol. R. of various chlorides of alcoholic radicles. By similar methods of cal-culation values for Mol. R. of HBr and HI were obtained. The three results are:

The value for HCl was confirmed by measuring Mol. R. of HCl dissolved in isoamyl oxide; the result was Mol. R. HCl = 2.24.

Values were then obtained for the three soids in aqueous solutions. The numbers increased as dilution increased; in any case they were much larger than the values obtained by the method stated above. The following table gives the minimum and maximum values for each acid:

Mol. R. in aqueous solutions.	Maximum.	Minimum.
HCl	4.419	4.045
(15.63 p.c. HCl)	(41.7 p.c. HCl)
HBr	8.519	7.669
(15·47 p.c. HBr)	(65.99 p.c. HBr)
ш	18:451	17.769
	(31·77 p.c. HI)	(67·02 p.c. HI)

Compound and water	Mol. R. observed	Mol. R. calculated for	Diff.
HCO,H.H.O CH,CO,H.H.O C,H,CO,H.H.O H.SO,H,O H.SO,2H,O H,SO,3H.O HNO,2-67H.O CCI,CHO.H.O	2:666 3:554 4:512 3:188 4:113 5:064 8:656 7:037	H.CO,H+1=2:671 CH,CO ₂ H+1=3:525 C ₂ H,CO ₄ H+1=4*462 H ₂ SO ₄ +1=3:315 H ₂ SO ₄ +2=5:188 H.SO ₄ +3=6:188 HNO ₃ +2:67=3:85 CCI_CHO+1=7:591	- ·005 + ·029 + ·05 - ·127 -1·076 -1·124 - ·194

water were mixed in the ratio shown by the formula given, and the Mol. R. of the product was determined; the Mol. R. of the product was then calculated by adding one unit for each molecule H.O to the observed Mol. R. of the original compound without water.

It is evident that the magnetic mol. rotatory powers of HCl, HBr, and HI in aqueous solutions are much greater than the values calculated from those obtained for the same three acids from observations made with compounds of them with C and H; in the case of HCl, the Perkin thinks that when water is added to value of Mol. R. in aqueous solution is much

greater than the value for the same compound in solution in isoamyl oxide. There must be an action of some kind between water and these three compounds.

It has been shown already that addition of

It has been shown already that addition of water to H₂SO₄ results in a value for the Mol. R. of the acid different from that observed for the pure acid itself; but in this case addition of water reduces the Mol. R. of the acid. A similar reducing effect was noticed as accompanying the addition of water to HNO₃.

Perkin was unable to explain these results. Ostwald, however, has shown that they are in keeping with the electrolytic dissociation hypothesis (C. J. 59, 198). According to this hypothesis strong acids are dissociated in aqueous solutions into their ions. Aqueous solutions of

HCl, HBr, and HI, contain the ions H and Cl,

H and Br, and H and I, each with its electric charge. The observed rotatory powers of these solutions, minus the value for the water contained in them, therefore represent the rotatory powers of these ions, and not of the compounds themselves; and the rotatory powers of these ions are considerably greater than those of the non-dissociated compounds. An aqueous solution of H₂SO₄, or HNO₂, must also contain dissociated, electrically charged, ions—according to the hypothesis; but Perkin's observations (ante, p. 259) show that the rotatory powers of the ions of these acids are slightly smaller than those of the acids themselves.

Now, the hypothesis of electrolytic dissociation asserts that the metallic salts of acids are dissociated into electrically charged ions in dilute aqueous solutions; hence determinations of Mol. R. for aqueous solutions of metallic salts of HCl, HBr, HI, H₂SO₄, and HNO₂ ought to give results different from the values obtained for these salts themselves. But the values obtained for aqueous solutions of salts of HCl, HBr, and HI ought, on the whole, to be greater than the calculated values, whereas the values obtained for salts of H₂SO₄ and HNO₄ ought, generally, to be slightly smaller than the calculated values. This deduction is partly confirmed by Perkin's results.

The values of Mol. R. for NH,Cl is calculated by Perkin as follows (C. J. 55, 743). The value for HCl is found from determinations of Mol. R. of alcoholic chlorides, which enable values to be found for H and Cl in combination; the value for NH, is taken as 1.818, which is the mean of the values found from observations on NH, in water and alcohol (ante, p. 259); the sum of the values for HCl and NH₃, with the subtraction of 5, gives the calculated Mol. R. of NH₄Cl. The number .5 is taken from the sum of the values for HCl and NH, because observation has shown that this is about the difference between the values for N^{III} and N^v, and in NH, the N atom is trivalent, while in NH,Cl it is supposed to be pentavalent. The values for the other salts of NH, are calculated in a similar way. Perkin's results for Mol. R. of NH,I, NH,Br, and NH,I show that practically the same values are obtained for solutions containing from c. 80 to c. 60 p.c. of the salts. The results with the six salts were as follows:

	Calculated	Observed, in aqueous solu- tions	Differences
NH,Cl	4·305	6·096	+1.791
NH,Br	6·096	7·997	+1.901
NH,I	8·149	9·896	+1.747
NH,NO,	2·298	2·320	+ .022
NH,HSO,	3·433	3·455	+ .022
(NH,)2SO,	4·551	4·980	+ .439

With regard to NH, NO, and the two sulphates, it is to be observed that the calculated values are found by adding the values for the acid and the base (NH3), then deducting 5 for the change of NIII to Nv, and then deducting 2 for the change from the free acid and base to the combination of these compounds; now, 5 is merely an approximate value for the change from N^{III} to N^V, and 2 is also merely a rough approximation for the value of the process of combination of acid and base. As the differences between the observed and calculated values for NH,Cl, NH, Br, and NH, I are large, small errors in the method of calculating Mol. R. for these compounds do not materially affect the differences in question; but as the differences are small in the cases of the nitrate and sulphates, small errors in the method of calculating Mol. R. for these compounds do materially affect those differences. Moreover, the observations of Mol. R. of the nitrate and the sulphates of ammonium in aqueous solutions were made with a single solution in each case (59.7 p.c. NH, NO₃, 66.6 p.c. NH, HSO₄, and 40 p.c. (NH₄)₂SO₄); hence it is not certain that the numbers set down as the values of Mol. R. of these compounds in aqueous solutions are the true values.

Perkin has also (C. J. 59, 981) made measurements of the magnetic mol. rotatory powers of the ammonium salts of formic, acetic, and propionic acids in aqueous solutions, and compared the results with the values calculated. He gives the results as follows:

	Observed, in aqueous solution	Calcu- lated	Dif- ferences
Ammonium formate ,, acetate ,, propionate	3·363	3·489	- ·126
	4·247	4·343	- ·096
	5·259	5·280	- ·021

The interpretation which the electrolytic dissociation hypothesis gives of these results is that, as in their aqueous solutions the salts examined are dissociated into their ions, and as the observed results are smaller than the calculated values, therefore the magnetic mol. rotations of the ions of HCO₂H, OH₂CO₂H, and C₂H₃CO₂H are slightly less than the rotations of the acids themselves (v. Ostwald, Z. P. C. 9, 513; cf. Ostwald, C. J. 59, 201).

But it seems to me that the numbers given by Perkin as the calculated values of Mol. R. for the three salts cannot be accepted as correct. For these values were found by adding the values of Mol. R. for the free acids to the value for free NH_a ; no deduction was made for the change of rotation accompanying the combination of the acid and the base, and no deduction was made | for the change of NIII to Nv. Either these values cannot be accepted as the true values, or the values calculated for the salts of NH, with the halogen acids, and with HNO, and H.SO., are not correct (ante, p. 260). If the values of Mol. R. for the salts of formic acid &c. are calculated by the same method as was used in the cases of the other salts of ammonium, then the results of this investigation are as follows:

	Observed in aqueous solution	Calcu- lated	Dif- ferences
Ammonium formate ,, acetate ,, propionate	3·363	2·789	+ ·574
	4·247	3·643	+ ·601
	5·259	4·580	+ ·679

If these results are accepted, then the differences are much greater than those given by Perkin, and they are in the opposite direction.

Measurements of the Mol. R. of formic, acetic, and propionic acid in aqueous solution would enable the question to be settled as to the effect of water on these acids; at present it seems that the magnetic rotations of the ions of these acids would be found to be greater than the rotations of the acids themselves.

This conclusion is confirmed by combining the results obtained by Perkin (C. J. 59, 986) for Mol. R. of sodium salts of formic and other acids with the value calculated by him for sodium (C. J. Proc. 1890, 141). In the following table I have calculated the values for the salts as Perkin calculated the values for NII, Cl, NH, NO, &c., by deducting 2 from the sum of Mol. R. of acid and At. R. of Na, and then further deducting .254 for the loss of H:

		Observed in aque- ous solu- tion	Calcu- lated	Differ- ences
Sodium formate .	•	2.347	1.775	+ .572
" acetate .	•		2.629	+ .652
" propionate		4.308	3.566	+.742
" butyrate.		5.332	4.576	+ .756

In a more recent communication (C. J. 63, 57) Perkin gives the Mol. R.s of aqueous solutions of H,SO, HNO, Na,SO, and Lino, of varying degrees of concentration. His results show that the Mol. R.s of these solutions do not vary with dilution in the same way as the electrical conductivities vary. The most dilute solution of H2SO, examined by P. contained c. 9.2 p.c. H₂SO₄, and the most dilute solution of HNO₃ contained c. 22·5 p.c. HNO₃. Now it has been shown repeatedly, by Ostwald and others, that measurements of the conductivities of fairly conc. solutions of acids and salts cannot lead to just conclusions regarding the amount of electrolytic dissociation of the compounds in solution; hence it is not to be expected that the amount of dissociation of H.SO, and HNO, should be calculable from the Mol. R.s of these compounds as deduced from observations on solutions so concentrated as those used by Perkin. What the observations of P. show is that the magnetic rotations of certain compounds diverge from the calcu-

lated results in all cases wherein electrolytic dissociation occurs. The laws which express the electric dissociation of compounds are to be deduced from the study of very dilute solutions. and as no measurements of magnetic rotations have yet been made for such solutions, it is not justifiable to draw detailed quantitative conclusions concerning the electrolytic dissociations of compounds from the measurements of the magnetic rotations of those compounds which P. M. M. P. M. has made.

VIII. OSMOTIC PRESSURE, METHODS BASED ON; v. Molecular weights, vol. iii. p. 418; and Electrical methods, this vol. p. 185.

IX. PHOTOGRAPHIC METHODS:

Photographic chemistry, this vol. p. 154.
X. SPECIFIC HEATS OF 80 SOLIDS. METHODS BASED ON; v. ATOMIC AND MOLE-CULAR WEIGHTS, vol. i. p. 342.

XI. THERMAL METHODS. Determinations of the quantities of heat which are produced, or which disappear, in chemical reactions help to elucidate the nature of these reactions. There are two sides to every chemical operation; there is a change in the form or distribution of matter, and a change in the form or distribution of energy. Light is thrown on the second of these changes by thermo-chemical investigations, and the connections between the two parts of the complete occurrence, and the mutual dependence of both, are thus made clearer. Thermo-chemical methods rest on the principle of the conservation of energy. When a chemical reaction occurs, heat may be produced, electricity generated, mechanical work done by expansion, and sound or radiant heat may leave the system; the sum of these forms of energy, added to the energy remaining in the system at the close of the reaction, must equal the energy originally present in the system at the moment when the change began. As a large part of the energy set free during any chemical reaction usually takes the form of heat, it follows that measurements of the heat produced during the reaction must give information regarding the differences between the initial and final energies of the system. The primary aim of thermo-chemical measurements is to determine such energy-differences; the secondary aim is to connect these differences with the differences of composition, constitution, and properties which the reacting systems undergo.

The loss or gain of energy which accompanies the passage of a system from one defined state to another is independent of any intermediate states through which the system may pass. This generalisation was proved experimentally for several cases, so far as heat energy was concerned, by Hess in 1840 (P. 50, 885); the generalisation may be deduced from the principles of energy. On this statement rest the methods for determining the thermal values of chemical changes when these values cannot be observed directly.

Notation used in thermo-chemistry. Thom sen's notation is followed in this DICTIONARY; the formulæ of the reacting substances are taken to represent grams of these substances-thus HCl means 36.5 g. of hydrogen chloride; the formula are inclosed in a square bracket, and the figures representing the number of atoms of each ele-

ment are placed above the symbols; the reacting substances are separated by a comma. The unit of heat is that quantity which raises the temperature of 1 g. of water at c. 18° through 1°. Ostwald, in his Lehrbuch der Allgemeinen Chemie, employs a unit almost exactly 100 times greater than this, viz. the quantity of heat given out by 1 g. of water in cooling from 100° to 0°. The symbol Aq means that a large quantity of water is present. Thus [H,Cl] = 22,000 means that 22,000 gram-units of heat are produced when 1 g. H combines with 35.5 g. Cl; [H,Cl,Aq] = 30,660 means that 30,660 gramunits of heat are produced when 1 g. of H combines with 35.5 g. of Cl in presence of a large quantity of water in which the HCl dissolves; [HCl,Aq] = 17,320 means that 17,320 gramunits of heat are produced when 36.5 g. of HCl dissolve in a large quantity of water; and [HClAq,KOHAq] = 13,750 means that the neutralisation of 36 5 g. HCl, dissolved in much water, by 56 g. KOH, dissolved in much water, the products of neutralisation being allowed to remain in solution, is accompanied by the production of 18,750 gram-units of heat. The symbol H.O is used as in ordinary notation to represent 18 g. of water; thus [As O,3HO] = 6,800 means that 6,800 gram-units of heat are produced during the formation of 284 g. H₂AsO₄ by the combination of 230 g. As₂O₅ with 54 g. water; and $[As^2O^3.3H_*O,Aq] = -800$ means that 800 gram-units of heat disappear during the solution of 284 g. H, AsO, in a large quantity of water. Thomsen's notation does not indicate the products of the reaction, the thermal value of which is set down; nor does it show the physical states of the reacting substances, or of the products of the reaction, except in the one case when the substances are dissolved in much water. Ostwald (Lehrbuch) uses the ordinary notation, and adds figures to express the quantities of heat which are produced or disappear in the reactions; he employs ordinary type for liquids, thick type for solids, and italies for gases. Thus, $H_2 + Cl_2 = 2IICl + 44,000$ means gases. Thus, $H_2 + Cl_2 = 2HCl + 44,000$ means that 44,000 gram-units of heat are produced when 2 g. gaseous hydrogen combine with 2 x 35.5 g. gaseous chlorine to form 2 x 36.5 g. gaseous hydrogen chloride; $2H_2S + 2I_2$ = 4HI + 2S - 34,000 means that 34,000 gram- $2H_2S + 2I_2$ gaseous units of heat disappear when 2×34 g. gaseous hydrogen sulphide react with 2×254 g. solid iodine to form 4×128 g. gaseous hydrogen iodide and 2 × 32g. solid sulphur; and 2H2SAq + 2I2Aq = 4HIAq + 2S + 34,000 means that 34,000 gram. units of heat are produced when 2 × 34 g. hydrogen sulphide dissolved in much water react with 2 × 254 g. iodine dissolved in much water, to form a dilute aqueous solution of 4 x 128 g. hydrogen iodide, and 2×32 g. solid sulphur. Ostwald sometimes indicates the temperature by figures in brackets placed after the formula of the substances: thus, $H_2O_{(0)} = H_2O_{(0)} + 1440$ means that

1440 gram-units of heat are produced when 18 g. liquid water at 0° become 18 g. solid water at the same temperature.

Measurements of thermal values of chemical changes. The quantities of heat produced during shemical processes are measured by causing the processes to take place in vessels arranged so it is known at another temperature, s. 72.1, 60-72. changes. The quantities of heat produced during

that the whole of the heat is used in raising the temperature of known masses of water, or of water and a solution the specific heat of which is known. When the process consists in a reaction between substances in aqueous solutions, the calorimeter employed usually consists of a vessel of platinum holding 500 to 1000 c.c. placed inside another vessel of silver, or thin sheet iron, with water between the two vessels. The reacting liquids are brought to the same temperature, and are then mixed in the platinum vessel, and the rise of temperature of the contents of this vessel is noted, any change in the temperature of the outside water being also measured. When the thermal value of a process of combustion is to be determined, the combustion is caused to proceed in a vessel, usually made or platinum, surrounded by a determinate quantity of water; if the products of combustion are gases, an apparatus is attached wherein these gases are absorbed, and thus the quantity of substance burnt is. determined.1

To calculate the thermal value of a reaction. it is necessary to know the initial temperatures of the reacting bodies, the final temperatures of the products of reaction, the masses of the reacting substances, the specific heat of water, the specific heat of the liquid formed by the reaction if the reaction be one wherein a solution is produced, and the water-equivalent of the calorimeter. The water equivalent of the calorimeter must be determined; it is equal to the number of unitweights of water which would be raised to the same temperature as that to which the calorimeter and its accessories-thermometer, stirrer, &c .- are raised by the heat produced in the process. When dilute solutions of acids and alkalis, or similar compounds, react, the specific heat of the dilute salt-solutions produced may be taken as equal- to the specific heat of the water they contain, without appreciable errors.

Let Q be the quantity of heat produced in a reaction between two solutions; let t be the initial temperature of one solution, t' the initial temperature of the other solution, and T the final temperature of the solution produced; further, let a be the calorimetric equivalent of one solution, i.e. mass x spec. heat, b the calorimetric equivalent of the other solution, and c the water-equivalent of the calorimeter; then

Q = (T - t)a + (T - t')(b + c).In the cases of dilute aqueous solutions, a and b represent the masses of water in the solutions mixed. If a change occurs in the state of aggregation of some of the constituents of the reacting system, e.g. if liquid water is formed from gaseous hydrogen and oxygen, the quantity of heat which is produced or disappears in this change must be taken into account in the calculation of the thermal value of the reaction. If contraction or expansion occurs, without change of state, the thermal value of such contraction or expansion must be determined and allowed for.3

Heats of combustion, and of formation, of compounds. The heat of combustion of an element or compound is the thermal value of the reaction which takes place when that element or com-

pound is completely oxidised to those masses of the product, or products, of exidation which are represented by the formulæ of these products. Thus $[H^2,O] = 68,360$; [CO,O] = 67,960. In this Dic-TIONARY the quantities represented by formulæ are taken in grams.

The heat of formation of a compound is the thermal value of the reaction whereby the formula-weight of the compound is produced from the formula-weights of its constituents. Thus, the heat of formation of ILSO, varies according to the constituents from which it is produced; we have the following statements: [SO3,HO] = 21,320; $[SO^2,O,H^2O] = 53,480$; $[SO^2,O^2,H^2] = 121,840$; $[S,O^3,H^2O] = 124,560$; $[S,O^1,H^2]$ = 192.920.

It is often practicable to measure heats of combustion directly; but in very many cases it

[KOHAq,HClAq] = -[K,O,H,Aq] - [H,Cl,Aq] + [K,Cl,Aq] + [H,H,O,Aq];

is necessary to determine heats of formation by indirect methods. These indirect methods rest on the principle, deduced from the laws of energy, that the total change of energy, and therefore the total thermal change, which accompanies the passage of any system from a definite initial composition to a definite final composition is independent of the intermediate states. Suppose that a system changes from a certain arrangement or configuration A to another configuration B, and that x units of heat are produced in this change. Suppose also that the same initial system then passes from the state A to a new state a, from that to b, from that to c, and, lastly, from that to B, and that there are x' units of heat produced in the first of those intermediate changes, x" units produced in the second, and x" units in the third; then x - (x' + x'' + x''') gives the thermal value of the change from the state c to the state B. If then the thermal value of a chemical process, whether the formation of a compound, or other process, cannot be determined by direct measurement, it may be determined if the process can be made a portion of a series of changes, the total thermal value of which is measurable, and the thermal values of all the portions of which are measurable with the exception of the value of that portion which is sought.

For instance, formic acid, CH,O; cannot be directly produced from C, H, and O, and, therefore, the heat of formation of this acid cannot be determined by direct measurement; but C and H can be burnt to CO₂ and H₂O, and CH₁O₂ can also be burnt to CO₂ and H₂O; hence we can acquire the data needed for calculating the value of [C,H²,O²]. The data are these: [C,O²] = 96,960; [H²,O] = 68,360; sum = 165,320; [CH²O²,O] = 65,900. Now, suppose that the first stage of the combustion of C and H, consists in the formation of CII,O2, and that this is then burnt to CO, and H,O, we should have the statement: $[C,O^2] + [H^2,O] = [C,H^2,O^2] + [CH^2O^2,O] = 165,320$. But $[CH^2O^2,O] = 65,900$; and also $[C,O^2] + [H^2,O] - [CH^2O^2,O] = [C,H^2,O^2]$. Hence $[C,H^2,O^2] = 165,320 - 65,900 = 99,420$.

Another example will show the application of the principle to a more complicated case. It is required to find the heat of formation of gaseous hydrogen bromide from gaseous H and Br, i.e. the thermal value of the reaction H + Br = HBr. To begin with: let [H,Br,Aq] = x, and let [H,Br]=x'; direct measurement gives [HBr,Aq] = 19,900. x-19,900=x'=heat of formation of HBr. Hence it is necessary to determine x.

Now, the thermal values of the neutralisation of HClAq and HBrAq respectively by KOHAq are found to be the same, i.e. [KOHAq,HClAq] =[KOllAq,HBrAq]. If these reactions are analysed, the first is seen to consist in (1) the splitting of HClAq into H and Cl in presence of water; (2) the separation of KOHAq into K, O, and H in presence of water; (3) the combination of K and Cl, in presence of water, to form KClAq; (4) the combination of II, H, and O, in presence of water, to form water; and the second is similar to this, only putting Br in place of Cl. These reactions may be stated in thermo-chemical notation thus:

(2) [KOHAq, HBrAq] = -[K, O, H, Aq] - [H, Br, Aq] + [K, Br, Aq] + [H, H, O, Aq].

The first and fourth terms on the right side are the same, and the total thermal values are the same. Are the values of the second and third terms the same? To answer this question we pass Cl into KBrAq, forming KClAq and BrAq, and measure the thermal disturbance; we then analyse the reaction, and see what information it has afforded. These are the results:

[KBrAq,Cl] = 11,500, i.e. -[K,Br,Aq] + [K,Cl,Aq] + [Br,Aq] = 11,500. Now, [Br,Aq] = 500, by direct measurement, [Er,Aq] = [K,Br,Aq] + [K,Cl,Aq] = 11,000, i.e. to form KCl, in solution, from K and Cl produces 11,000

units of heat more than to form KBr, in solution, from K and Br.

Now, turning back to equations (1) and (2) above, and remembering that the thermal values of these are the same, it is evident that, since 11,000 more heat-units are produced in forming KClAq than in forming KBrAq, each from its elements, 11,000 more heat-units must disappear in splitting up HCl, in presence of water. into H and Cl, in presence of water, than in similarly separating HBr into H and Br in presence of water; and therefore, since the heat energy required to decompose a stated mass of a compound is equal to the heat energy that is produced when the same mass of that compound is formed, 11,000 more heat-units will be produced in the formation of HClAq from H, Cl, and Aq than in the formation of HBrAq from H, Br, and Aq; or, stated in thermo-chemical notation: [H,C],Aq]=11,000=[H,Br,Aq]. Now [H,C],Aq]=39,300 by direct measurement, $[H,Br,\Lambda q] = 39,300 - 11,000 = 28,300.$

At the beginning of this calculation we had H.Br.Aq]-19,900 = [H.Br]. We can now substitute the value of [H.Br,Aq], and write [H.Br]=28,300-19,900=8,400. That is to say, 8,400 gram-units of heat are produced when 81 g. gaseous hydrogen bromide are formed from 1 g. gaseous hydrogen and 80 g. gaseous bromine. Exothermic and endothermic reactions. Chemical changes which are accompanied by production of heat are sometimes classed together as exothermic reactions, and are distinguished from changes accompanied by disappearance of heat, which changes are called endothermic reactions. The terms endothermic and exothermic are sometimes useful. It should not be forgotten that most chemical reactions consist of portions which are exothermic and portions which are endothermic. Substances which are formed with the disappearance of heat are generally more readily decomposed by the application of outside forces than substances which are formed with the production of heat.

Interpretation of thermo-chemical measurements. Thermo-chemical measurements aim at determining the quantities of heat which are produced or disappear during definite and defined chemical changes. But every chemical change is inextricably bound up with more or less extensive physical changes; hence some portion of the thermal value of a chemical occurrence is always due to a process which is not, strictly speaking, chemical. A purely chemical change is a change in the distributions, configurations, and motions of atoms. But in only some cases are we able to form clear conceptions as to the configurations and motions of atoms; therefore, even if it were possible always to disentanglethe purely chemical from the accompanying physical parts of a change, we should still very frequently be unable to connect the thermal values of purely chemical processes, in a clear and definite

way, with measurable changes in the distribu-

tions, configurations, and motions of atoms.
The heats of formation of HCl, HBr, and HI
are said to be 22,000, 8,440, and -6,050 gramunits respectively. But these thermal values
are not strictly comparable, because the first represents the heat produced in forming gaseous
HCl from gaseous H and Cl; the second represents the heat produced in forming gaseous HBr
from gaseous H and liquid Br, and the third represents the heat which disappears when gaseous
HI is formed from gaseous H and solid I. In
other words, more heat is used in the second
change than in the first, and still more in the
third than in the second, in accomplishing subsidiary physical changes. Steam is decomposed
by chlorine, with formation of hydrogen chloride
and oxygen. All the reacting substances are
gases. This change, which is stated in formule
as 2H₂O+2Cl₂=4HCl+O₂, when analysed
thermo-chemically, is found to consist of four
parts, thus: [2HO,2Cl²]
= -2(H,H,O)-2[Cl,Cl]+ {O,0}+4[H,Cl],

= -2[H,H,0] -2[OI,CI] +[O,0] +4[H,CI]. We measure the thermal value of this complete change, but we cannot at present separate the portions of the change and assign to each its proper thermal equivalent; hence we cannot give a complete explanation of the thermochemical measurement we have made.

Notwithstanding these difficulties, attempts have been made to generalise from thermochemical measurements to statements of universal applicability. The most widely known of such attempts is that which finds expression in Berthelot's 'law of maximum work.'! This so-called law asserts that 'Every chemical change accomplished without the addition of energy from without tends to the formation of that body, or system of bodies, the production of which is accompanied by the development of the maximum quantity of heat.' In another place Berthelot states the law more rigidly, thus: 'Every chemical change which can be accomplished without

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the aid of a preliminary action, or the addition of energy from without the system, necessarily occurs if it is accompanied by disengagement of heat."

The same generalisation was stated by Thomsen (v. Th. 1, 12-16) some years before it was enunciated by Berthelot. Thomsen's statement took this form: 'Every simple or complex reaction of a purely chemical kind is accompanied by production of heat.' None of these statements is strictly applicable to actually occurring chemical changes, because we never have to deal with reactions of a purely chemical kind, but with reactions that are partly chemical and partly physical-that is, with reactions which consist in part in changes in the arrangement and motions of atoms, and partly in changes in the arrangement and motions of molecules. A consideration of the way in which the so-called law is applied, especially by Berthelot and his school, shows that it is taken to mean that measurements of the thermal values of various possible chemical changes enable us to predict which of these will occur. Thus, suppose we start with a system A + B + C, and suppose that from this may be formed AB+C, AC+B, or ABC; suppose also that x thermal units are produced in the first of these changes, x' thermal units in the second, and x" thermal units in the third; finally, suppose that x'' > x' > x; then the law of maximum work is taken as asserting that the reaction A + B + C = ABC will occur, and will occur to the complete, or almost complete, exclusion of the two other possible reactions.

It is easy to show that many reactions are known to occur which would be impossible were this 'law' a true generalisation. But it is better to treat the law as a deduction from the principles of energy, and to show that it is not a warrantable deduction.

The statements made by Thomsen and Berthelot are true only when an arbitrary separation is made of chemical changes into two parts, and one of these parts is alone called chemical. Every chemical change, however simple, consists of at least two parts, the first of which is the necessary antecedent of the second; the 'law of maximum work' ignores this duality, or, it might be more accurate to say, the law assumes that the second part of a chemical process may occur without the first. A process of chemical change may be compared to the flight of a stone from, and its return to, the surface of the earth. During the first part of this process there is a continual transference of kinetic energy from the moving stone to the surrounding medium and during the second part there is a continual transference from the medium to the stone, until the stone comes to rest, when its energy becomes a part of the total energy of the system earth plus stone. If the final resting-place of the stone is nearer the centre of the earth than the spot from which it was projected in its upward flight, then the stone contains less energy, relatively to surrounding systems, at the close of the trans-action than at the beginning. On the other hand, if the starting-point is nearer the earth's centre than the final point of rest, then the transaction has resulted in a gain of energy to the stone. In both cases the second part of the transaction, that which occurs between the turnIng-point and the coming to rest of the stone, is attended with loss of energy to the stone; but this second part does not represent the complete transaction. The 'law of maximum work,' if applicable at all, is applicable only to the second part. And, moreover, this law ignores the fact that the stone, or chemical system, does not leave its initial resting-place of its own accord; the law assumes that no work need be done, no energy need be expended, in the passage of the stone, or chemical system, from its original position to that whereat the energy-relations between it and surrounding systems come within the cognisance of the law.

The 'law of maximum work' asserts a certain condition of equilibrium for a chemical system, for the law states that equilibrium results when that change has occurred which is attended with the maximum production of heat. But the true condition of equilibrium of a material system undergoing a reversible change is laid down in the statement that equilibrium results when the entropy of the system has attained the maximum value under the conditions which prevail.

Let Q = quantity of heat added to a body at constant temperature T, then $\frac{Q}{T}$ = gain of entropy to the body; let Q_1 = quantity of heat lost by a body at constant temperature T_1 , then $\frac{Q_1}{T_1}$ = loss of entropy to the body. All chemical and physical changes which occur spontaneously increase the entropy of the system. This statement holds good for non-reversible changes; and as no actually occurring change is completely reversible, the statement holds for all changes.

Suppose that one of two bodies is lotter than the other and loses heat to the colder body; the hotter body at temperature T_1 loses, heat Q, therefore its entropy is diminished by $\frac{Q}{T_1}$; the colder body at temperature T_2 gains heat Q, therefore its entropy is increased by $\frac{Q}{T_2}$; but as $T_1 > T_2$, it follows that $\frac{Q}{T_1} < \frac{Q}{T_2}$; in other words, the entropy of the system is increased by the passage of heat from the hotter to the colder

body. Now, a system is in equilibrium when its entropy has attained the maximum value possible under the conditions. But, inasmuch as entropy is measured by a quantity of heat divided by a temperature, it is only at the absolute zero of temperature that dS=dQ (S=entropy, Q=quantity of heat); hence it is only at the absolute zero that thermal changes directly measure changes of entropy. When a chemical change is accompanied by the production of much heat, and the change occurs at a low temperature, the thermal change will roughly measure the change of entropy; therefore, if such a change be possible, it will occur. But if the quantity of heat produced in a chemical process is small, the change of entropy may be conditioned, to a large extent, by changes other than the thermal change. Indeed, in some cases, heat may disappear from the system, and yet the total change of entropy may be positive; in such cases, chemical change will occur with the disappearance of heat, because the decrease in the entropy of the system caused by the loss of heat will be more than balanced by the increase in the entropy caused by the changes of state which the system undergoes.

The general conception of chemical change which is given by applying the law of entropy is that of a system attaining equilibrium as the result of processes taking place in opposite directions. According to van't Hoff (Dynamique Chimique, 153), the directions of chemical processes which result in equilibrium vary with variations of temperature in such a way that the lower the temperature the more is equilibrium established with the production of heat, but the changes can take place wholly in one direction only at the absolute zero. The law of maximum work' would then hold good for the limiting case that the changes should occur at -273°. As the temperatures at which most chemical changes occur are not very high, many chemical processes are accompanied by production of heat.

The 'law of maximum work' is not, then, a law of nature. But it is true that most chemical processes which occur without the expenditure of much energy from without, and which take place at moderate temperatures, are accompanied by the disengagement of heat. If it is known that a certain chemical change would be attended by the disappearance of much heat, we may conclude that this change will be difficult to accomplish; that it will be brought about only by the expenditure of a considerable quantity of energy, and that the most successful way of accomplishing the change will be to make it one part of a series of changes the sum of which is attended with the disengagement of heat.

Applications of thermo-chemical methods.
The applications of thermo-chemical methods are many and varied. A few of the more important

will be briefly dealt with here.

Neutralisation of acids and bases. In 1842 Hess stated the principle of the thermo-neutrality of salts in solutions (P. 52, 79). He said that when aqueous solutions of two normal salts are mixed the thermal disturbance is nil; in other words, that the thermal value of the reactions consisting in the exchange of the acids and bases is equal to zero. Hess supposed that the heats of neutralisation of acids were independent of the nature of the bases used. Andrews (P. 54, 208; 59, 428) thought that the heats of neutralisation were dependent only on the bases, and were independent of the nature of the acid employed. Favre a. Silbermann (A. Ch. [3] 34, 357; 36, 1; 37, 406) put the law of thermo-neutrality in its proper form by showing that the differences between the heats of neutralisation of any two bases by any acid have a constant value, and the differences between the heats of neutralisation of two acids by any base are constant. Let the composition of various salts be represented by the scheme :

A" + B A"' + B $\mathbf{A} + \mathbf{B}$ A' + BA"+B' A"+B" A' + B' A' + B" A''' + B' A''' + B'' A + B'A + B" A + B" A' + B"' $\tilde{A}'' + \tilde{B}'''$ $\overline{A'''} + \overline{B'''}$ And let f(A + B), f(A' + B), &c., represent the quantities of heat produced by the union of the acid A with the base B, the acid A' with the base B, &c. Then the law of thermo-neutrality asserts that

$$f(A + B) + f(A' + B') - f(A + B') - f(A' + B) = 0$$
or $f(A + B) - f(A + B') = f(A' + B) - f(A' + B')$
and $f(A + B) - f(A' + B) = f(A + B') - f(A' + B')$

Exceptions have been found to this law, but these exceptions have all proved to be connected with some abnormality in the behaviour of the salts formed. The law may be stated by saying that, in the normal formation of a salt, in solution, by the reaction between an acid and a base, the acid contributes a definite portion of the total heat of neutralisation, independently of the nature of the base, and the base contributes a definite portion of the total heat of neutralisation, independently of the nature of the acid. If the statement is correct, then the heat of neutralisation of an acid, in solution, must be independent of the nature of the base, and the heat of neutralisation of a base, in solution, must be independent of the nature of the acid, unless there be some divergence from the normal condition of affairs. By the heat of neutralisation of an acid is meant the quantity of heat produced when an equivalent weight of the acid reacts with an equivalent weight of a base, both being in dilute aqueous solution. If A' represents a formula-weight of a monobasic acid, A" a formula-weight of a dibasic, and A" a formulaweight of a tribasic, acid; and if B represents a formula-weight of a mono acid base; then the heats of neutralisation of these three acids are the thermal values of the reactions,

[A'Aq,BAq]; [',A''Aq,BAq]; and [',A'''Aq,BAq]. Sometimes it is more convenient to take the thermal values of the reactions [A''Aq,2BAq] and [A'''Aq,3BAq] to represent the heats of neutralisation of the dibasic and tribasic acids respectively.

The following table, taken chiefly from Thomsen's results, shows that the heats of neutralisation of the strong acids are practically independent of the base, provided the base used is strong; the numbers all refer to reactions between dilute solutions of the acids and bases:—

Acid	NH,	NMe,	NH,OH	
HCl HNO _s	12,200 12,300	8,700	9,200	

When weak acids neutralise strong bases, the thermal values differ from those obtained for strong acids; and when weak acids neutralise weak bases the reactions have different values from any of the preceding cases. The following numbers illustrate this:

Acid	NaOH strong	NH, weak base	
₹ { CO₂Aq	10,100	10,900	8,400
	7,700	7,800	6,200

The electrolytic dissociation hypothesis gives an explanation of the facts concerning the thermo-chemical reactions between acids and bases. According to this hypothesis, a dilute aqueous solution of a salt contains the ions of the salt each with its electric charge; the salt is dissociated into its ions; when two dilute salt solutions are mixed, the ions remain as they were, there is no change, and therefore heat is neither produced nor consumed. The law of thermo-neutrality holds. The hypothesis looks on a dilute aqueous solution of a strong acid, or a strong base, as containing the ions of the acid or the ions of the base; when the solutions of the strong acid and strong base are mixed, a salt is not formed in the solution, because in dilute solutions salts are wholly dissociated, but water is formed by the union of the ion H of the acid with the ion OH of the base. Thus, the composition of dilute solutions of HCl and NaOH. before and after mixing, are represented by the hypothesis as follows:

Acid	NaOH	кон	Lioit	TIOII	BaO,H,	łСаО.Н,	lSrO,Π,	Pt(NH ₃),(OH),	S(C,H,),OH	N(CH,)OH
HCI	13,300	13,300	13,300	13,300	13,300	13,300	13,300	13,600	13,700	13,600
HBr HI	13,300	13,300 13,300	-	-			-	=	=	=
HNO. HClO.	13,500 13,600	13,500 13,600	=	13,500	14,000 14,000	13,900	-	=	=	=
HBrO. HIO. HOIO.	13,600 13,600	13,600 13,600	=	=	=	=	_	_	=	=
HOIO.	14,000 13,500	14,000	_	=	13,800	=	_	=	=	=
H.S.O. H.PtCl. H.O.H.SO.	13,600 13,500	=	=	=	13,600	=	_	_	=	

If concentrated solutions are employed, the heats of neutralisation, even of the strong acids, show considerable differences with different bases. If the salt which is formed by neutralising an acid by a base is allowed to precipitate, then the apparent heat of neutralisation as thus determined is not the true heat of neutralisation (v. Th. 1, 440). The following numbers represent the heats of neutralisation of two strong acids by weak bases; these numbers differ from one another, and also from the values given in the preceding tables in which strong acids and strong bases only were included;

Or, generally, if M represent the positive ion of a strong base, and A the negative ion of a strong acid; we have the composition of the dilute aqueous solutions, before and after mixing, ropresented by the two schemes:

$$M + OH + H + A$$
 and $M + A + HOH$

Hence, as the only process wherein heat can be produced consists in all cases in the union of H with OH, the quantity of heat produced is always the same. The hypothesis asserts that HOH is produced because water is a non-dissociable, or nearly a non-dissociable, compound; pure water is, approximately, a non-electrolyte.

But when a weak acid is mixed, in dilute aqueous solution, with a strong base, or when dilute solutions of a weak acid and a weak base are mixed, the processes are more complex; for, according to the hypothesis, only a portion of the weak acid is dissociated into ions, and only a portion of the base is dissociated if the base is weak. In such cases the state of matters, before and after mixing, would be represented thus (supposing both acid and base to be weak)—

$$\frac{\text{HA} + \overset{+}{\text{H}} + \overset{-}{\text{A}} + \text{MOH} + \overset{+}{\text{M}} + \text{OH}}{\text{before inixing}}$$
and
$$\frac{\text{HA} + \text{MOH} + \overset{+}{\text{M}} + \overset{+}{\text{A}} + \text{HOH}}{\text{after mixing}}$$

But the process does not necessarily stop here; there is a striving towards the formation of the comparatively non-electrolytic compound HOH, therefore more of the acid and more of the base become dissociated, so that we have, as a final condition, less or more of the acid HA, and less or more of the base MOH, remaining in the solution. The dissociation of the acid and the base, when these are mixed, is accompanied by a thermal change; and as the degree to which this dissociation proceeds depends on the nature of the acid and the base, the values of the heats of neutralisation of weak acids and weak bases differ one from another (cf. Electrical Methods, p. 189 in this vol.).

If this treatment of the heats of neutralisation of acids and bases is accepted, it is evident that the thermal values of the neutralisations of acids by a base do not necessarily measure the affinities of these acids for that base. If the acids were all equally dissociated in solution, they would all be equally strongor their affinities would be equal-and their heats of neutralisation would be equal. The statement Q = about 13,500 + A + B expresses the heat of neutralisation of any acid by any base in dilute aqueous solution. A represents the heat of dissociation of the acid, and B is the heat of dissociation of the base, into their ions; A and B may be positive or negative at any specified temperature. Under the conditions of the experiment only a portion of the acid, or of the base, may be dissociated; therefore the observed heat of neutralisation cannot measure the affinity of the acid for the base. But at the same time, it is evident that there is a connection bctween the heats of neutralisation and the affinities of acids and bases. On the one hand, measurements of the thermal values of the reactions between acids and bases enable conclusions to be drawn as to the distribution of two acids between one base, or two bases between one acid, and such measurements therefore lead to determinations of the affinities of acids and bases (v. infra); on the other hand, although the affinity of an acid for a base probably consists in a striving towards electrical equilibrium among the ions, yet, as electrical and thermal phenomens are closely connected, measurements of the heats of dissociation of acids and bases, in aqueous solutions, must help us to understand the relative affinities of acids and bases, to classify acids and bases in accordance with their affinities, and to connect the affinities of these substances with their constitution (cf. Electrical Methods), especially pp. 208 and 209).

Monobasic and polybasic acids. When an equivalent of a monobasic acid is added to an equivalent of a base, both in dilute solutions, a certain quantity of heat is produced, and there is no further thesmal disturbance on adding more of the acid to the neutral solution; but heat is either produced or disappears when a polybasic acid is added to a solution of the same acid which has been neutralised by an equivalent quantity of a base. This behaviour enables a thermo-chemical distinction to be drawn between monobasic and polybasic acids (cf. Actus, Basicity or, yel. i. p. 51).

Basicity or, vol. i. p. 51).

Distribution of an acid between two bases.

Thomsen found the following data:

[H²SO¹Aq,2NaOHAq] = 31,380; [2HNO³Aq,2NaOHAq] = 27,230;

 $[Na^2SO^4Aq, 2HNO_3Aq] = -8,500.$ Now, supposing that the reaction of equivalent quantities of Na₂SO₁ and HNO₃, in dilute solution, produced NaNO, and H.SO,, and these compounds only, this reaction would be attended by the disappearance of 31,380 - 27,230 = 4.150 thermal units; but as only 3,500 thermal units disappear in the reaction, it is evident that some change has occurred wherein heat has been produced, or that the whole of the Na SO, has not been changed to NaNO, by the reaction of the equivalent quantity of HNO,. If we suppose that the discrepancy in the quantity of heat consumed is due to the partial decomposition of the Na SO₄ by the IINO₃; in other words, if we suppose that when equivalent quantities of Na SO, and HNO, react in solution, some of the base remains united with the II,SO, and some goes into combination with the HNO, and that no other reaction occurs, it is easy to calculate the distribution of the base between the two acids. For it is evident that, on this supposition, 8500 4150 = 845 of the quantity of Na_zSO₄ present

statement $[nH^*SO^*Aq, Na^*SO^*Aq]$ = 31,380 - $\frac{n}{n+8}$ 3,300. These data give a means for calculating the distribution of the base between the two acids. The complete reaction between equivalent quantities of Na,8O, and HNO, will consist of three parts: (1) the decomposition of a equivalents of Na,8O, attended with the disappears of a. 31,380 thermal units; (2) the formation of a equivalents of NaNO, attended with the production of a. 27,230 units of heat; (3) the reaction of a equivalents of H,SO, with 1-a equivalents of Na,SO, attended with the disappearance of

has been decomposed. Thomsen found that II,SO, reacts with Na,SO, to form NaHSO, with disappearance of heat. He also found that this

reaction is expressed thermo-chemically by the

led with the disappearance of
$$1-a = \frac{\frac{a}{1-a}}{1-a} 8,800 \text{ units of heat.}$$

The complete thermo-chemical change may be stated thus:

[Na²SO¹Aq,2HNO¹Aq] = -3,500
=
$$a(27,230-31,380)-(1-a)$$
 $\frac{a}{1-a}$ 3,300.
 $\frac{a}{1-a}$ + '8

Thomsen found that if a is taken as $\frac{2}{3}$, the number - 3550 is obtained, which is almost identical with the observed value. Hence Thomson concluded that $\frac{3}{3}$ of the base, NaOH, went to the nitric acid, and $\frac{1}{3}$ to the sulphuric acid; or, that the affinity of nitric acid for soda (Thomsen used the term avidity) is twice as great as the affinity of sulphuric acid for the same base.

The relative affinities of various acids for different bases have been measured by Thomsen by this method (v. Affinity, vol. i. pp. 74-75).

Allotropy and isomerism. The generally

accepted views regarding the allotropy of ele ments and the isomerism of compounds would lead us to expect that the formation of one allotropic form of an element from another form, or the formation of one isomeride from another, should be accompanied by changes of energy, and, therefore, probably by the produc-tion or disappearance of heat. This expectation is confirmed by thermo-chemical measurements. The following tables present some typical data:-

Combustion of allotropic forms of sulphur,

phosphorus, and carbon. [8,0"] to form gaseous SO2 71,220 for S crystallised from CS, 71,720 rhombie S 72,300 native opaque S [P2,O3] to form solid P.O 369,500 ordinary P for 362,800 red P [C,O²] 96,900 to form gaseous CO, amorphous C for 93,200 diamond Combustion of isomeric carbon compounds.

[C'H',O's] to form 6CO, + 3H,O 787,900 for benzene 883,200 dipropargyl [C2H6O,O5] to form 2CO, +3H,O 330,400 ethylic alcohol for 344.200 methylic ether [C⁹H⁴O,O⁸] to form 3CO $_2$ + 3H $_2$ O

allyl alcohol

propaldehyde

acetone

for

442,600

424,000

420,000

These values, and many more might be given, show that the quantity of heat produced in the change from the combination of a certain number of atoms to certain other combinations of these atoms is dependent, in part, on the arrangement of the atoms in the initial combination. Isomeric molecules differ in the arrangements of their parts; and they also differ in the quantities of energy which are associated

with the different atomic arrangements. The attempts which have been made, chiefly by Thomsen (v. Th. vol. iv.), to connect in a definite way the thermal values of the combustion and formation of carbon compounds with

the constitutions of these compounds have not led, as yet, to any very satisfactory results (v. also Armstrong's criticism of some of Thomsen's conclusions; P. M. Feb. 1887. 73).

Dissociation.—This very important branch

of the subject is fully discussed in the article Dissociation in vol. ii. pp. 385-410.

References.

I. Descriptions of apparatus.

BERTHELOT, Essai de Mécanique Chimique, vol. i. Book ii. and Supplt.; also A. Ch. [5] 23, 160.

THOMSEN, Th. 1, 18, 27; 2, 8, 45, 68, 305, 339; 3, 222, 349; 4, 15.

FAVRE 8. SILBERMANN, C. R. 66, 788; 73, 717; also A. Ch. [3] 31, 359; 36, 44.

Bunsen, P. 141, 1; also in connection with Bunsen's ice-calorimeter v. B. 8, 1011; 10, 1298; 11, 385; 12, 744; and W. 13, 85.

Andrews, P. M. [3] 32, 321.

Frankland, P. M. [4] 32, 182.

STOHMANN, J. pr. [2] 19, 115; 39, 503.

Pickering, P. M. [5] 29, 247. Petersen, Z. P. C. 8, 601 (special app. for studying certain allotropic changes).

II. General principles and methods.

Hess, A. 31, 79 (1839); P. 50, 385 (1840).

GRAHAM, C. S. Mem. 1, 106 (1842).

Andrews, T. 1818; P. M. [3] 32, 321 (1848). Woods, P. M. [4] 2, 268; 3, 43, 299; 4, 370 (1851-52).

FAVER B. SILDERMANN, A. Ch. [3] 34, 357; 36, 1; 37, 406 (1852-53).

Berthelot, Essai de Mécanique Chimique, fonde sur la Thermochimie, 1879 (with supplement).

Thomsen, Thermochemische Untersuchungen (1882-86).

Jahn, Die Grundsätze der Thermochemie (1882). NAUMANN, Lehr- und Handbuch der Thermo-

chemie (1882).

Nutr. The Elements of Thermal Pattison Muir, Chemistry (1885).

OSTWALD, Lehrbuch der Allgemeinen Chemie, vol. ii. book i. (1887; 2nd edition, 1892-93). M. M. P. M.

XII. VAPOUR-PRESSURES OF SOLU-TIONS, METHODS BASED ON, v. MOLECULAR WEIGHTS, vol. iii. p. 420; ELECTRICAL METHODS,

this vol. p. 185; and Solutions, this vol.
XIII. VISCOSITY OF LIQUIDS. A per fect fluid, if such existed, would offer no resistance to a change of shape, and if its parts were set in motion relatively to each other by the action of any forces, the work done would be exactly equal to the kinetic energy produced. Moreover, this energy of motion would continue unchanged in amount if the fluid were then left to itself, and would not die away by being converted into heat as is the case with every known fluid. The property which causes this subsidence of relative motion is called viscosity. In consequence of the existence of viscosity a continual expenditure of energy is required to maintain the parts of a fluid in a state of steady motion relatively to each other, just as the existence of friction makes it necessary to apply a constant force to a body to keep it moving uniformly over another. From this resemblance in the two

cases the viscosity of a substance is often called its internal friction.

Imagine a layer of a liquid one cm. thick, contained between two flat plates, one of which is at rest and the other is moving parallel to the first. The liquid in contact with the plate which is at rest is at rest also, and the successive layers have velocities which increase uniformly as we go towards the moving plate, so that the liquid is being sheared, and this requires a continual supply of work; which is proportional to the area and velocity of the moving plate. If this velocity is one cm. per second, the coefficient of viscosity is defined as the tangential force which must be applied per sq. cm. to the moving plate to maintain the motion, or if the relative velocity of the two surfaces is v, and their distance apart is l, the tangential force T per unit area required

to maintain the motion is given by $T = \eta_l^v$ where η is the coefficient of viscosity.

From this definition it can be proved that if a circular plate or other solid of revolution be set vibrating about its axis of figure in a liquid, the amplitudes of successive vibrations will bear a constant ratio to each other, and the experimental verification of this is the best proof we have of the proportionality of the viscous forces to the relative velocity of the parts of the fluid.

The coefficient of viscosity is regarded by Maxwell (P. M. [4] 35, 133) as being the product of two factors, a coefficient of elasticity and a If between the parallel time of relaxation. plates spoken of above we have an elastic solid without viscosity, instead of a liquid, the result of moving one of the plates parallel to the other will be to distort the solid, and give rise to a force or stress tending to restore it to its original shape, and this force will be proportional to the amount of distortion and to the coefficient of rigidity of the body. Now, if the body is a viscous substance like pitch, the stress will soon die away, even though the surfaces be held in the new position, the molecules rearranging themselves so that this position becomes one of equilibrium. The time required for this to take place is what Maxwell called the time of relaxation. For solids it may be very large, extending to several hours or even days, but for ordinary liquids it is a small fraction of a second, while for a gas, such as air, Maxwell estimated it at the fifty thousand millionth of a second. The rate at which this internal stress is disappearing at any moment is proportional to the strain at that moment. If the upper surface is moved uniformly, relatively to the lower one, the strain will never disappear entirely, for, although the rearrangement of the molecules is continually going on andthe substance is tending towards its equilibrium state, the strain is being continually set up again by the relative motion of the two surfaces we are considering, and the body will soon get into a steady state in which the rate whereat the strain is being produced is equal to the rate whereat it is dying away. The stress produced by this constant strain is the tangential force required to maintain the motion, and Maxwell proved that this stress is proportional to the coefficient of rigidity of the substance and to the time of relaxation.

For the determination of coefficients of viscosity, Coulomb and others allowed some solid of revolution, such as a circular plate or a sphere immersed in the fluid, to vibrate about its axis of figure, and observed the ratios of the amplitudes of consecutive vibrations, from which the coefficient can be calculated. O. E. Meyer (W. 43, 1) modified the method by hanging a flat cylindrical box by a bifilar suspension, filling it with liquid, and observing the rate at which the vibrations died away. This method has been used by Mitzel (W. 43, 15), and is capable of considerable accuracy. For absolute measurements it has some advantages in the fact that the lengths to be measured are not very small; but in most cases only relative values are required, and for obtaining these the transpiration method described below is preferable, as it is more readily applied, requires a smaller quantity of material, and lends itself better to accurate adjustment of temperature.

In the common form of the experiment the liquid is caused to flow through a capillary tube in consequence of a constant difference of pressure, P. between the ends, and the time, t, is observed which is required for a volume, v, to flow through the tube; then the coefficient of viscosity, η , is given by the equation $\eta = \frac{\pi}{8} \frac{Prt}{lv}$,

where r is the radius and l is the length of the tube. Hence the coefficients for two liquids will be in the ratio of the times required for the outlow of the same volume with the same difference of pressure. If the liquid flows through the tube in consequence of its own weight, P will be proportional to its specific gravity, and the coefficients of viscosity will be proportional to the product of specific gravity and time of flow.

The formula given above assumes that the work done by the pressure is entirely converted into heat inside the tube, or, in other words, that the liquid flows out without any appreciable kinetic energy. If the tube is very long and narrow this may be taken to be the ease, but generally a small correction has to be applied for the energy of the issuing fluid. The form of this correction is doubtful. Hagenbach (P. 109, 385) has given a formula which has been largely used, but Wilberforce (P. M. 1891, 407) has pointed out an error in his assumptions which makes the correction probably too small.

The coefficient of viscosity falls off very rapidly with rise of temperature, the average rate of fall for water between 0° and 10° being nearly 3 p.c. per degree, which shows the necessity for very accurate adjustment of the temperature during an experiment.

Using Maxwell's conception of the nature of viscosity, and making certain assumptions as to the way in which the rigidity and the time of relaxation vary with the temperature, Graetz (W. 24, 25) deduced the formula $\eta = A \frac{t_0 - t}{t - t}$, where

 t_i is some low temperature at which η is infinite, and t_o is the critical temperature. The formula expresses the facts very well over a moderate range, but, as we might as reasonably assume the connection between η and t as between the time of relaxation and t, it can only be regarded as empirical.

Extensive observations of the viscosity-coefficients of organic liquids have been made by Graham (T. 1861), Relistab (Inaug. Diss. Bonn, 1868), Guerout (C. R. 81, 1025; 83, 1291), Pribram a. Handl (Sitz. W. 1878 and 1879), and Gartenmeister (Z. P. C. 6, 524); but few laws have been observed beyond qualitative relations applicable to small classes of compounds. In general the viscosity increases with the molecular weight, but formic acid is an exception, as it is more viscous than acetic acid. Isomeric esters have nearly the same viscosities, that with the higher alcohol radicle having the greater. Normal compounds are generally more viscous than the corresponding iso- compounds, but the propyl halogen compounds, and a few others, form exceptions. At high temperatures these differences are less marked than at lower ones, rise of temperature tending to efface the distinction between normal and iso- compounds. Pribram a. Handl endeavoured to find the conditions of temperature under which the results are comparable; by determining the coefficients of viscosity of a number of liquids at various temperatures up to 50°. Taking the series PrCl, EtBr, PrBr, EtI, and PrI, they plotted the curve connecting vis-cosity with molecular weight, and found that while at the lower temperatures it was distinctly curved it got gradually flatter with rise of temperature, till at 50° it was almost a straight line. showing that at this temperature the increase of viscosity is proportional to the increase of molecular weight, whether this be due to the introduction of CH., or of a halogen.

Though sulphuric acid is much more viscous than water, the first effect of adding water to it is, as Graham showed, to increase its viscosity, and this continues till 18 p.c. of water has been added, when a maximum is reached, and further addition of water causes a rapid diminution of viscosity. The mixture with maximum viscosity corresponds to the proportions given by the formula H2SO, H2O, and there is a maximum in the electrical resistance near the same point. Similar relations are shown by nitric and acetic acids. For mixtures of alcohol and water Graham showed that the particular proportion of the constituents which gives the greatest contraction has maximum viscosity, and Traube (B. 19, 871) showed further that aqueous solutions of most alcohols and acids of the fatty series have maxima which occur at different concentrations according to temperature.

Arrhenius (Z. P. C. 1, 285) has investigated the relation between the concentration of a solution and its viscosity; he finds that for indifferent substances the exponential formula $\eta = A^{1-x}B^x$ expresses the results, where η is the viscosity, x the proportion by volume of the dissolved substance, and 1-x that of the solvent, so that A is the viscosity of the pure solvent, and B is a constant for the dissolved substance which is independent of the concentration up to about 10 p.c. As the solvent is usually water, and its viscosity is taken as the unit in comparative measurements, the formula can be written in the form $\eta = B^z$. In every case investigated by Arrhenius B proved to be greater than unity, showing that the viscosity of water is increased by the addition of a small quantity of an indif-

ferent substance. The same is generally true of salts, but not quite invariably so. A viscous fluid like glycerin has less effect than ether has; there seems, in fact, to be no relation between the value of B and the viscosity of the dissolved substance alone.

The latest and most comprehensive determinations of the viscosities of salt solutions are by Reyher (Z. P. C. 2, 744), Wagner (Z. P. C. 5, 31), and Lauenstein (Z. P. C. 9, 417). The formula of Arrhenius in the form $\eta = \Lambda^x$, where x is now the number of gram-molecules in a litre of solution, or A is the viscosity of a normal solution, is found to hold moderately well, but for many salts of acids of the aromatic series it shows divergences if the strengths of the solutions are greater than half normal.

Wagner worked with sulphates, nitrates, and chlorides of metals, and found that the viscosities of solutions of equivalent quantities of the various salts are additive quantities, the part which the base or the acid contributes being approximately constant. A further relation is shown by table lating the viscosities of normal solutions of the chlorides arranged according to the periodic law, when the coefficients are found to diminish in any group as the molecular weight increases. From this arrangement it would seem that copper and manganese should be put in the eighth group, for their coefficients are almost exactly equal to those of nickel and cobalt.

Reyher determined the viscosities of a number of acids and their sodium salts, and found they could be divided into two classes. The strong mineral acids have viscosities about 3 p.c. less than those of the sodium salts, while the weaker mineral acids and organic acids have coefficients from 20 to 30 p.c. less.

I auent tein has found the viscosity-coefficients of solutions of the sodium salts of many organic acids. In the fatty series he found that substitution of CH₄ for H increases the viscosity, while the replacement of H by COOH or OH diminishes it. The change from succinic to malcic acid diminishes the viscosity, but if we remove two more atoms of hydrogen, giving acetylene dicarboxylic acid, we get a large increase.

In the aromatic series the results are less regular. Introduction of a carboxyl group into the ring still diminishes the viscosity, and this diminution is greater in the para-position than in the meta-, and greater in the meta- than in the ortho-; thus the viscosity diminishes regularly in the series shown by the formulæ at the top of p. 271.

According to the usual theory, the electricity which constitutes the current in an electrolyte is carried by charged ions, and it might be expected that the conductivity would be greater the more easily these ions were able to move along under the influence of the electromotive force—that is to say, the less the frictional resistance they had to overcome. On this account Wiedemann thought there would prove to be a connection between the viscosities and conductivities of solutions. Some experiments which he made seemed to point to the conductivity being inversely proportional to the viscosity, but though this was found at a later time to hold only in a few special cases, it has been shown that there is

$$\textbf{C_{e}H_{s}.COONa}, \ \textbf{C_{e}H_{s}} \\ \underbrace{\textbf{COONa}}_{\textbf{COONa}} \\ \textbf{1:2}, \ \textbf{C_{e}H_{s}} \\ \underbrace{\textbf{COONa}}_{\textbf{COONa}} \\ \textbf{1:3}, \ \textbf{C_{e}H_{s}} \\ \underbrace{\textbf{COONa}}_{\textbf{COONa}} \\ \textbf{1:4}.$$

With other replacing groups we have the following series. each being arranged in order of diminishing viscosity : -

$$\begin{array}{l} \textbf{1:2} \ C_{o}H_{4} < \begin{matrix} \text{COONa} \\ \text{NO}_{3} \end{matrix}, \ \textbf{1:3} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{NO}_{2} \end{matrix}, \ C_{o}H_{3}\text{COONa}, \ \textbf{1:4} \ C_{s}H_{4} < \begin{matrix} \text{COONa} \\ \text{NO}_{2} \end{matrix}\\ \textbf{1:4} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{OH} \end{matrix}, \ C_{v}H_{3}\text{COONa}, \ \textbf{1:3} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{OH} \end{matrix}, \ \textbf{1:2} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{OH} \end{matrix}\\ \textbf{1:2} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{OH} \end{matrix}, \ \textbf{1:4} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{OH} \end{matrix}, \ C_{v}H_{3}\text{COONa}, \ \textbf{1:3} \ C_{v}H_{4} < \begin{matrix} \text{COONa} \\ \text{OH} \end{matrix}. \end{array}$$

undoubtedly a close connection between the two

properties.

This connection is shown very clearly by the work of Grotrian (P. 157, 130, 237; 160, 238), who determined the proportional rate of change with temperature of the viscosity and conductivity of salt solutions for various concentrations that is, he calculated from his observations the

values of $\frac{1}{f}\frac{df}{dt}$ and $\frac{1}{h}\frac{dk}{dt}$, where f is the coeffi-

cient of viscosity and k is the electrical conductivity, and found that though not equal they always vary in the same way with the concentration. If curves be drawn with the values of these coefficients at a fixed temperature for ordinates, and the concentrations for abscisse, W. N. Shaw (Camb. Phil. Proc. 7, 21) has shown that the two curves run almost exactly parallel. any peculiarities in the shape of one being repeated in the other.

That the conductivity is not dependent on the viscosity alone is shown by the fact that if we add to an electrolyte such quantities of different non-conductors, as alcohol, sugar, glycerin, &c., as increase the viscosity by the same amount, the conductivity will generally be affected differently by the different substances. Arrhenius (Z. P. C. 9, 495) has investigated this effect at some length. He finds that the conductivity can be expressed by the equation: $l = l_0 \left(1 - \frac{a}{2}x\right)^2$,

where lo is the conductivity of the electrolyte alone, and I that which it has when x p.c. of the water is replaced by a non-conductor. may be taken as defining the change in the conductivity. The change in the viscosity of the electrolyte on the addition of 1 p.c. of non-conductor is the same as the change would be with water alone, and is hence equal to A-1, where A is the constant of the formula $\mu = \mathbf{A}^x$.

On tabulating the values of 1000a and 1000 (A-1) for a number of different salt solutions and non-conductors, it appears that the equation, $1000 \alpha = c + 1000 c'(A-1)$ holds as a first approximation, and the electrolytes fall into four classes, for the members of any one of which the constants c and c' are the same. These classes are:

(1) Solutions of strong acids and bases; (2) Solutions of salts of the type KCl;

K₂SÓ₄; BaCl2. ,,

Arrhenius considers the relation not to be exact, but thinks it should include a term depending on the degree of dissociation, which can be neglected only in the cases of the more completely dissociated salts.

XIV. VOLUME-CHANGES,

BASED ON, v. VOLUMES, SPECIFIC; this vol. PHYSODIN C1011,1007. [125°]. Extracted by ether from the dried lichen Parmelia physodes (or Ceratophylla] and crystallised from alcohol (Gerding, N. Br. Arch. 87, 1). Mass of minute prisms, insol. water. Forms a yellow solution in KOHAq.

PHYSOSTIGMINE v. ESERINE. PHYTO-ALBUMOSES v. PROTEÏDS.

PHYTOLACCIC ACID. Occurs as K salt in the Poke Berry, the fruit of Phytolacca decandra (Terreil, C. R. 91, 856; cf. Claesson, Ph. [3] 10, 566). Extracted by dilute alcohol. Yellowishbrown resin.

PHYTOSTERIN v. vol. ii. p. 149. PHYTO-VITELLIN v. PROTEÏDS.

PIAZTHIOLE $C_6 II_4 < \stackrel{N}{N} > S$. [44°]. (206°).

Formed by heating o-phenylene-diamine with aqueous SO₂ at 190° (Hinsberg, B. 22, 2899). Colourless crystals, sl. sol. hot water. Feeble base. Reduced by tin and HCl to o-phenylenediamine.

Reference.—METHYL-PIAZTHIOLE.
PICENE C₂ H₁₁. [345° cor.]. (520°). V.D.
9:8 (obs.). Occurs in the highest holling portions of brown-coal tar (Burg, B. 13, 1834), and in the residues of Californian petroleum (Graebe a. Walter, B. 14, 175). Appears also to be formed by the action of ethylene bromide and AlCl₃ on naphthalene (Lespeau, Bl. [3] 6, 238). White plates with blue fluorescence, insol. alcohol and ether, sol. boiling solvent naphtha (150°-170°). On oxidation with CrO, it yields picoquinone C₂₂H₁₂O₂, which crystallises from HOAc as a dark orange-red powder, sublimes in red needles, and forms a green solution in pure

H₂SO₁.
Di-bromo-picene C₁₂H₁₂Br₂. [206°]. Necdles.

(from xylene), insol. alcohol.

Picene hydrides C.H., (over 360°) and C.H_{3e} [175°] (over 360°) are got by heating piecne with HIAq and red P at 250° (Liebermann a. Spiegel, B. 22, 781). C₂₂H_{3e} is liquid.

PICHURIN OIL contains the glyceryl ether lauric acid (Sthamer, A. 53, 390).

PICOLINE v. METHYL-PYRIDINE.

PICOLINIC ACID v. Pyridine Carboxylic

Dipicolinic acid v. Pyridine dicarboxylic ACID

DIPICOLYL v. DI-METHYL-DIPYRIDYL. PICRACONITINE v. ACONITE ALKALOIDS. PICRAMIC ACID v. DI-NITRO-AMIDO-PHENOL. PICRAMIDE v. TRI-NITRO-ANILINE.

PICRASMIN C₂₅H₄₆O₁₀. [204°]. A bitter substance which, together with C₂₆H₄₀O₁₀ [209°-

212°], may be extracted by dilute alcohol from Picræna excelsa (Massute, Ar. Ph. [3] 28, 147; C. J. 58, 791). HClAq converts it into picrasmic acid C₃₁H₄₀O₆(CO₂H)₂, while fuming HIAq displaces three methyls.

PICRIC ACID v. TRI-NITRO-PHENOL.

PICRO-ACONITINE v. ACONITE ALKALOIDS. PICROCROCIN C₃, H₃₀O₁₇, [75°]. Obtained by extracting saffron with ether (Kayser, B. 17, 2233). Colourless prisms. V. sol. water and alcohol, sl.sol. ether. Bitter taste. By heating with baryta-water or with dilute acids it is split up into crocose and the ethereal-oil of saffron C₁₀H₁₀,
PICROERYTHRIN v. ERYTHRITE.

PICROLICHENIN $G_{12}\Pi_{20}O_6$. [100°] (A.). **S.G.** 1·176. Extracted by alcohol from the lichen Variolaria amara (Alms, A. 1, 61; Vogel, J. 1857, 515). Trimetric octahedra, sl. sol. hot water, v. sol. alcohol and ether. Tastes very Its alkaline solutions turn red in air.

PICROROCCELLIN C₂,H₃₀N₃O₃. [194°]. Occurs in a variety of the lichen Roccella fuciformis (Stenhouse a. Groves, A. 185, 14). Prisms, insol. water, m. sol. boiling alcohol, sl. sol. ether. Yields benzoic acid when oxidised by chromic acid mixture. Converted by boiling with HOAc and HCl into xanthoroccellin C₂|H₁₈N₂O₂, which crystallises from alcohol in yellow needles [183°]. Boiling dilute (1\), p.c.) NaOHAq converts picroroccellin into C₂|H₂N₂O₃ crystallising from alcohol in prisms [154°].

PICROSCLEROTIN. Occurs in ergot of ryo Dragendorff, C. C. 1878, 125, 141; Blumberg, Ph. [3] 9, 23, 66, 147). Dissolved in acids and is reppd. by ammonia. It is an active poison

with bitter taste. V. ERGOTININE.

PICROTOXIN C₃₀H₃₁O₁₃ (P. a. O.; S.); C₁₃H₁₆O₆ (B. a. K.). Occurs in Cocculus Indicus, the seeds of Menispermum cocculus (Boullay, A. Ch. [1] 30, 209; Casaseca, A. Ch. [2] 30, 307; Oppermann, Mag. Pharm. 35, 233; Pelle-J. Conerbe, A. Ch. [2] 54, 181; Liebig, A.
Logo; Regnault, A. Ch. [2] 68, 160; Barth,
J. pr. [1] 91, 155; Paterno a. Oglialoro, G. 6, 521; 7, 193). It is accompanied by anamirtin picrotin (Barth a. Kretschy, M. 1, 99, 2,796).

Preparation. - 1. The grains are exhausted with boiling alcohol, the extract evaporated, and the residue boiled with water. The aqueous solution is ppd. by lead acctate and the filtrate, freed from lead by H.S, evaporated. The residue is crystallised from benzene and water successively (B. a. K.).-2. The powdered seeds are boiled with water, the filtrate treated with lead acetate and H.S successively, and evaporated to crystallisation. The product is recrystallised from water and alcohol successively (Schmidt, A. 222, 313).

Properties. - Colourless needles, v. sl. sol. cold water, sl. sol. ether and chloroform, v. sol. alcohol. Very poisonous and very bitter. Sol. alkalis. Reduces Fehling's solution and ammoniacal AgNO_a.

Reactions.—1. When boiled with benzeue

for some time it is split up into picrotin and picrotoxinin (Schmidt). Probably the picrotoxin employed was a mixture of these two bodies .- 2. IICl passed into an ethereal solution forms picrotoxide. - 3. Cold AcCl also forms

picrotoxide, but on boiling it vields a crystalline acetyl derivative [185°].—4. NaOAc and Ac₂O form $G_{11}H_{12}G_{2}$ [227°].

Picrotoxinin $G_{13}H_{16}G_{4}$ aq. [201°]. S. 14 at 15°; S. (benzene) 34 at 21°. Obtained from piero-

toxin by treatment with benzene, CHCl, or AcCl. It constitutes about 30 p.c. of crude picrotoxin (Barth a. Kretschy). Colourless needles or plates. Very bitter and very poisonous. V. sol. hot water. Colours H₂SO₄ orangered. Mixed with dry KNO₃ (3 pts.), moistened with H.SO, and saturated with conc. NaOHAq it gives a red colour (Langley, Am. S. [2] 34, 109). After heating with milk of magnesia, the cold filtrate is coloured red by FeCl, the colour being destroyed by HCl. Bromine forms $C_{13}H_{13}BrO_{8}$ [250'-255']. BzCl gives a crystalline compound (not the benzoyl derivative) [238°]

[above 310°]. Picrotoxide (C₁₃H₁₆O₆)x. [above 310°]. Formed by the action of AcCl on picrotoxin, and by passing HCl into its ethereal solution (P. a. O.). Crystalline, insol. ordinary solvents. According to Schmidt, pierotoxide obtained by means of AcCl crystallises in needles [225°], sl.

sol, cold water and alcohol.

Pierotin $C_{25}H_{30}O_{12}$. [c. 247°]. S. 16 at 17°; S. (benzene) 023 at 22° (Schmidt). Constitutes 60 p.c. of crude picrotoxin (B. a. K.). Crystallises with 23 aq, 3 aq, and 4 aq. It is very bitter, but not poisonous. Reduces hot Fehling's solution and ammoniacal AgNO, H2SO forms a yellow solution. BzCl forms a benzoyl

derivative [245°] (S.).

Anamirtin $O_{10}H_{21}O_{10}$. Constitutes 2 p.c. of crude pierotoxin (Barth a. Kretschy, M. I, 131). Short needles (from water), v. sl. sol. benzene. Neither bitter nor poisonous. Turns brown at 260° and black at 280° without melting.

Cocculin C₁₀H₂₆O₁₀. Occurs in small quantity in Cocculus Indicus (Löwenhardt, A. 222, 353). Slender needles, sl. sol. hot water, nearly insol. alcohol and ether. Does not give Langley's reaction. Is perhaps identical with anamirtin.

PICRYL. The radicle tri-nitro-phenyl.
PICRYL CHLORIDE v. CHLORO-TRI-NITRO-

PIGMENTS, ANIMAL.

BILE PIGMENTS. Bile contains bilirubin, bilifuscin, biliprasin, and probably also biliverdin, which is a product of oxidation of bilirubin. Nitric acid changes the colour of the bile pigments through green, blue, and red to yellow (Gmelin). These colours may be observed by adding nitric acid to a dilute solution of the bile pigments in aqueous alkali, or by gently pouring H.SO, into a solution of the pigments mixed with NaNO₃ (Fleischl, Fr. 15, 502). The changes in the absorption spectra produced by nitric acid have been studied by Jaffé (Z. [2] 5, 666). An alcoholic solution of bromine also produces a play of colours with bile pigments (Capranica, G. 11, 430). The absorption spectra of the bile pigments have been studied by Heynsius a. Campbell (Pf. 4, 497) and McMunn (Pr. 35, 388). Bilirubin, hæmoglobin, and chlorophyll all absorb the violet end of the spectrum, giving an abrupt edge: biliverdin transmits more green; biliprasin, bilifusoin, and bilihumin absorb up to between D and E. The colouring matters of bile are probably got by reduction of hæmatine.

itself formed by the action of bile acids on hæmoglobin (McMunn, Pr. 31, 206). According to Latschenberger (M. 9, 52), hæmoglobin yields simultaneously meianin and bile pigments. All the colouring matters of bile, including hæmatine, urobilin (in bile), and bilirubin, are oxidised to choletelin, which body apparently passes into blood serum, and is then excreted by the kidneys. The absorption bands of bile are due to choletelin and urobilin.

Bilirubin C_{r.}H_{s.}N_{*}O₆ (Städeler, A. 132, 323; Maly, A. 181, 106), or C₁₅H₁₈N_{*}O₃ by Raoult's method (Nencki a. Rotschy, M. 10, 568). S. (chloroform) 17 (Thudiohum, Z. [2] 4, 554). Ox gall stones are often largely composed of the lime compound of bilirubin (Maly, A. 175, 76).

Preparation.—Brown human gall stones are powdered and extracted with ether; the residue is boiled with water, and treated with dilute HCl. The mass is washed, dried, and extracted with chloroform; the chloroform is distilled off, and the residue treated with absolute alcohol. It is then treated with ether and alcohol repeatedly, again dissolved in chloroform, and precipitated by absolute alcohol (Burdon-Sandorson).

Properties .- Orange powder, insol. water, nearly insol. ether, v. sl. sol. alcohol, sol. benzene and chloroform. The colour of the skin in jaundice is probably due to bilirubin. Bilirubin dissolves in alkalis, forming an orange solution, which gradually absorbs oxygen from the air, and then gives a green pp. of biliverdin on adding an acid. An alkaline solution of bilirubin mixed with an equal bulk of alcohol gives, on adding HNO, containing nitrous acid, a green colour changing through blue to red. Sodiumamalgam forms hydrobilirubin. Bromine-vapour yields various brominated products (Thudichum, C. J. 28, 389; 30, 27). Br in chloroform gives C. H., Br. N. O., a dark bluish green fowder, forming a dark-blue solution in alcohol or other (Maly, A. 181, 106). Chlorine passed into a solution of bilirubin in CHCl, forms several chlorinated bodies (Thudichum). A solution of p-diazobenzene sulphonic acid added to a solution of bilirubin in chloroform mixed with alcohol gives a red colour changing to blue on adding conc. HClAq, and turned red again on adding an alkali (difference from other bile-pigments) (Ehrlich, Fr. 23, 275).—CaC32H31N4O6. Occurs in gall stones. Obtained also by ppg. an ammoniacal solution by CaCl2, as brown flakes drying to a lustrous dark-green mass, which yields a dark-blue powder.

Hydrobilirubin C32II,0N,O7. Obtained by reducing bilirubin in alkaline solution with sodium-amalgam (Maly, A. 163, 77). According to McMunn it is not, as had been stated, identical with the urobilin which is found in normal urine, in the urine of febrile patients (Jaffé, Virchow's Archiv, 47; Disqué, II. 2, 271), and in excrement (Vaulair a. Masius, Centralbl. f. d. Med. Wissensch. 1871, No. 24). A similar substance is formed by reducing hamoglobin, hamatine, or hamatoporphyrin in alcoholic solution with tin and HCl (Hoppe-Seyler, B. 7, 1065; Le Nobel, C. C. 1887, 538; McMunn, Proc. Physiol. Soc. 1888, 1), and by the action of H.SO, on a solution of albumen in HOAc (Michailoff, J. R. 16, 269). Reddish-brown powder with green lustre, sl. sol. water, v. sol. alcohol, m. sol. ether. Its alkaline

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solutions are brown, its solution in chloroform is yellowish-red. The alcoholic solution shows an absorption-band near F. Does not give Gmelin's reaction with HNO₂. May be reduced by sodium-amalgam or by tin and HOI to a colourless product, which in acid solutions is reoxidised by air to hydrobilirubin.

Choleteliu $O_{i_1}H_{i_1}N_{i_2}O_{g}$. Occurs in normal urine, and is obtained by passing nitrous vapours into a solution of bilirubin in alcohol (Heynsius a. Campbell; McMunn, J. Th. 1881, 213). Brown amorphous 'powder, sol. alkalis and alkaline carbonates, alcohol, ether, and chloroform. Ammoniacal AgNO₃ ppts. reddish-brown $C_{15}H_{18}Ag_{i_2}N_{i_3}O_{g}$. Does not give Gmelin's reaction. Its absorption spectrum contains a broad band

from b to F.

Biliverdin C₂,H₃,N₄O₈. Formed by oxidation of a solution of bilirubin by air or by PbO₂. Dark-green powder, iusol. water and chlorotorm, sl. sol. ether, v. sol. alcohol, CS₂, and benzeno. Its solutions are green. Its alcoholic solution gives dark-green pps. with buyta-water, ammoniacal CaCl₂, and AgNO₃. Ag₂O added to its alcoholic solution ppts. bilipurpin, sol. NH₂Aq and reppd. by HCl as a purple powder. Prolonged treatment with Ag₂O converts bilipurpin into yellow biliflavin. HNO₃ added to an alcoholic solution of biliverdin gives a bluish-violet, red and, finally, yellow colour (Thudiclum).

red, and, finally, yellow colour (Thudichum).

Bilifuscin C₁, H₁₀N₁O₂. Prepared by washing gall stones with ether, hot water, and chloroform, adding dilute HClAq, and extracting with hot chbroform. The extract is evaporated and the bilifuscin dissolved in alcohol, which leaves bilirubin undissolved (Brücka, J. pr. 77, 72; Städeler, A. 132, 325). Almost black mass, which yields a dark-brown powder. Forms a brown solution in alcohol and alkalis, nearly insol. water, ether, and chloroform. Gives Gmelin's colour-reaction. Ppd. by ammoniacal CaCl₂. Simony (Sitz. W. [3] 73, 181) obtained from the bile of a corpse a bilifuscin which did not give Gmelin's reaction, and which formed an olive-brown solution in alcohol, HOAc, and alkalis.

Biliprasin C₁₀II.₂N₂O₂. Extracted by alcohol from the residue of gall stones from which bilirubin and bilifuscin have been removed by chloroform (Städeler). Nearly black mass, yielding a greenish-black powder, insol. water, ether, and chloroform, v. e. sol. alcohol, forming a green solution which, unlike one of biliverdin, is turned brown by ammonia. Gives Gmelin's reactic a.

Bilihumin. Left after extracting biliprasin with alcohol (S.). Black powder, m. sol. warm NaOHAq. Exhibits Gmelin's reaction.

Bilicyanin. A product of partial oxidation of bilirubin and other bile pigments (Maly, Sits. IV. [2] 59, 597). Prepared by adding an alcoholic solution of Bit to a colution of bilirubin in chloroform. Occurs in gall stones. Its alcoholic solution is blue, but turned dingy green by alkalis, the blue colour being restored by acids. Bile also contains a blue substance strongly resembling indigo, forming a yellowish solution in alkalis (Ritter, Bl. [2] 13, 212; Andouard, Bl. [2] 31, 139).

URINARY PIOMENTS. Urine usually contains urobilin (v. supra). After urine, containing urobilin, has been mixed with its own bulk of

HClAq and heated to boiling, and then allowed to cool, the urobilin may be extracted by ether and recognised by its absorption band (Grimbert, J. Ph. [5] 18, 481). According to McMunn (Proc. Physiol. Soc. 1888, 5), there are two kinds of urobilin, one in normal urine and the other in pathological urine, and neither is identical with hydrobilirubin. Normal urobilin is identical with a pigment got from acid hæmatin by successive treatment with H2O2 and sodium-amalgam. By the action of oxidising agents indigo-blue and indirubin can be obtained from urine (v. Indigo). Pigments can also be obtained by boiling urine with HClAq.

Uromelanin. Prepared by evaporating urine to one-sixth of its bulk at 60°, adding 10 p.c. HCl, and, after two days, removing uric acid by filtration. The filtrate is then boiled for 18 hours, and the ppd. pigment washed with water, alcohol, and ether, dissolved in NaOKAq, and reppd. by H₂SO₄ (Udranski, *II.* 11, 537; 12, 33; cf. Plosz, *H.* 8, 89). Brownish-black plates, insol. cold water, ether, and chloroform, sl. sol. alcohol and HClAq, v. sol. isoamyl alcohol and alkalis. Not decomposed at 115°. Potash-fusion yields NH, formic, acetic, butyric, and protocatechuic acids and pyrocatechin. Urine contains '03 p.c. of this substance, which appears to be a humous body formed by decomposition of the reducing substance of normal urine.

Urofuscohematin C₃₁H₃₁N₁O₁₃ (?) and urorubrohematin C₃₁H₃₂N₄FeO₁₃ (?) were obtained by Baumstark (B.7, 1170) from the urine of a patient suffering from Lepra. Urofuscohæmatin is a black pitchy substance, insol. water, alcohol, ether, chloroform, acids, and NaClAq, sol. alkalis, alkaline carbonates, and alkaline phosphates, forming brown solutions. Urorubrohæmatin is a light blue-black mass, which differs from urofuscohematin in not being ppd. when HCl is added to its solution in NaOHAq.

Black pigment in Mclanuria, v. vol. iii. p. 199.

Urorosein. An unstable substance which can sometimes be extracted from acidified pathological urine by isoamyl alcohol, to which it imparts a rose colour. The solution shows an absorption band in the green (Nencki a. Sieber, J. pr. [2] 26, 333). A similar substance (urorubin) was extracted by ether from urine that had been boiled 15 minutes with 7 p.c. HCl, exposed to air (Plosz, H. 8, 85). It was left on evaporation as a dark cherry-red mass. Apparently the same pigment, or rather its leuco-compound, occurs in urine of dogs after administration of skatole (Mester, H. 12, 130). The pigment itself is then got by adding HCl to an alcoholic, ethereal, or aqueous extract of the evaporated urine.

OTHER PIGMENTS. Blood pigments v. H.EMOGLOBIN. Muscle pigments v. Muscle.

Eye pigment v. Melanin. A purple pigment occurs in the retina of animals. It is insol. ordinary solvents, but dissolves in bile, and in an aqueous solution of the bile acids. its colour in daylight, but recovers it in the dark (Boll, J. Th. 1877, 318; Kühne, J. Th. 1877, 318; 1878, 279; Ayres, J. Th. 1879, 259).

Yellow pigment of animals v. Lutrig.

Tetronerythrin. A red pigment extracted by chloroform from the red spot in the eye of the blackcock and red grouse (Wurm, J. 1872, 842; 1875, 885; Merejkowski, J. Th. 1881, 871). H.SO, gives a blue colour changing to black.

Pyocyanin. Occurs in blue pus (Fordos, J. 1860, 596; Lücke, J. 1863, 658; Gessard, J. Th. 1882, 55). It is formed, together with other pigments, by Bacillus pyocyanicus in peptonised geiatin (Babès, C. R. Soc. Biol. [9] 1, 438). Blue trimetric prisms or needles (from CHCl,) which become green on keeping, v. sol. chloroform, alcohol, and water. Turned red by acids, but becomes blue again on adding alkalis. It shows two absorption bands, one being in the ultraviolet:

Pigments of Purpura lapillus. The pigments are furnished by a yellowish-white fascia which extends along the rectum (Letellier, C. R. 109, 82). This contains two green substances, applegreen monoclinic crystals turned dark blue by light, and dull-green trimetric crystals turned violet or crimson by light. The green substances are sol. ether and chloroform, but become in-soluble on exposure to light. The change to purple (punicin) is accompanied by absorption of oxygen (Schunck, B. 12, 1359).

Pigments of sea anemones. Actinia mesembryanthemum contains a pigment allied to hemo-chromogen and hemato-porphyrin, and to harmatine. It also contains biliverdin. Actinia cercus, Bunodes ballii, and Sagartia bellis contain a green pigment resembling chloro-fucin, but not identical with any animal or plant chloro-

phyll (McMunn, Pr. 38, 85).
PIGMENTS, VEGETABLE, v. CHLOROPHYLL, ALKANET, BETH-A-BARRA COLOUR, BIXIN, BRAZILEÏN, CHICA, COLEÏN, CURCUMIN, DRAGON'S BLOOD, ILE-MATOXYLIN, LITHOSPERMUM ERYTHRORHIZON, LIT-MUS, LUTEIC ACID, PALMELLIN, and SANTALIN.

Anthocyanin. The blue pigment of flowers is sol. water and alcohol, insol. ether. It is free from N, and is turned red by acids and green by alkalis (Fremy a. Cloez, J. Ph. [3] 25, 249; Filhol, C. R. 39, 194; 50, 345, 1132; Schönn, Fr. 9, 328).

Anthoxanthin. Yellow flowers contain anthoxanthin, which is insol. water, and anthoxanthein, which is sol. water. Both are sol. alcohol and ether. The petals of Rosa gallica contain a pigment sol. alcohol, insol. ether, which forms amorphous Pb2C21H30O30 (?) (H. Senier, Ph. [3] 7, The colouring matter of the berries of Phytolacca decandra has been examined by Hilger

and Bischoff, L. V. 23, 456; B. C. 1879, 875).
PILIGANINE. A very poisonous alkaloid occurring in piligan, a Brazilian lycopod (Adrian, C. R. 102, 1322). Soft mass, with alkaline reaction, fuming with HCl. Sol. water, alcohol, and chloroform, sl. sol. ether. Emeto-cathartic in action. Its hydrochloride forms minute deliquescent crystals.

PILOCARPENE $C_{10}H_{18}$. (178°). S.G. 18 852. V.D. 4°0. $[a]_{D}=1$ 21. Obtained by steam distillation from jaborandi leaves (Hardy, BL, [2]) 24, 498). Fragrant oil. Dextrorotatory. Yields

CH_CH_2HCI [49:5°].

PILOCABPINE C₁₁H₁₂N₂O₂ i.s.

CH_CH_CH_CC.CMe
CO.CMe
CO.CMe [1599] (Blyth). [a]n = 101.6 in a 7.24 p.c. solution.

Occurs in the leaves and bark of jaborandi (Pilocarpus) (Gerrard, Ph. [3] 5, 865, 965; Hardy, Bl. [2] 24, 497; Kingzett, C. J. 30, 367; Harnack a. Meyer, A. 204, 67). Prepared synthetically from a-oxy-a-pyridyl-propionic acid CH₃.C(OH)(C₅H₄N).CO₂H by treatment with phosphorus tribromide and heating the resulting CH₂.CBr(C₃H₄N)CO₂H with NMe₂ at 150°. In this way pilocarpidine C10H11N2O2 is formed, and this is converted into pilocarpine by heating with MeI and MeOH, and oxidising the product with aqueous KMnO, (Hardy a. Calmels, C. R. 105, 68; Bl. [2] 48, 233).

Preparation.-Jaborandi leaves are digested with 1 p.c. HClAq, the extract treated with Pb(OAc)₂, filtered, and the filtrate ppd. by phosphomolybdic acid. The pp. is decomposed by baryta-water at 100° (Pöhl, Bl. [2] 34, 340).

Properties .- Crystalline; begins to sublime at 153°; at 160°-170° the sublimate consists of yellow drops (Blyth). Dextrorotatory. Pilocarpine may be estimated by means of the aurochloride (Christensen, Ph. [3] 12, 400). Poisonous, being diaphoretic. Forms resinous compounds with potash, NaOH, and baryta; these compounds are v. sol. water, v. sl. sol. alcohol, and are decomposed by acids, even by CO2. They may be considered to be salts of

pilocarpic acid C11H18N2O3.

Reactions .- 1. Fuming HNO, (300 pts.) converts it into pilocarpidine nitrate (Chastaing, C. R. 94, 968). -2. Boiling with water for twelve hours splits it up into trimethylamine and oxypyridyl-propionic acid (Hardy a. Calmels, C. R. 102, 1562).-3. Boiling HClAq forms McOH and pilocarpidine.—4. KMnO₄ forms NMe₃ oxypyridyl-malonic acid, and finally pyridine (β)-carboxylic acid.—5. Bromine added to a chloroform solution forms C11H15N2O2Bra, crystallising in minute prisms, converted by moist Ag.O into di-bromo-pilocarpine C₁₁H₁₁Br₂N₂O₂ (Chastaing, C. R. 97, 1435). Chlorine forms C₁₁H₁₂N₂O₂Cl₃, which is amorphous, and slowly forms crystalline $C_{11}H_{15}N_2O_2Cl_3$.—6. Yields NMc_3 when distilled with potash (Harnack a. Meyer; cf. Chastaing, C. R. 94, 223).—7. The barium compound on distillation yields jabonine C₉H₁₁N₂, an oil with fætid odour, yielding the amorphous salts

B'AuCl, B'HAuCl, B'.PtCl, and B'2H.PtCl, Salts.—B'HCl: needles, v. sol. alcohol. B'HNO: trimetric lamelle. -B',H,PtCla: golden tablets (from hot water).—B'PtCl;: crystals.—B'HAuCl4: minute needles.—B'AuCl3 [88°]: slender needles.—B'2AuCl₂: small needles.—B'HAu₂Cl₂: minute needles.—B'AgNO₂: minute B'CrN,H₁(SCN)₁: red silky needles, sol. alcohol (Christensen, J. pr. [2] 45, 368).—B'₂CuO₂II₁; green powder, ppd. by adding CuCl₂ to a solution of nilegenies in the statement. of pilocarpine in baryta-water.—B'AgOH: curdy pp.—B'Me,PtCl,: crystals.—B'EtI. [c. 30°].—
B'EtBr. [c. 60°]. Very hygroscopic (Chastaing,

C. R. 101, 507).

Pilocarpidine C₁₀H₁, N₂O₂ i.e. NMe₂.CMe(C₃H₁,N).CO₂H. Occurs in jaborandi leaves (Harnack, A. 238, 230). Formed by the action of HClAq or fuming HNO, on pilocarpine, by heating dry pilocarpine for twenty-four hours at 120°, by boiling pilocarpine or its baryta com-pound with water for forty eight hours, and by heating the baryta compound for thirty minutes

at 150°. Prepared synthetically by heating CH_,CBr(C,H,N).CO,H with trimethylamine at 150° (H. a. C.). Very deliquescent, m. sol. water, v. sol. alcohol. Acts physiologically like pilocarpine, but not so strongly. Its alkaline salts are gummy, sol. water, insol. alcohol, and deare gmmy, sot. water, msot. accord, and decomposed by CO₂.—B'HCl: radiating needles, v. soluble in water.—B'HAuCl, aq. Rectangular prisms. — B'AuCl₃. [145°]. Yellow plates. —B'H.PtCl, aq: small red prisms.—B'MeI.— B'McAuCl, [153°]. Prismatic needles. Changes when fused into McCl and B'AuCl,

PIMARIC ACID $C_{y_0}H_{y_0}O_{y_0}$ [211°]. [a]_p = 72.5 in a 3.8 p.c. (saturated) alcoholic solution at 15°. Occurs in galipot, the hardened resin of Pinus maritima (Laurent, A. Ch. [2] 72, 384; [3] 22, 459; Sievert, Z. f. d. g. Naturwiss. 14, 311; Maly, A. 129, 94; 132, 253; Strecker a. Duvernoy, A. 148, 143; 150, 131; Cailliot, Bl. [2] 21, 387; Bruylante, B. 11, 447; Haller, B. 18, 2165; Vesterberg, B. 18, 3331; 19, 2167; 20, 3248).

Preparation.—Finely-divided galipot is stirred with half its weight of dilute (70 p.c.) alcohol, left for some days, and squeezed in a cloth. The press-cake is treated several times in this way, finally with 80 p.c. alcohol. The residue is dissolved in somewhat more than the calculated quantity of hot dilute (3 p.c.) NaOHAq. The mixture of Na salts that separates after some days is recrystallised from water, decomposed by HCl, and the free acids crystallised from alcohol or HOAc. (\$)-Pimaric acid remains in the mother-liquor.

Properties .- Rectangular plates, insol. water, v. sl. sol. alcohol, ether, and HOAc, m. sol. hot ligroin, m. sol. hot NaOIIAq, sl. sol. NH,Aq. On shaking the ethereal solution with a drop of ammonia the NH, salt separates in slender needles. Not reduced by sodium-amalgam. May be distilled in vacuo. Dextrorotatory. HIAq (S.G. 1.96) forms C20H3, (320°-330° uncor.). By distillation of the (crude) Ca salt Bruylants obtained ethylene, propylene, amylene, acetone, methyl ethyl ketone, di-ethyl ketone, toluene, xylene, ethyl-toluene, terebene, and diterebene.

Salts.-All the salts are insol. ether. KA' (dried at 100°). Soapy mass of pliant needles .-NaA' 5aq. Slender needles (from 80 p.c. alcohol), sl. sol. cold water. - CaA', aq: needles. -BaA', 9aq: pliant needles. — CuA', — PbA', — AgA': amorphous pp., becoming crystalline.

Ethers.—Med. [69°].—Eth. [52°].

Chloride C₂₀H₂₀OCl. [66°]. Got by adding
PCl, to a solution of the acid in CS. Small prisms, v. e. sol. ether and CS2.

prising, v. e. soi. tenior and C_{3x} . (3). Finario acid $C_{3x}H_{3x}O_{2x}$. [140°-150°]. S. 9·26 in 98 p.c. alcohol at 15°. [a]_{3x} = -272° in a 3·17 p.c. alcoholic solution. Obtained as above (Vesterberg, B. 20, 3248). Trimetric prisms; a:b:c=*810:1: '614, insc'. water, v. sol. NH₃Aq. Lævorotatory.—NaA': m. sol. ether.—PbA'; needles, insol. alcohol and ether. Haller (B. 18,

2165) obtained an inactive pimaric acid [c. 149°], which was perhaps a mixture of the dextro- and lævo- varieties.

PIMELIC ACID C,H₁₇O₄ i.e.
CO,H.CHPr.CH_.CO₂H. Isopropyl-succinic acid.
Mol. w. 160. [114°]. Electrical conductivity:
Walden, B. 24, 2037. Formed by fusing camphoric acid with potash (Hlasiwitz a. Grabowski,

A. 145, 205; Kachler, A. 169, 168). Formed ! also by heating either of the following isopentane tricarboxylic acids: (CO₂H)₂CP₇.CH₂CO₂Hor CO₂H₃.CH₂P₇.CH₃CO₄Hor CO₂H₃.CH₄P₇.CH(CO₂H)₂. (Waltz, B. 15, 609; A. 214, 60; Hjelt, B. 16, 2622; Schleicher, A. 267, 123). Obtained also by the action of KOHAq on isopropyl-acetyl-succinic ether (Roser, A. 220, 276). According to Arppe (J. 1864, 377) it is not formed, as stated by Laurent (A. Ch. [2] 66, 168), by oxidation of oleïc acid. Nodules (from water) or triclinic crystals; a:b:c=497:1: 599; $a=81^{\circ}$ 50'; $\beta=100^{\circ}$ 2'; $\gamma=85^{\circ}$ 6' (Wreden, A. 163, 323; Von Zepharovitch, Sitz. W. [1] 73, 7). V. sol. water, alcohol, and ether. Yields butyric

said when fused with potash.

Salts.—(NH₄)_AA". Hygroscopic leaflets.—
Na_AA" (dried at 130°).—CaA" aq: sandy crystal-Na_A" (dried at 130°).—CaA"aq: sandy crystal-line powder. S. 47 at 9°; '25 at 100° (Bauer a. Schuler, J. 1878, 734; B. 10, 2031; M. 4, 345); '30 at 13° (Roser).—SrA": necrly insol. hot water, v. e. sol. cold water.—Ag_AA": pp. Ethyl ether EtA". (236°240°). Chloride C,H₁₀O₂Cl₂. (210°). Anhydride C,H₁₀O₂Cl₂. (216°). Got by distilling the acid. Becaused into the acid.

distilling the acid. Reconverted into the acid by alkalis.

Imide C.H₁₁NO₂. [60°]. Got by heating the ammonium salt. Tables (from water) or small needles (from alcohol-ligroin). Insol. ligroin, v. sol. alcohol and ether.

n-Pimelic acid CH2(CH2.CH2.CO2H)2. [103°]. (272° at 100 mm.) (Krafft a. Noerdlinger, B. 22, 818). S. 4·2 at 20°. H.C.p. 828,900. H.F. 243,100 (Stohmann, J. pr. [2] 45, 480).

Formation.—1. By heating suberone with HNO₂ (Dale a. Schorlemmer, C. J. 35, 686; A. 199, 147) .- 2. By heating furonic acid with HIAq and P at 200° (Baeyer, B. 10, 1858).-8. By heating pentane ω-tetra-carboxylic acid (Perkin, jun., C. J. 51, 242; 59, 825; B. 18, 3249).—4. By oxidation of myristic acid with HNO, (Noerdlinger, B. 19, 1898).—5. By reducing CO(CH, CH, CH, H), (cf. FURFURYL-ACRYLIC ACID) (Marckwald, B. 21, 1398).

Properties. - Rectangular trimetric plates (from water), v. sol. alcohol, ether, and hot benzene. May be sublimed. NaOEt forms C₁,H₂₀Na₂O₃, a white powder, insol. ether, sol. water. Not converted into anhydride by AcCl

or by POl, (Volhard, A. 267, 82). Salts.—BaA"aq.—CaA". Deposited as

granular powder when a cold saturated solution is heated.— Ag,A": white pp.

Ethyl ether Et,A". S.G. ‡ 1:0080; †5
9988; ‡ 9920. M.M. 11:424. Oll with penetrating odour (Perkin, C. J. 59, 826).

Pimelic acid C,H₁₁O₄, [103° cor.]. Got by heating chelidonic acid with HIAq at 205° (Haitinger a. Lieben, M. 5, 358). Monoclinic tables, v. sol. hot benzene. Perhaps identical with n-pimelic acid.

(8)-Pimelic acid C, H10(CO2H)2. [106°]. Occurs among the products of oxidation of castor oil and earth-nut oil with nitric acid (Gantter a. Hell, B. 17, 2212). Large tables (from water). Readily forms supersaturated solutions.

BaA"aq: plates.—PbA".—CuA".—Ag,A": pp.

Iso pimelie acid 'O,H., (CO,H). [104°].

Formed from amylene bromide by successive treatment with alcoholic KCy and HClAq at 170° (Bauer, M. 4, 345; Hell, B. 24, 1389). Prisms,

v. sol. water and alcohol. Begins to form an v. sol. water and atcomot. Degins to form an anhydride at 185.— (NH₄)₂A".— BaA" 1₂aq; sandy powder.—CaA". S. 2 at 22°; 14 at 100°.— SrA" 4aq.—NiA" 2½aq.—ZnA".—PbA". S. 01 at 10°.—CuA"aq. S. 04 at 16°; 07 at 100°. Bluish-green plates.—CdA"2aq: needles. S. 12 at 15°; 13 at 100°.—Ag₂A".

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An amorphous pimelic acid was got by Bauer, as well as the preceding acid, from amylene bromide. Its Ca salt was more soluble (S. 4·7).

Pimelic acid C,H₁₂O₄. [87°]. Got by oxidising menthol with KMnO₄ in acid solution (Arth, A. Ch. [6] 7, 455; C. R. 107, 107). Needles, v. sol. water. Can be extracted by ether from its aqueous solution.—Ag2'\".

Isomerides — v. DI-METHYL-GLUTARIC ACID,

METHYL-ETHYL-SUCCINIC ACID, TRI-METHYL-SUC-CINIC ACID, and PROPYL-SUCCINIC ACID.

PIMENTO. The volatile oil obtained from the pods and seeds of Myrtus Pimenta contains eugenol and a terpene (255°) S.G. 18 98 (Bonastre, J. Ph. 11, 187; Oeser, A. 131, 277).

PINACOLIC ALCOHOL v. Sec - HEXYL PINACOLIN v. METHYL tert - BUTYL RETONE.

PINACULIN v. METHYL Lett-BUTYL RETONE.
Benzpinacolin v. vol. i. p. 488.
PINACONE C₄H₁, O. i.e. CMe₂(OH). CMe₂(OH).
Hexylene glycol. [38°]. (170° cor.). S.G. 45
9672; 35 9609. M.M. 7-245 (Perkin, C. J. 45,
506). H.C. 897,697 (Louguinine, A. Ch. [5] 25,
143). Formed by the action of Na or sodum. amalgam on aqueous acetone (Fittig, A. 110, 25; 114, 54; Städeler, A. 111, 277; Friedel, A. 124, 324; Bl. [2] 19, 289; Linnemann, A. Suppl. 8, 374). Formed also from CMe, Br.CMe, Br by successive treatment with AgOAc and baryta (Pawloff, A. 196, 122). Small needles (from CS₂), v, sol. cold alcohol and ether, sl. sol. cold CS₂. Sl. sol. cold water, but v. sol. hot water, separating on cooling as a hydrate $C_0H_{14}O_2$ 6aq [46.5°], crystallising in four-sided tables, decomposed by distillation into water and

Reactions .- 1. Chromic acid mixture reconverts it into acetone. -2. Gaseous HI yields PrI and some hexane (Linnemann, Sitz. W. [2] 63, 255). HIAq at 100° forms C₆H₁₁I (Bouchardat, Z. 1871, 699).—8. Boiling dilute H₂SO₄ converts it into pinacolin. Heating with HOAc has the same effect.—4. POCl, forms di-chloro-hexane [160°] (Friedel a. Silva, B. 6, 35).—5. Does not form an acctal when heated with aldehyde (Lochert, A. Ch. [6] 16, 60).-6. When passed through a A. Oh. [6] 10, 00).—0. When passed whough a red-hot tube it yields acctone and isopropyl alcohol (Thorner a. Zincke, B. 18, 645).

PINACONES. Compounds of the form HO.CRR'.CRR'.OH, where R and R are alkyls.

They are obtained by reduction of ketones. On treatment with dehydrating agents they yield (β)-pinacolins CRR', CO.R or isomeric (α)-pinacolins OCRR' or CRR'.O.CRR'. If in these formulæ R = H, the (β)-pinacolin will be an aldehyde; while if at the same time R'= H, we find that glycol is the simplest pinacone, aldehyde the simplest (8)-pinacolin, and ethylene oxide the simplest (a)-pinacolin (Zincke, A. 216, 296). Some (\$)-pinacolins are decomposed by heating with soda-lime or alcoholic potash, thus: PhOX, COPh + HO = PhOX, H + HOBs | Zincke

a. Thorner, B. 11, 65; Zagumenny, J. R. 12. 429); but phenyl (a) naphthyl (B) pinacolin reacts with alcoholic potash, thus: PhC(C, H, J, OOPh+ H, O=PhC(C, H, J, OH+Ph.CO.H (Elbs, J. pr. [2] 35, 506).

PINE-APPLE OIL. Artificial pine-apple oil may be made by dissolving butyric ether in alcohol (Hofmann, A. 81, 87). PINENE v. TERPENES.

PINEY TALLOW. A fat obtained by boiling the fruits of Valeria indica (of Malabar). Melts at 30° to 38°. Its fatty acids consist of palmitic acid (75 p.c.) and oleic acid (25 p.c.) (Dal-Sie, G. 8, 107)

PINIPICRIN C₂H_{3e}O₁₁. Occurs in the needles and bark of the Scotch fir (*Pinus sylvestris*) and in the green parts of *Thuja occidentale* (Kawalier, *Sitz. W.* 11, 350; 13, 515). Bright-yellow amorphous powder, beginning to soften at 55°, and quite liquid at 100°. Hygroscopic. Tastes bitter. V. sol. water, sol. alcohol, insol. ether. Boiling dilute H,SO, yields glucose (2 mols.) and ericinol C10H16O (1 mol.), v. vol. ii. p. 458.

PINITANNIC ACID C₁₄H₁₆O₈? Occurs in

the needles of the Scotch fir and in the green parts of the Arbor vitee (Thuja occidentale) (Kawalier, Sitz. W. 11, 357; 29, 19). Reddish-yellow powder, v. sol. water, alcohol, and ether. FeCl, colours its aqueous solution brown. Gives yellow pps. with lead acetate and subacetate.

Not ppd. by gelatin.

PINITE C,H,10. Methyl ether of dextrorotatory inosite. [186°]. [a], = 65° 51'. Supposed to be extracted by water from the hardened sap of Pinus lambertiana of California (Berthelot, A. Ch. [3] 46, 76; Johnson, Am. S. [2] 22, 6; Combes, C. R. 110, 46; Maquenne, A. Ch. [6] 22, 264). Crystalline crusts, v. e. sol. water, almost insol. alcohol. Tastes sweet. Dextrorotatory. Non-fermentable. Does not reduce Fehling's solution. HIAq splits it up into MeI and dextrorotatory inosite [248°]. Pinite is identical with materite and sennite.

PINOL $C_{10}H_{10}O$ *i.e.* $C_{0}H_{0}OMeFr$. (184°). S.G. 2º .953; $\mu_{D} = 1.469$. Formed, together with pinene nitroso-chloride when oil of turpentine is treated with HOAc, nitrous ether, and HCIAq (Wallach, A. 253, 251; 259, 322; 268, 222; B. 24, 1552). Purified by conversion into the di-bromide C₁₀H₁₆Br₂O [94°], which is dissolved in dry benzene and treated with sodium-wire.

Liquid, smelling like cineol.

Reactions.-1. Oxidised by KMnO, to CO, oxalic acid, and terebic acid [176°].-2. Br forms C₁,H₁,Br₂O and C₁,H₁,Br₂O [160°]. — 3. HBr forms an addition product converted by water into the hydrate C₁,N₁OH₂O [131°] which is not attacked by Ac₂O, but is reconverted into pinol by warming with dilute H.SO., and yields terpenylic acid [57°] on oxidation by KMnO.

Dibromide C₁₆H₁₆Br₂O. [94°]. (144° at

11 mm.). Trimetric crystals; a:b:c = 570:1:1.555. Insol. water, volatile with steam. Converted by alcoholic potash into 'pinol glycollic ether' C₁eH_{1e}(OEt)₂O [53°] (c. 115° at 14 mm.). AgOAc forms O_{1e}H_{1e}(OAc)₂O [98°] (127° at 13 mm.), which on saponification by hot dilute H₂SO, yields 'pinol-glycol' O_{1e}H_{1e}(OH)₂O [125°], crystallizing in matted needles, v. e. sol. chloroform. Boiling with water and Pb(OH), also converts the dibromide into the glycol. Silver propionate yields C10H16(O.COEt), [106°]. Formic acid at 100° reduces the dibromide to cymene.

Nitroso-chloride C, H, ONOCI. [108° Formed by the action of amyl nitrite and HCl on pinol in HOAc (Wallach, A. 253, 261). Converted by alcoholic NH, into the nitrolamine C_{1e}H₁₆ONONH₂ (130° at 14 mm.), a viscid mass which yields a crystalline hydrochloride, B'HCl. Aniline, piperidine, and benzylamine form the three analogous bodies $C_{10}H_{10}O.NO.NHPh$ [175°], $C_{10}H_{10}O.NO.NC_{1}H_{10}$ [154°], and the compound $C_{10}H_{10}O.NO.NC_{1}H_{10}$ [136°], each of which forms a crystalline hydrochloride. (β)-Naphthylamine forms, in like manner, pinol-nitrol-naphthylamine C₁₀H₁₆O.NO.NHC₁₀H, [195°].

PINYLAMINE C₁₀H₁₃NH₂. (208°). S.G. M. 943. Formed by reducing with zinc-dust and HOAc nitroso-pinene C10 H13NO [1320], which is got from C, H NOCl and alcoholic NaOH (Wallach a. Lorenz, A. 268, 197; B. 24, 1550). Oil, turning yellow in air, and giving off NH: Absorbs CO, from air, forming a solid carbonate Benzoic aldehyde forms C₁₀H₁₃N:CHPh [58°] furfuraldehyde gives C₁₀H₁₃N:CH.C₄H₃O [81°] whilst salicylic aldehyde forms the compound C₁₀H₁,N:CH.C₂H₄.OH [109°].—B'HCl. [230°]. Needles (from water). Yields cymene on distilla-tion.—B'₂H₂PtCl₃. Yellow plates or needles.— B'HNO,. Crystals, sl. sol. cold water. - B', H, SO. -B'HCyS. [136°]. Prisms (from water).-B'₂H₂C₂O₄. [248°]. Scales.

Acetyl derivative C₁₀H₁₅NHAc. [109°] Benzoyl derivative. [125°]. Needles.

PINYL-UREA NH CO.NHC HIS. [160° Formed from pinylamine hydrochloride and potassium cyanate (Wallach, A. 268, 204). Needles, v. sol. alcohol.

PIPECOLINE v. METHYL-PYRIDINE HEXA-HYDRIDE.

PIPERAZINE v. Pyrazine HEXAHYDRIDE. PIPERHYDRONIC ACID v. Methylene derivative of DI-OXY-PHENYL-VALERIC ACID.

PIPERIC ACID C12H10O4 i.s.

CH₂<0>C₆H₂.CH:CH:CH:CH:CO₂H. Mol. w. [217°]. S. (alcohol) :37 in the cold; 2 at 78°. Formed, together with piperidine, by boiling piperine with alcoholic potash (Von Babo; Strecker, A. 105, 317; 118, 280; G. C. Foster, C. J. 15, 17; Fittig a. Mielk, A. 152, 25; 172, 134). Yellowish needles (from alcohol). After fusion it melts at 213°. Nearly insol. water, m. sol. hot alcohol and ether.

Reactions .- 1. Reduced by sodium-amalgam to two hydropiperic acids, which are the methylene derivatives of di-oxy-phenyl-angelic acids CH.O.:C.H., CH., CH.; CH., CO.H. [78°] and CH.O.:C., H., CH., CH.; CH., CH.; CH., CO.H. [131°] (Regel, B. 20, 414).—2. Dilute alkaline potassium permanganate at 4° oxidises piperic acid to piperonal CH.O.: C.H. CHO and racemic acid (Doebner, B. 23, 2375).-3. Potash-fusion yields protocatechuic, oxalic, and acetic acids .- 4. Bromine in CC2 forms a tetrabromide which decomposes at 160°-165°.

Salts. – NH,A'. Satiny scales. — KA'. — BaA'. S. '02 in the cold.—AgA': powder. Ethyl ether EtA'. [78°]. Plates. · Reference .- BRONO-PIPERIC ACID.

PIPERIDEINE. A name for Pyridine tetra-

slowly adding v-chloro-piperidine to a boiling 10 p.c. solution of potash in alcohol (Lellmann a. Schwaderer, B. 22, 1000, 1318). Monoclinic crystals, sl. sol. water, v. sol. alcohol and ether. Between 200° and 230° it begins to dissociate into (2 mols. of) pyridine tetrahydride; hence it has no constant boiling-point. Slightly volatile with steam. Ac,O forms an acetyl derivative (220°). S.G. 105 1.0531. Tin and conc. HClAq reduce it to piperidine. Phenyl thiocarbinide gives $C_{10}H_{11}N_2$ CS.NHPh [144°]. CS₂ forms $C_{10}H_{18}N_2$ CS₂, crystallising in needles, and melting at 150° with evolution of gas.

Salt.-B"H,Cl, 2aq. [150°]. Plates, liquefies c. 80° when quickly heated. .

Isodipiperideïne $C_{10}H_{18}N_2$. Formed by heating diazobenzene piperidide at 250° (Heusler, A. 260, 239). Thickish liquid, miscible with water, but can be extracted therefrom by ether. Reduces Fehling's solution and ammoniacal AgNO. Its salts are hygroscopic.

PIPERIDIC ACID C.H., NO. [184°], which is got by oxidising piperidine ν-carboxylic ether with fuming HNO, and heating the product with HClAq at 140°, is γ-amido butyric acid (Schotten, B. 16, 643; Gabriel, B. 23, 1770).

PIPERIDINE CHINN i.e.

CH. CH, CH, NH. Pyridine hexahydride. Mol. w. 85. (106°). S.G. 15 8664; 25 8591. M.M. 5·810 (Perkin, C. J. 55, 700). S.V. 108·76. S.H. 533 (Colson, Bl. [3] 3, 8). H.F.v. 24,090. H.F.p. 26,990 (Thomsen, Th. 4, 145). Appears to occur in the husks of pepper (Johnstone, C. N. 58, 235; An. 14, 41).

Formation. -1. By distilling piperine with potash-lime or soda-lime, or by boiling it with alcoholic potash (Wertheim, A. 127, 75; Anderson, A. 75, 82; 84, 345; Cahours, A. Ch. [3] 88, 76; Von Babo a. Keller, J. pr. 72, 53). 2. By reduction of pyridine in alcoholic solution by sodium-amalgam; the yield being 75 p.c. of the theoretical (Ladenburg a. Roth, A. 247, 51). 8. By heating pentamethylene-diamine hydro-chloride (Ladenburg, B. 18, 3100).—4. By heating hygric acid C₆H₁₁NO₂ with H₂SO₄ for a few minutes at 300° (Liebermann a. Kühling, B. 24,

Properties.—Liquid, with ammoniacal and peppery smell, miscible with water. Alkaline in reaction. Caustic taste. Ppts. salts of zinc and copper, but does not redissolve the ppd. hydrates. Not attacked by funing HClAq at 300° or by boiling HNO₄ (S.G. 1·5). Piperidine acts as an anæsthetic (B. 14, 713). Oxidised by H.O. to glutaric acid and its imide and δ-amido-valeric aldehyde (Wolffenstein, B. 25, 2777).

Reactions .- 1. Bromine and water at 200° yield di-bromo-oxy-pyridine and some CHBr, (Hofmann, B. 12, 984). Piperidine hydrochloride, heated with dry Br at 180, yields dibromo-pyridine (Schotten, B. 15, 427). Bromine and NaOHAq give crystalline C.H.Br.NO (Hof-mann, B. 16, 560). Bromine and lime-water yield bromo-piperidine C.H.,BrN [284°] (Lell-

mann, B. 22, 1327). -2. Chlorine acts with explosive violence on dry piperidine. In presence of water or chloroform it yields v-chloro-piperidine, which may also be got by using bleachingpowder. It is an unstable, heavy oil (52° at 25 mm.), with pungent odour, and deposits piperidine hydrochloride when kept for some time (Bally, B. 21, 1/72).—3. Conc. H.SO, at 800° forms pyridine (Kenigs, B. 12, 2341). Nitrobenzene at 260° also oxidises it to pyridine (L.). 4. Chloroform, on boiling for some days, yields 4. Choroform, on boiling for some days, yields CH(C₃H₁₀N)₃ aq (98° at 15 mm.) (Busz a. Kekulé, B. 20, 3'246).—5. CH₁CCl₃ forms, on boiling, ethenyl tripiperidine CH₂C(C₃H₁₀N)₃, a liquid (262°) yielding B"H₂Cl₃ and B"₂3H₂PtCl₃ (B. a. K.).—6. Boiling oxalic ether (1 mol.) yields piperidyl-oxamic ether C₃H₁₀N.CO.CO₂Et (289°) (Wallach, A. 214, 278; 237, 247). The corresponding axial March 11 coordinates of the corresponding axial March 12 coordinates of the corresponding axia sponding acid [129°] splits up on fusion into CO. and the formyl derivative of piperidine. PCI, yields CO₂ and C₂H₁₀N.COCI (238°), which acts upon piperidine forming (C₂H₁₀N)₂CO[43°] (298°). NH3Aq converts the ether into piperidyl-oxamide C₃H₁₀N.CO.CO.NH₂ [127°], crystallising in monoclinic prisms, converted by P₂O₃ into clinic prisms, converted by P₂O₃ into C₃H₁₀N.CO.CN, a heavy oil (264°). When piperidine (2 mols.) is distilled with oxalic ether (1 mol.) there is formed oxalyl-piperidine $C_3H_{10}N.CO.CO.C_1H_{10}N$ [89°] (above 350°).— 7. By heating with phthalic acid (2 mols.) as long as phthalic anhydride sublimes there is formed 'piperilene-amine-phthaleïn ' O18H21N2O2 or $C_0H_1<\frac{\hat{C}(NC_5H_{10})_2}{CO}$, an oil which yields crystalline C₁₈H₂₁Br₂N₂O₂ (Piutti, G. 13, 535; A. 227, 197).—8. Phthalic anhydride unites in the cold with piperidine, forming a mixture of ' piperilene-phthalamic acid' C_{H_10} N.CO. C_g H, CO. H_1 and its piperidine salt (P.). On shaking with other and water the acid goes into ethereal solution, and the salt into aqueous solution. Piper-

ilene-phthalamic acid is a heavy oil, v. sol. alcohol. It yields AgA', C.H., NHA' [c. 150°], and C18H28Br, N2O2, crystallising in long needles. 9. Alloxan and aqueous sulphurous acid give (C₁H₂N₂O₄)C₅H₁₁NH₂SO₃, crystallising in plates (l'ellizzari, A. 248, 150).-10. On heating with isatin and alcohol on the water-bath there is formed the compound C₈H₅NO(C₅H₁₀N)₂ or C_uH₄ C(NC₃H₁₀)₂, crystallising in flat colour-

less prisms, m. sol. hot alcohol, turned red by HCl, and yielding a blue dye (indigo 2) when treated with Ac₂O, or when rapidly heated to 125°-160°. Bromo-isatin forms, in like manner, C.H.BrNO(C.H.0N)2, crystallising in needles, while di-bromo-isatin reacts with production of C.H.Br. (NH.).CO.CO.NC. H. [152] (Schotten, B. 24, 1367, 2605).—11. A solution of diazobenzene chloride and sodium acetate forms Ph.N:N.NO, H10, which yields phenol and piperidine when treated with dilute H.SO., and phenyl-hydrazine and piperidine when reduced by SuCl, and HCl (Nölting a. Binder, B. 20, by Such and Hol (Noting a. Bines, B. 20, 3016). Other diazo-compounds act in like manner. Diazobenzene piperidide is decomposed on heating to 250°, yielding benzene, N, and isopiperidein (Heusler, A. 260, 239).—12. Potassium cyanate converts piperidine sulphate into NH₊CO.NC.H₁₄, crystallising from alcohol in needles (Cahours). Methyl and ethyl cyanates prisms [172°]. O,H,NH.COOl gives rise to O,H,NH.CO.NC,H, [102°], crystallising from dilute alcohol in needles (Kühn a. Riesenfeld, B. 24, 3818).—13. Methyl thio-carbimide forms NHMe.CS.NO₅H₁₀ [129°] (Hecht, B. 23, 287; 25, 815), while ethyl-, propyl-, and phenyl- thiocarbimides form corresponding thio-ureas [46°], [75°], and [99°] respectively. Phenyl-, o-, and p-tolylthiocarbimides form C3H10N.CS.NHPh [983] (G.); [104°] (Skinner a. Ruhemann, C. J. 53, 558) and C₃H₁₀N.CS.NHC,II, [98°] and [132°] respectively. Potassium sulphocyanide reacts with piperidine sulphate, forming C₃H₁₀N.CS.NH₂ [92°] Gebhardt, B. 17, 3039). Allyl-thiocarbimide forms oily C, H, N.CS.NHC, H, which is converted by conc. HClAq at 100° into C₃H₁₀N.C S.CHMe, a liquid (277°) yielding B'C H,N₃O, [112°] and B'MeI [67°] (Avenarius, B. 24, 262).—14. Benzoul-thiocarbimide added to a solution of piperidine in dry benzene forms C, H, N.CS.NHBz [123°], crystallising in needles, sol. alcohol and ether (Dixon, C. J. 55, 624). Benzyl-thiocarbinide gives C.H., N.CS.NHCH, Ph [88°] (Dixon, C. J. 59, 568).—15. Tri-methyl-trithiocyanurate at 200° forms C₁,H₂,N₃S [107°], which gives B'₂H₂PtCl_a (Hofmann, B. 18, 2779).—16. Quinone forms red needles [178°], which are probably C₆H₂O₂(NC₅H₁₀)₂ (Lachovitch, M. 9, 506).— 17. Benzoic aldehyde in presence of K₂CO₃ forms OHPh(NC₃H₁₀)₂ [80°] crystallising from alcohol in flat needles (Ehrenberg, J. pr. [2] 36, 130; Lachovitch, M. 9, 695).—18. Tri-oxy-methylene forms CH₁(NC, H₁₀)₂ (230°), which unites with CS₂ giving C₁(H₂₀N₂CS₂ [58°]. — 19. Pinene nitroso-chloride in alcoholic or aqueous solution yields crystalline C10H10NONC3H10 [119°] which forms B'HCl. The corresponding terpine and dipentinene derivatives melt at 154° (Wallach, A. 241, 320; 245, 253). -20. Amylene nitrosonitrate in boiling alcoholic solution forms CMe2(NC3H10). CMe: NOII, which crystallises from ether in prisms [96°], and is converted by boiling dilute H₂SO₄ into CMc₂(NC₅H₁₀).CO.CH₂, an oil (220°), μ_D = 1.934, volatile with steam, yielding a very hygroscopic hydrochloride (Wallach, Δ. 248, 172). -21. Fluorescein chloride at 220° forms $C_{\bullet}H_{\bullet}:C_{\bullet}O_{\bullet}$ $C_{\bullet}H_{\bullet}(NC,H_{\circ})$ O which yields $B''H_{\bullet}PtCl_{\bullet}$ and $B''H_{\bullet}Cl_{\bullet}$ which is purple in dilute solution and yellow in conc. HClAq (Lellmann a. Bütner, B. 23, 1387).—22. Bromo-phen-anthrene at 260° forms crystalline C₁₁H_oNC₂H₁₀ [113°] which yields B'₂H₂PtCl_a 6aq (L. a. B.).— 23. Bromo-anthracene at 260° reacts forming C_{1,}H_aNC₃H₁₀ crystallising from other in yellow prisms and giving B'₂H₂PtCl₅ 2aq (L. a. B.).— 24. Chloro-acetic acid forms C₃H₁₀N.CH₂CO₂H, which forms hemihedral prisms (containing aq) and yields CuA', 4au, HA'HCl, HA'HBl, (HA'),3HAuCl, and HA'BaCl, (Kraut, A. 157, 66).—25. a-Chloro-propionic ether produces C.H., N.CHMe.CO.H crystallising from water and alcohol in prisms and yielding HA'HAuCl, acconol in prisms and yielding HA'HAuCl, (Brühl, B. 9, 34).—26. Benzene sulphochloride and NaOHAq form C.H., SO, NC.H., [93°] (Hinsberg, A. 265, 182; Schotten a. Schlömann, B. 24, 8689). This body is oxidised by KMnO, to O.H., SO, NH.CH., CH., CH., CO.H..

yield corresponding ureas. Phenyl cyanate forms NHPh.CO.NO, H., or crystallising from alcohol in

27. Picryl chloride forms C.H., N.C.H. (NO.). [106°] (S. a. S.).—28. Glycerin dichlorhydrin forms liquid O₁H₂N₂O (280° 290°) which yields B"H₂PtCl_a (Ladenburg, B. 14, 1879).—29. CS₂ forms (O₂H₁N₁O₂O or O₂H₁N₁OS.SNO₂H₁, crystallizing analysis [174] tallising in slender monoclinic needles [1740]. converted by an alcoholic solution of iodine to (C₃H₁₀N.CS)₂S₂[130°]. — 30. Dicyandiamide reacts on 'piperyl-biguanide' with formation of C,H₁₅N₅, on 'piperyl-bignanide' with formation of C,H₁,N₂, c. C,H₁, N, C(NH), NH, C(NH), NH, [163° 7] orystallising in silky needles, and yielding the salts B'H,Cl₂ [2170], B'H,SO, [173°], B'H,SO, [219°], B'H,PiCl₂ [252°], B'H,AuCl₃, and the copper compound Cu(C,H₁,N₃,H,SO₄ crystallising in rose-red needles (Bamberger, B. 24, 605, 904). Piperyl-biguanido is converted by CHCl, and caustic potash into 'piperyl-formoguanamine' $C_1H_{10}N.C \leqslant N.C(NH_2) > N$ [194.5°] which yields N=CH
the salts B'HCl [201°], B'.H.SO.aq [222°],
B'2C,H.N.O. [A88°], B'.H.PtCl, [219°], B'HAuCl,
[90°] and [158°], and B'.AgNO, [229°-238°]
(Hjelt, B. 25, 529). Piperyl-bignanide sulphate heated with NaOAc at 200° yiells piperyl-aceto-guanamine C₃H₁₀N.C N:CMe N: [179°] (Hjelt, B. 25, 533). The acetyl derivative of piperyl-biguanideC₃H₁₆N.C(NAc).NH.C(NH).NH₂ [193°] is got by heating the copper salt with HOAc.

Salts.—B'HCl. [237°]. M.M. 10 034 in a 53 p.c. solution (Perkin, C. J. 55, 716). Needles, v. sol. water and alcohol. -B'HAuCl, [206°]. Not decomposed by boiling water (De Coninck, Bl. [2] 45, 131). B', H.PtCl, [196°] (Ladenburg, B. 18, 3100); [200°] (Wallach a. Lehmann, A. 237, 241). Red needles. Not decomposed by boiling water (De Coninck, Bl. [2] 45, 131). Crystallises also with EtOH in orange needles [191°]. - B'₂PtCl₂. B'Zn OCl2: amorphous pp. got by adding piperidine to a solution of ZnCl2 (Lachovitch, M. 9, 517) .- B'HBr. Plates (Lellmann, B. 20, 680) .-B'HI. Long needles.—(B'HI), 2BiI, Scarl plates (from alcohol) (Kraut, A. 210, 819). Scarlet B'ICL [143°]. White needles. - B'ICIHCl. BTCI. [143°]. White nection.—BICHCI. [190°]. Yellow crystals (from water) (Pictet a. Krafit, Bl. [3] 7, 72).—B'HNO., Small needles.—B'.H.C.O.; needles.—B'.H.FcCy, 3aq. Yellow triclinic crystals.—Piperate B'C₁₂H.₁₀O., Silky lamine [100°] (Babo a. Keller).—B'.H.₂SO., Nitrosamine C.H.₁₀N.NO. (218°). S.G.

185 1-066. Formed from piperidine and nitrous acid (Wertheim, A. 127, 75; Schotten, B. 15, 425; Knorr, A. 221, 298). Pale-yellow liquid, 8l. sol. water, v. sol. conc. HClAq, but reppd. on dilution. Zinc and HClAq reduce it to piperidine and NH₁. Heated in a current of HCl at 100° it gives piperidine and NOCl. Sodium-amalgam forms C₂H₁₀N.NH₂ and piperidine.—B"H₂Cl₂: syrupy.—*B"HCl: crystalline mass.

Hydrazine C.H., N.NH. Piperyl-hydrasreducing the nitrosamine with zinc-dust and HOAc (Knorr, B. 15, 859; A. 221, 299). Liquid, with ammoniacal odour, miscible with water, alcohol, and ether. Volatile with steam. Oxidised by HgO in the cold to the tetrazone C₁₆H₂₀N₄ [45°], which yields B'₂H₂PtCl₃. Reduces cold ammoniacal AgNO, and hot Fehling's solution. Nitrous acid converts it into piperidine. CS, gives rise to (C,H,eN.NH),CS [181]. The compound

C.H.o.NH.CS.NC, H.o [86°] may also be obtained. BzOl in ether forms C,H₁₀N.NHBz [196°]. Benzole aldehyde forms C,H₁₀N.N:CHPh [63°]. Salt.—B'HCl. [162°]. Tables (from alcohol). Reacts with potassium cyanate forming $C_bH_{10}N.NH.CO.NH$, [136°] and with potassium sulphocyanide forming CAHION.NH.CS.NH. [167°].—Methylo-iodide B'Mel.[215°]. Begins to decompose at 150°.

Formyl derivative C,H, N.CHO. (222°). 8.6. 23 10193. Formed by the distillation of $C_5H_{10}N.CO.CO.H.$ (v. Reaction 6) (Wallach a. Lehmann, A. 228, 251; 237, 252). Got also by heating piperidine with formamide (Lachovitch, M. 9, 699). Liquid, miscible with water, alcohol, and ether. PCl, yields a base C11H20N2- B'HCl:

and ether. For young abserting and states are deliquescent needles. — B', H, PtCl. [172°]. Plates.—B'HgCl. [149°]. Needles. Acetyl derivative C, H, Nac. (227°). S.G. 2 1011 (Wallach a. Kamensky, A. 214, 238; cf. Schotten, B. 15, 426). Liquid, miscible with water. When heated with BzCl it gives AcCl and benzoyl-piperidine (Pietet, B. 23, 3014). On heating with bromine it gives pyridine, bromo-pyridine, and di-bromo-pyridine (Hofmann, B. 16, 587). When Cl is passed into cooled acetyl-piperidine and the product is warmed with water, there is formed C,H₁₁Cl₂NO₂

[122°] (Bally, B. 21, 1772).

Benzoyl derivative C,H₁₀NBz. [48°]. (above 360°). Formed from piperidine, BzCl, and NaOHAq (Cahours; Schotten, B. 17, 2544; 21, 2238). Triclinic prisms (from alcohol). Oxidised by KMnO, to benzoyl-8-amido-valeric acid dised by KMnO, to benzoyl-6-amido-valeric acid [94°]. Benzoic aldehyde forms the compound NH C(CHPh).CH₂>CH₂ [89°], which yields B'HCl [166°] and B'HNO₃ [98°], both being crystalline (Rügheimer, B. 24, 2186).

Bromo-benzoyl derivative CaH10N.CO CaH4Br. The o-compound is an oil, while the p-compound crystallises from alcohol in rectangular monoclinic tables [95°] (Schotten,

B. 21, 2248).

m-Nitro-bensoyl derivative

C.H. N.CO.C. H. NO₂. [34°]. (184° at 54 mm.). S. (alcohol) 33 in the cold, 50 at 78°. Darkyellow monoclinic crystals. Crystallises from water with about 5aq, and then melts at 84°. Yields, on reduction, the m-amido-benzoyl derivative [125°].

Oxy-bensoyl derivative v. Piperidide

of OXY-BENZOIC ACID.

Cuminyl derivative C15H21NO. Tables. Cinnamyl derivative C, H, CO.NC, H10. • [122°]. Formed from the anhydride and piper-idine (Herstein, B. 22, 2265). Stellate needles.

Alkyl-piperidines. On heating the alkylo-iodides of pyridine, a pair of alkyl-pyridines is produced, that of lower boiling-point being (a)-alkyl-pyridine, and the other (γ) -alkyl-pyridine. On reduction these give the corresponding alkyl-piperidines. The same isopropyl-pyridines are obtained both from pyridine isopropylo-iodide, and pyridine n-propylo-iodide, an intramolecular change taking place in the propyl group in the latter case. Conyrine is (a)-propyl-pyridine, conline is (a)-propyl-piper-idine (Ladenburg, B. 18, 1587). By adding potash to piperidine alkylo-iodides, r-alkylpiperidines can be obtained.

Methyl-, Ethyl-, Propyl-, Phenyl-, and Tolyl-Piperidines v. METHYL, ETHYL, PROPYL, PHENYL, and Tolyl Pyridine HEXAHYDRIDES.

PIPERIDINE p-CARBOXYLIC ACID

CH₂CH₂CH₂N.CO₂H. Methyl ether MeA'. (201°). Formed from piperidine, ClCO₂Me, and Honry KOHAq (Schotten, B. 15, 425; 16, 647). Heavy oil. Converted by HNO, containing urea, into C,H,(NO,)N.CO,Me [103°], whence Br forms a compound [130°].

Ethyl ether EtA'. Piperul-urethane. Ethyl ether EtA'. Pyreyyl-urcunane.
(211°). Formed from piperidine and ClCO₂Et.
0il. Br in HOAc forms C.H.B.N.CO₂Et [140°],
while HNO, free from NO₂ forms 'nitrodehydropiperyl urethane' C₃H₁(NO₂)N.CO₂Et [52°],
whence Br in HOAc forms C.H.B.N.O₂, [157°].
Chloride C.H.₁₀N.COCl. (238°). Formed
from C.H.₁₀N.CO.CO.H and PCl, (v. PIPERIDIER,
Paration (1) Liquid shouly decomposed by cold

from C₂H₁₀N.CO.CO.H and PCl₄ (p. PIPERIDINE, Reaction 6). Liquid, slowly decomposed by cold water into piperidine, CO., and HCl.

Amide C.H.₀N.CO.NH.₂ [106°]. Got from piperidine sulplate and potassium cyanate.

Needles. Yields B'HNO., [67°] (Franchimont a. Klobbie, R. T. C. 8, 302).

Anilide. [172°]. Formed from piperidine and phenyl cyanate, or from the chloride and aniline (Gebhardt, B. 17, 3010; Wallach, A. 228, 250; 237, 250).

Piperidide (C.H., N), CO. [43°].
Isomeride v. Hexahydride of Pyriding CARBOXYLIC ACID.

DI-PIPERIDYL v. DIPYRIDYL dodecahydride

PIPERIDYL-CYANURAMIDE v. Cyanuramide in article Cyanic Acids.

PIPERIDYL-MELAMINE v. CYANIC ACIDS.

PIPERILENE v. vol. iii. p. 807.

PIPERILENE v. vol. iii. p. 807.

PIPERINE C. H. 10 NO. i.e.

C. H. 10 N. CO.C.H. C.H. C.H. C.H. C. H. 20 C.H. 2. Piperylpiperiline. Mol. w. 285. [128°]. Occurs in
black pepper (Piper nigrum), long pepper (P. longum), and in the black pepper of Western Congun), and in the black pepper of Western Africa (Cubeba Clusii) (Oersted, S. 29, 80; Pelletier, A. Ch. [2] 16, 344; 51, 199; Merck, N. J. T. 20, 1, 34; Wackenroder, Br. Arch. 37, 347; Duflos, S. 61, 22; Warrentrappa. Will, A. 39, 283; Wertheim, A. 70, 58; Gerhardt, Compt. Chim. 1849, 375; A. Ch. [3] 7, 253; Anderson, A. 75, 82; 84, 345; Cahours, A. Ch. [3] 38, 76; Staphones, A. 95, 166; Von Behoe, Kelley, Lee Stenhouse, A. 95, 106; Von Babo a. Keller, J. pr. 72, 53; Strecker, A. 105, 317).

Formation .- By heating piperidine with the chloride of piperic acid (Rügheimer, B. 15, 1390).

Preparation. - Ground pepper (1 pt.) is boiled with slaked lime (2 pts.) and water, the filtrate evaporated to dryness at 100°, and the piperine extracted with ether and recrystallised from alcohol (Cazeneuve a. Caillot, Bl. [2] 27, 290).

Properties .- Monoclinic prisms, v. sl. sol. hot water, m. sol. alcohol and ether. Inactive to light. Insol. dilute acids and alkalis. Decomposed by alcoholic potash into piperic acid and piperidine. Conc. H.SO, forms a blood-red solu-tion. HNO, gives a greenish-yellow colour changing to red. Phosphomolybdic acid gives a flocculent pp. Salts.—The hydrochloride is crystalline,

but decomposed by water.—B',H,PtCl,: roseate monoclinic crystals. Not decomposed by hot water (De Coninck, Bl. [2] 45, 131).—B', HHgCl, : triclinic crystals. -B'HI. r145°7. Steel-blue needles (Jörgensen, J. pr. [2] 3, 328).
PIPEROKETONIC ACID v. DI-OXY-BENZYL

ETHYL KETONE CARBOXYLIC ACID.

PIPERONAL v. Methylens derivative of PROTOCATECHUIC ALDEHYDE.

PIPERONYL-ACRYLIC ACID v. Methylene ether of CAFFEIG ACID.

PIPERONYL ALCOHOL v. Methylene derivative of DI-OXY-BENZYL ALCOHOL.

PIPERONYLIC ACID v. Methylene derivative of PROTOCATECHUIC ACID.

PIPEROPROPIONIC ACID v. DI-OXY-PHENYL-

PIPER-PROPYL-ALKINE v. OXY-PROPYL-PIPERININE.

PIPERYL. This name is given to radicle CH2O.:C8H3.CH:CH.CH:CH.CO. Piperyl has also been used to denote C, H10, the divalent radicle which is united to NH in piperidine; many of the derivatives of this divalent 'piperyl' are described under PIPERIDINE.

PIPERYLENE v. Pentinene.
PIPERYLENE TETRABROMIDE v. Tetra-BROMO-PENTANE

PIPITZAHOIC ACID C₁₃H₂₀O₃. Perezone. [104°] (A. a. L.); [107°] (Mylius, B. 18, 480). May be extracted by alcohol from Pipitzahuae root or Radix Peresia (De la Sagra, C. R. 42, 873, 1072; Weldt, A. 95, 188; Anschütz a. Leather, C. J. 49, 715; B. 18, 709, 715). Flat golden plates (from alcohol), nearly insol. water, v. sol. alcohol and ether. May be sublimed. Volatile with steam. Aqueous alkalis form a violet solution. Aqueous methylamine forms methyl - amido - pipitzahofo acid C₁₅H₁₉(NIIMe)O₂ [114°], crystallising in blue needles, while aniline forms C₁₅H₁₉(NHC·H₂)O₂ [139°], o-toluidine gives C₁₅H₁₉(NHC·H₂)O₄ [110°] a toluidine gives C₁₅H₁₉(NHC·H₂)O₄ [110°], p-toluidine yields p-tolyl-amido-pipitzahore acid [134°]. Bromine forms C12H. Br.O2 [109°].

Salts.-PbC15H18O2.-CuA'2.-AgA': purple

Ethyl ether EtA'. [141°].

Acetyl derivative C_{1.}H₁₉AcO₃. [115°]. Trimetric plates; a:b:c=629:1: 845.

Oxim? C_{1.}H₂₁NO₃. Amidopipitzahoic acid.

[154°]. Flat violet-brown needles. Formed from the scid and alcoholic hydroxylamine (Mylius, B. 18, 936). The same body is got by boiling phenyl-amido-pipitzahoïe acid (v. supra) with NH₂Aq (A. a. L.).

Oxypipitzahoïc acid C_{1,}H_{1s}(OH)₂O₂. [129'] (A. a. L.); [134°] (M.). Formed by warming phenyl-amido-pipitzahoïc acid (v. supra) with alcoholic H.SO. Orange plates, nearly insol. water. Its alkaline solutions are violet. Bromine forms an unstable dibromide [140°-146°]. On warming with H₂SO₄ it is converted into perozinone O₁₅H₁,O₂ [144°], which crystallises in yellow needles or prisms, and yields C15H1, NaO2, crystallising in easily soluble yellow tables.

PIRYLENE C.H. i.e. $CH \ll_{CH:CH^2}^{CH,CH_2}$. (60°).

Formed by distilling with solid NaOH the methylo-iodide of the base obtained by the action of Ag.O on the iodide formed from di-methyl-pyridine hexahydride and iodine (Ladenburg, A. 247, 60). Oil. Does not ppt. ammoniscal Ou,Ci,

PISCIDIN C., H.,O. [192°]. The poisonous principle of Jamaica dogwood (Piscidia Erythrina), from which it can be extracted by lime-water (Hart, Am. 5, 39). Six-sided prisms (from alcohol), insol. water, sl. sol. cold alcohol, sol. benzene, CHCl., and conc. HClAq. Sedative and narcotic.

PITTAKAL v. EUPITTONIC ACID.

PITURINE is NICOTINE.

PLASMINE v. PROTEÏDS.

PLATINAMMINES v. PLATINUM-AMMONIUM сомроимов, р. 292.

PLATINATES. Pto II, acts as an acidio hydroxide towards strong bases, forming compounds of the type xPtO2.yMO. These platinates are generally obtained by reacting on PtCl, Aq with caustic or carbonated alkalis, and sometimes by fusing PtCl, with bases and then washing with water.

Barium . platinates. 2PtO...3BaO was obtained, in hexagonal crystals, by Rousseau (C. R. 109, 144) by heating PtCl. with BaO for some time, then adding BaCl, equal to the quantity of BaO used, and heating to c. 1100° (m.p. of Cu) in a Pt dish for some hours, and washing with water. The crystals are insol. acetic acid, but sol. HClAq. The salt decomposes at an orange-red heat, in presence of BaCl₂, with separation of Pt. Topsöe (B. 3, 462) obtained PtBaO₃.4H₂O by decomposing H2PtCl, Aq by excess of BaO2H2 in sunlight; to the pp. thus obtained Johannsen (A. 155, 204) gave the composition

3PtBaO3.BaCl2.PtOCl2.11H2O.

Calcium platinates. According to Herschel (A. 3, 317), CaOAq added to PtCl, Aq in sunlight produces a white pp. of

PtCaO3.CaO.PtOCl2.7H2O.

Sodium platinates. When a mixture of Na₂CO₃Aq and H₂PtCl₈Aq stands for some days in a warm place, a pp. of 3PtO2. Na O.6H,O separates (Döbereiner a. Weiss, A. 14, 21). Rousseau (C. R. 109, 144) obtained crystals of Na platinate by heating a mixture of equal weights of NaOH and NaCl with some Pt black, in a Pt crucible, to c. 1100 for two or three hours.

For descriptions of the bromoplatinates, chloroplatinates, iodoplatinates, &c., v. Platini-BROMIDES, PLATINI-CHLORIDES, PLATINI-IODIDES,

THIOPLATINATES. PtS, combines with some more basic sulphides to form salts which may be called thioplatinates; some salts are also known containing Pt and Sn combined with alkali metal and S, these may be called thiostanuoplatinates. The alkali thioplatinates are obtained by fusing together spongy Pt, S, and alkali carbonate, and washing with water, wherein the thioplatinates are insoluble. Other thioplatinates - of Cd, Cu, Fe, Pb, Mn, Hg, Ag, Tl, Platinates—or Cd, Cd, Fe, Fe, Mi, Hg, Ag, Ag, Sr, and Zn—arc obtained by double decomposition from the alkali salts. The thioplatinates belong to the forms M¹_Pt_sS_and M⁴_Pt_sS_a; the corresponding thioplatinic acids H_Pt_sS_a H,Pt,S, are obtained by decomposing K,Pt,S, and Na,Pt,S, respectively by dilute HClAq.

Potassium thioplatinate K.Pt.S. = K.S.3PtS.PtS. (Potassium platin-thioplatinate). Blue-grey, metal-like crystals; S.G. 6:44 at 15°. Glows like tinder when heated in air, forming K,SO, and Pt; reduced in H with

evolution of H_sS and formation of Pt. Obtained by fusing an intimate mixture of 1-2 parts Pt black with 12 parts of a mixture of equal parts of S and K_sCO_s in a porcelain crucible, keeping the molten mass over the blowpipe for a few minutes and extracting with water when cold.

Sodium thioplatinate

Na,Pt,S,=2Na,S.2PtS.PtS, (Disodium platinthioplatinate). Copper-red, rhombic needles; decomposed in air. Obtained similarly to the K compound mentioned above.

For details regarding thioplatinates, and also thiostannoplatinates, v. Schneider, P. 136, 105; 138, 604; 139, 661; 141, 519; 148, 633; 149, 881 (cf. E. von Meyer, J. pr. [2] 15, 1).

PLATINITES, derivatives of; v. Platino-BROMIDES, PLATINO-CHLORIDES, PLATINO-NITRITES, &co.

PLATINI- and PLATINO- GOMPOUNDS. Such compounds as platini-bromides, called also bromoplatinates, and platino-nitrites will be tlesorthed here.

PLATINI. COMPOUNDS. These compounds are derived from platinic compounds, especially from PtCl, PtBr, and Ptl, they generally react as salts of acids containing tetravalent atoms of Pt in their acidic radicles.

Platini-bromhydric acid H₂PtBr₂.9H₂O (Bromoplatinic acid). Formed by heating spongy Pt with Br, and HBrAq (b.p. 126°), in a sealed tube, to 180° (Meyer a. Züblin, B. 13, 404; Halberstadt, B. 17, 2962). Also by dissolving Pt black in HNO₃Aq mixed with HBrAq, heating with repeated additions of HBrAq, evaporating over CaO, and washing the crystals, on an asbestos filter, with CS₂ (H., l.c.). Large, clear, carmine-red, monoclinic crystals; v. sol. water, alcohol, ether, acetic acid, and CHCl₂. Melts at 100° with partial decomposition (Topsüe, Ar. Sc. 35, 58; 45, 223).

50, 58; 40, 220;.

Platini-bromides M'.PtBr. (Bromoplatin.
ates). Thomsen (Th. 3, 430) gives [Pt, Br, 2RBrAq]

= 57,160 and [Pt, 0°, 6RBrAq] = 80,360, where
R = H, Na, K, Am, \(\frac{1}{2}\text{Ca}, \(\frac{1}{2}\text{Ba}, \(\frac{1}{2}\text{Sr}, \(\frac{1}{2}\text{Mg}, \) These
salts are generally formed by evaporating
H.PtBr.Aq, or a solution of Pt in Br and
HBrAq, with metallic bromides. They are red
crystalline solids, isomorphous with the corresponding Cl salts. As solutions of these salts
give a pp. of Ag.PtBr. and not AgBr, with a
limited quantity of cold Ag.NO.3Aq, and on electrolysis of their solutions the Pt goes with
the Br to the positive electrode, they are better
regarded as ordinary salts than as double salts
2MBr.PtBr.

AMMONIUM PLATINI-BROMIDE Am,PtBr. Red cotahedra; S.G. 4-2; sl. sol. cold water. S. at 20° = 59 (Halberstadt, B. 17, 2962). Formed by evaporating H,PtBr,Aq + NH,Br.

POTASSIUM PLATINI-BROMIDE K,PtBr. Red octahedra; S.G. 4.54 (Topsöe, Ar. Sc. 35, 58; 45, 228). S. 2.07 at 20°, 10 at 100° (H., l.c.). Obtained by ppg. H,PtBr,Aq by KBr, or by evaporating H,PtCl,Aq with KBr. Thomsen (Th. 8, 480) gives [Pt,Br,2KBr] = 59,260; [K*PtBr*Aq] = -12,260.

Double compounds with K.PtCl, are described by Pitkin (C. N. 41, 118).

Sonium Platini-Bromide Na,PtBr.,6H.O. Dark-red, triolinic prisms; S.G. 3-323; very sol.

water and alcohol. Obtained by evaporating PtCl, Aq with HBr till the Cl is turned out, adding NaBrAq, evaporating to dryness, dissolving in a little water, and crystallising (Thomsen, J. pr. [2] 15, 294). Thomsen (Th. 3, 480) gives [Pt,Br*,2NaBr,6HO] = 65,830; [NaPtBr*,6H*O] = 18,540; [NaPtBr*,6H*O,Aq] = -8,550. Platini-bromides of Ba with 10aq, Ca with 12aq, Co with 12aq, Cu with 8aq, Ph. Mg with 12aq, Mn with 12aq, Ni with 6aq, Sr with 10aq, and Zn with 12aq, are described by Topsöe (Ar. Sc. 35, 58; 45, 223); von Bonsdorff (P. 19, 343) describes a Mn salt with 6aq.

Platini-bromonitrites (Nitro-bromoplatinates. Platini-nitrobromides). Salts derived from the platini-bromides by replacing Br by NO. Bygently heating K.pt(NO.). (v. Platino-nitrites, P. 284) with Br. polassium platini-dibromonitrite, K.ptBr.(NO.)., is obtained as a yellow powder, sl. sol. cold, more sol. hot, water (Vèzes, C. R. 112, 616). When an aqueous solution of this salt is concentrated at a gentle heat, it yields crystals of potassium platini-tribromonitrite, K.ptBr.(NO.). (V. C. R. 115, 44). Polassium platini-tetrabromonitrite, K.ptBr.(NO.).; is obtained by the regulated action of Br on K.pt(NO.).; it forms red prisms, sol. water with partial decomposition (V., C. R. 115, 44).

Platini-chlorhydric acid H,PtCl,.6H.O (Chloroplatinic acid). A solution of this compound is the starting-point for the preparation of very many Pt compounds. Formed by dissolving Pt in aqua regia, repeatedly evaporating with cone. HClAq till every trace of HNO, is expelled, and allowing to crystallise (Weber, P. 131, 441; Jörgensen, J. pr. [2] 16, 345; Topsöe, Ar. Sc. 35, 58). Red-brown, very deliquescent crystals; S.G. 2-431. Easily sol. alcohol, forming crystals; S.G. 2-431. Easily sol. alcohol, forming H.PtCl_(OEt), (Schützenberger, A. Ch. [4] 31, 362). Heated to 230', gives PtCl, (v. Platinum digitioning, Freparation, p. 289). Heated in Cl to above 350' gives PtCl, (v. Platinum tetral-cultoride, Formation, p. 289). By adding much H_SO, to H_PtCl_oH_O in a little water, Pigeon (C. R. 112, 1919), abtained the heater (1). (C. R. 112, 1218) obtained the hydrate with HI,O; and by heating in vacuo at 100°, over fused KOH, he obtained HPtCl, 2H,O. Thomsen (Th. 3, 430) gives [2HClAq,Pt,Cl] = 84,620; [6HClAq,Pt,Cl] = 64,660. Pigeon (C.R. 110,77) gives [H-PtCl*-6HTO,Aq] = 4,340. H.PtCl*Aq reacts as a dibasic acid; the platinic-hlorides are numerous and important; the Am and K salts are only sl. sol. water and insol. alcohol, and are much used as forms for estimating K and ammonia. Very many organic bases replace H and form salts analogous with the metallic platinichlorides.

Platini-chlorides M¹-PtCl_s (Chloroplatinates),
Thomsen (Th. 3, 430) gives [Pt,Cl¹,2RClAq]
=84,620; and [Pt,O¹,6RClAq]=64,060; where
R=H, Am, K, Na, 3Ba, 3Ga, 3Sr, 3Mg. Pigeon
(C. R. 110, 77) gives [PtCl¹,2HClAq]=24,800.
These salts are generally obtained by evaporating
H,PtCl,Aq with metallic chlorides. Most of
them are yellow-red, crystalline solids; usually
e. sol. water and alcohol. They are better
regarded as ordinary salts than as double chlorides (cf. Platini-browides, supra). The platinichlorides were investigated by von Bonsdorff
(P. 17, 250); later by Cleve (Bl. [2] 21, 118, 197,
247, 845); also by Tope6e (Ar. So. 85, 58); and

by Nilson (B. 9, 1056, 1142). Crystallographically considered, these salts fall into four groups:—(1) M.PtCl, where M = Am, Cs, K, Rb, Tl (and Pt may be replaced by Pd, Ir, or Sn); regular, isomorphous with Am2(or K2)PtBr2, Am, (or K,)PtI,, fluosilicates, fluostannates, fluozirconates of similar composition. (2) MPtCl. 6aq, where M = Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn (and Pt may be replaced by Pd or Sn); hexagonal. (3) MPtCl₆.12aq, where M = Mg or Mn; hexagonal; isomorphous with corresponding platini-bromides.
(4) M(PtCl_{*})₂·24aq, where M = Ce₂ or La₂; hexagonal.

Ammonium Platini-chloride Am2PtCla (Ammonium chloroplatinate. Platinsalammoniac). Ppd. on adding NH,Cl to H,PtCl,Aq, PtCl,Aq, or a solution of Pt in cone. HClAq with a little a solution of Pt in cone. Florid with a fittle HNO₂. Yellow, regular, octahedral crystals. S.G. 3-065 (Topsöe, l.c.). S. -665 at 20°, 1-25 at 100° (Michaelis, G.-O. 1, 1187). Scarcely sol. alcohol or ether. Decomposed at red heat, leaving Pt black. For reactions with NH₃ v. PLATINUM-AMMONIUM COMPOUNDS, p. 292.

POTASSIUM PLATINI - CHLORIDE (Potassium chloroplatinate). Ppd. by adding KCl, or other K salt, to conc. H₂PiCl₈Aq, or to a solution containing Pt which has been evaporated with excess of HČlAq. Reddish-yellow regular octahedra. S.G. 3-586 (Bödeker). S. 74 at 0°, 1-12 at 20°, 2-17 at 50°, 3-79 at 80°, 5-13 at 100° (Michaelis, *l.c.*). Almost insol. alcohol, or alcohol and ether. Slightly sol. dilute acids; sol. KOHAq. Reduced to Pt and KCl by heating to redness; more quickly by heating with reducing agents such as oxalic acid or sulphurous acid, or by heating in a stream of hydrogen. Vèzes (C. R. 110, 757) describes a nitroso- derivative, (C. R. 110, 757) describes a narrows derived $K_2Pt(NO)Cl_5$. Pigeon (C. R. 110, 77; 112, 791) gives [Pt,Cl',2KClAq] = 83,330; [PtCl',2KClAq] = 95,330; [PtCl',2KClAq] = 95,330; [PtCl',2KCl] = 29,700. Thomsen (Th. =25,330; [PtCl $^{4},2$ KCl] =29,700. 3, 430) gives [Pt,Cl4,2KCl] = 89,500.

Potassium platini-bromochloride K2PtBr2Cl4; by ppg. H2PtCl6Aq by KBr (Pitkin,

C. N. 41, 118).

The following platini-chlorides have also been isolated: AlCl. PtCl. 15aq (Welkow, B. 7, 804; Salm-Horstmar, P. 99, 638); Ba, with 4aq (Topsöe; Bornsdorff, Precht, Fr. 1879; 509); Be, with 8aq (Welkow, B. 6, 1288; Thomsen, B. 3, 827); Cd, with 6aq (Topsöe); Cs (Crookes, C. N. 9, 37; Bunsen, P. 119, 371); Ca, with 9aq (Topsöe); Breath! (Topsöe; Procht); Ge, various salts (Cleve, Marignae, Holzmann, J. pr. 81, 80); CrCl, PtCl, 10aq (Nilson, B. 9, 1056, 1142); Co, with 6aq (Topsöe); Cu, with 6aq (T.); Di, various salts (Frerichs a. Smith, A. 191, 331); 2InCl, 5PtCl, 36aq (Crookes, J. 1864. 256); Fe, various salts (T.; Bonsdorff; various salts (Cleve, Marignac, Nilson); La, Jolin, B. 11, 910); Pb, with 3 or 4aq (Birnbaum, J. 1867. 319; Topsöe); Li, with 6a4 (Scheibler, J. pr. 67, 485; Jörgensen a. Topsöe, Gm.-K. 3, 1174); Mg, with 6aq (T.); Mn, with 6aq (T.); Ni, with 6aq (T.); Rb (Crookes; Bunsen); Ag (Birnbaum); Na, with 6aq (Marignao, Topace, Precht; for thermal data v. Thomsen, and Pigeon, Le.); Sr, with 8aq (Bonsdorff); Tl rigeon, 4.5.; or, with 12aq (Cleve); Sn, with 12aq (Cleve); Sn, with 12aq (Cleve); Sn, with 12aq (Nilson). Compounds of PtCl, with chlorides of Rr (Nilson), Hg (Birnbaum), VO (Brauner, M. 3, 58), and ZrO (Nilson) probably exist. No com-

pounds are formed with PtCl, and chloride of Sb, As, or Bi.

(Platini-nitrochlor-Platini-chloronitrites Nitrochloroplatinates). Salts derived from the platini chlorides by replacing Cl by NO. A few of these salts are described by Vèzes (C. R. 115, 44); the principal are dichloronitrite K.PtCl₂(NO₂), trichloronitrite K.PtCl₂(NO₂), and pentachloronitrite K.PtCl₃(NO₂). H₂O (v. also Blomstrand, J. pr. [2]

3, 214). Platini-iodhydric acid H,PtI,9H,O (Iodoplatinic acid). Brown deliquescent crystals; probably monoclinic; by dissolving PtI, in HIAq, and evaporating. Easily decomposed, even in solution, rapidly at 100°, with separation of PtI, (Topsoc, Ar. Sc. 38, 297; Clementi, J. 1855. 420; Lassaigne, A. Ch. [2] 51, 113).

Platini-iodides Mr.PtI. (Iodoplatinates). Reddish-brown, metal-like salts; generally formed by evaporating H.PtCl.Aq with excess of (Iodoplatinates). metallic iodides, or by adding iodides to PtI Aq. The following have been described (v. Topsöc, Clementi, Lassaigne, l.c.; Am; Ca, with 12aq; Co; Fe; Mg, with 9aq; Mn; Ni, with 6aq; K; Na, with 6aq; Zn, with 9aq.

Platini-iodonitrites (Platini-nitro-iodides. Nitro-iodoplatinates). $M_2^1PtI_{e-x}(NO_2)_x$. A few of these salts are described by Vezes (C. R. 113, 696). A nitroso-platini-iodide, K,Pt(NO)I,, is

also described.

By boiling Pt(OH,) Platini-molybdates. with an acidified solution of Na molybdate, Gibbs (Am. S. [3] 14, 61) obtained a complex compound which may provisionally be classed as a platini-molybdate, 4Na,O.10MoO, PtO, 29H,O.

Platini-nitrobromides ; .v. PLATINI-BROMOмититея, р. 282.

Platini-nitrochlorides; v. PLATINI-CHLORO-NITRITES, supra.

Platini-nitro-iodides; v. PLATINI-IODO-NITRITES, supra.

Platini-tungstates. Complex compounds of PtO2, WO3, and strong bases (v. Gibbs, Am. S. [3] 14, 61; Rosenheim, B. 24, 2397).

These com-PLATINO. COMPOUNDS. pounds are derived from platinous compounds, especially from PtCl., PtBr2, and PtI2; they generally react as salts of acids of the form H2PtX4, where X is a monovalent negative radicle, generally Cl, Br, or I.

Platino-bromhydric acid H₂PtBr. (Bromo-tinous acid). This compound is probably platinous acid). contained in a solution of PtBr, in HBrAq.

Platino bromides M1.PtBr. (Bromoplati-nites). Only one of these salts, K.PtBr., has been isolated. Potassium platino-bromids is obtained by adding a very little water to a mixture of the corresponding Cl salt and NaBr, in the ratio K,PtCl,: 4NaBr, boiling, sucking up the clear liquid from ppd. NaCl, and allowing to cool, when the salt crystallises in dark-brown octahedra, or brown-red needles, which are very sol. water (Thomsen, J. pr. [2] 15, 294). Thomsen (Th. 3, 430) gives [2KBr, Pt, Br²] = 82,310.

Platino-bromonitrites v. Platino-mitrites, p. 284.

Platino-chlorhydric acid H.PtCl, (Chloroplatinous acid). This soid has not been isolated; but it almost certainly exists in a solution of PtCl, in HClAq, in the liquid obtained by decomposing BaPtCl, by the equivalent quantity of H₂SO,Aq (Nilson, J. pr. [2] 15, 260), and in the solution formed when conc. H.PtCl,Aq is added to hot conc. K.PtCl,Aq (Thomsen, J. pr. [2] 15, 294). When these liquids are evaporated in vacuo. a residue is obtained agreeing in composition with the formula HPtCl₃.2H₂O (= HCl.PtCl₃.2H₂O = H₂PtCl₂(OH).H₂O); at 100° this loses H₂O and HCl and leaves PtCl₂ (Nilson, *l.c.*).

Platino-chlorides M' PtCl, (Chloroplatinites). These salts are obtained by evaporating metallic chlorides with PtCl.Aq, or in many cases by reducing platini-chlorides. Most of the platinochlorides are very soluble in water, and crystallise only from very conc. solutions, generally forming dark-red crystals. Many of them are described by Nilson (J. pr. [2] 15, 260). Thomsen (Th. 8, 480) gives $[Pt,O]^2,2MClAq] = 41,830$; and [Pt,O,4MClAq] = 81,550; where M=H, K, Na, Am, Ba, Ca, Sr, or Mg.

Ammonium PLATINO-CHLORIDE Am.PtCl. (Ammonium chloroplatinite). Obtained, in four-sided prisms, by adding AmCl to PtCl, in HClAq, and evaporating; also by reducing hot Am2PtClaAq by SO2, or hot H2PtClaAq by SO2 and then adding AmCl (Peyrone, A. 55, 205; Thomsen, B. 2, 668; Grimm, A. 99, 95). $[Pt, Cl^2, 2AmCl] = 43,550$ (Th. 3, 430).

POTASSIUM PLATINO-CHLORIDE K.PtCl. (Potassium chloroplatinite). Large, ruby-red, foursided prisms; S.G. 3.2909 at 21°; easily sol. water, insol. alcohol (Nilson). An aqueous solution is not ppd. by soda or potash when cold; on boiling, all the Pt is thrown down as Pt(OH), (Thomsen, J. pr. [2] 15, 295). [Pt,Cl²,2KCl] - 45,170 (Th. 3, 430). Obtained by adding KCl to PtCl, in HClAq, and evaporating (Magnus, P. 14, 241); also by reducing K,PtCl,Aq by H.S. (Böttger, J. pr. 91, 251), or better by Cu₂Cl₂ (Thomsen, J. pr. [2] 15, 294). K₂PtCl₅ is made into a paste with water, warmed, and moist Cu₂Cl₂ is added, little by little, until a small excess is present; the liquid, which is nearly black, is filtered, the red crystals which separate on cooling are washed with alcohol and re-crystallised.

The following platino-chlorides have been isolated and described: Ba, with 3aq; Be, with 5aq; Ca, with 8aq; Cs (Böttger, J. pr. 91, 251);
Co, with 6aq; Cu, with 6aq (Thomsen, l.c.;
Millon a. Commaille, C. R. 57, 822); Fe^{cus}, with 6aq; Pb; Li, with 6aq; Mg, with 6aq; Mn, with 6aq; Ni, with 6aq; Rb; Ag; Na, with 4aq; Sr, with 6aq; Tl; Zn, with 6aq (Hünefeld, S. 60, 197).
Compounds of PtCl₂ with the chlorides of the following metals are also described by Nilson (l.c.); Al, Ce, Cr, Di, Er, La, Th, and Y.

Platino-chloronitrites; v. Platino-nitrites,

Platino-chlorophosphates (Phospho-platinochlorides). Several salts, and a few acids, containing Pt, Cl, and P have been isolated by Schützenberger (Bl. [2] 17, 482; 18, 101, 148). The classification of these compounds is very incomplete. The following scheme is accepted as provisional (cf. Seubert, Ladenburg's Hand-worterbuch der Chemie, 9, 314):

Platino-chlorophosphoric acid Cl.Pt:P(OH), by dissolving Cl.Pt.PCl, in water and crystal-

lising; (Cl.Pt:PO,),Pb,8aq, and various esters. isolated.

Platino-chlorodiphosphoric acid

P(OH) ; by the action of moist air on

Cl_Pt:| ; by the action of moist P(OH), Cl_Pt:Pcl_Pcl_; ethyl ester also isolated.

Platinochloropyrophosphoric acid

ClPt: d ; by warming a solution of

P(OH), Cl₂Pt:PCl₃.PCl₃.

Platino-chloro-anhydropyrophosphoric acid P(OH),

ClPt: Ò ; by heating the foregoing acid to P(OH)

150°. Ethyl diplatino-chloro-phosphate

Cl.Pt P(OEt), by dissolving Cl.Pt PCl, in alcohol; corresponding acid not isolated (Cochin. C. R. 86, 1402).

Platino-cyanides and derivatives : v. vol. ii. p. 344.

Platino-iodhydric acid H.PtI. (Iodoplatinous acid). This acid probably exists in a solution of PtL, in HIAq.

Platino-iodonitrites; v. Platino-nitrites.

Platino-nitrites, and derivatives. Platinous nitrite [Pt(NO2)2] has not been isolated; but several compounds are known in which the group Pt(NO₂)₂ forms part of the acidic radicle. These platino-nitrites belong to the form M2Pt(NO2); they are not to be regarded as double salts, but as derivatives of the acid H2Pt(NO2)4; the ordinary reagents for Pt do not show the presence of this metal in solutions of these salts, nor do these solutions give the reactions of nitrites; their solutions doubtless contain the ions M and Pt(NO2)4. Most of the platino-nitrites are obtained from the potassium salt K2Pt(NO2)4, which is formed by the reaction of equivalent weights

is formed by the reaction of equivalent weights of K_PtGl₄ and KNO₂.

PLATINO-NITROUS ACID H_Pt(NO₂)₄ has not been obtained pure, but it doubtless exists in the solution obtained by decomposing BaPt(NO₂)₄ by H_SO₄Aq; on evaporation, this solution gives red crystals (Lang, J. pr. 83, 415), but the process causes merical decomposition to but the process causes partial decomposition to triplatino-octonitrous acid H.Pt.O(NO2).2H20 (Nilson, B. 10, 934).

POTABSIUM PLATINO-NITRITE (Potassium nitroplatinite). Small, lustrous, colourless, monoclinic prisms; by mixing solu-tions of equivalent weights of K.PtCl, and KNO. and evaporating (Topsöe, J. 1879, 307). S. 3.8 at 15°; more sol. hot water. Combines with Br and Cl to form potassium platini-dibromo-[dichloro-] nitrites, K.PtBr. [Cl.] (NO.). Most of the other platino-nitrites are obtained from this salt, by adding AgNO,Aq, separating Ag,Pt(NO₂), and decomposing this by metallic ollorides; or making BaPt(NO₂), by the action of BaCl_Aq on the silver salt, and decomposing this by sulphates (Nilson, B. 9, 1722; 10, 980; 11, 879; v. also Blomstrand, J. pr. [2] 8, 186).

The other platino-nitrites which have been

isolated are: Al, Am, Cd, Ce, Cr, Co, Di, Sr, Fe, La, Pb, Li, Mg, Mn, Hg, Ni, Ag, Na, Tl, Y, and

PLATINO-BROMONITRITES M¹₂Pt(NO₂)_{4-x}Br_x.

A few of these salts have been obtained by Vezes (C. R. 113, 696; 115, 44). Potassium platino-bromonitrite K₂PtBr(NO₂)₂ and dibromo-nitrite K₂PtBr₂(NO₂)₂ are described.

PLATINO-CHLOROMITRITES M'_Pt(NO_1)_-_cCl_z. Vèzes (l.c.) has described the potassium monochloro-salt K_PtCl(NO_1),, and the dichloro-salt

K2PtCl2(NO2)2.

PLATINO-IODO-NITRITES M.Pt(NO₂)₄., I₂ (Nilson, B. 10, 930; 11, 879; Groth, Z. K. 4, 409; Vèzes, C. R. 115, 44). Potassium platino-di-iodo-nitrite K.PtI₂(NO₂)₂.Pl₂O is obtained, in small, black crystals, by the action of an alcoholic solution of I on K.Pt(NO₂)₄. The other salts isolated are those of Al, Am, Ba, Be, Cd, Cs, Ca, Ce, Co, Cu, Di, Fe, La, Pb, Li, Mg, Mn, Ni, Rb, Ag, Na, Sr, Tl, Y, and Zn.

Platino-nitrobromides; v. PLATINO-BROMO-

MITRITES, supra.

Platino-nitrochlorides; v. Platino-chloro-MITRITES. supra.

Platino-nitro-iodides; v. Platino-iodo-

NITRITES, supra.

Platino-oxalic acid and platino-oxalates $\mathbf{H}_{2}\mathrm{Pt}(\mathbf{C}_{2}\mathbf{O}_{4})_{2}$ and $\mathbf{M}^{1}_{2}\mathrm{Pt}(\mathbf{C}_{2}\mathbf{O}_{4})_{2}$ (Söderbaum, Bl. [2] 45. 188). The sodium salt Na,Pt(C,O₄),.4H₂O 45, 188). is obtained, in copper-coloured crystals, by he obtained, in copie-coloured trystalised oxalio acid, cooling the blue-coloured liquid, treating the brown needles which separate with hot water, and crystallising; sometimes the salt separates with 5H.O as golden-coloured crystals. The other salts are obtained by double decomposition from the Na salt; they seem to exist in two forms corresponding with the two sodium safts. Platino-oxalic acid H.Pt(C,O,),2H,O is obtained as red, lustrous, metal-like crystals by decomposing the silver salt with the equivalent weight of HClAq, filtering, and concentrating the blue solution in vacuo. Salts of the following metals are described by Söderbaum (l.c.): Am, Ba, Ca, Mg, Mn, Ni, K, Ag, Na, Sr, and Zn.

Platino-phosphochlorides v. Platino-chloro-

РИОЅРНАТЕS, р. 284.

Platino-seleno-stannates. Schneider (J. pr. [2] 44,507) has described two salts, K_Pt_SnSe, and Na_Pt_SnSe, which may be called platino-seleno-stannates. They are formed by heating together Pt black, SnSe, K_CO, or Na_CO, and Se.

Platine-stannates. This name may be given to some compounds derived from the acids H_Pt_Sn_O, and H_Pt_Sn_O, described by Schneider (P. 136, 105) and Schützenberger (C. R. 98, 985); cf. also Lévy a. Bourgeois (C. R. 94, 1365).

Platino-sulphocyanhydric acid, and salts v.

vol. ii. p. 857.

Platine-sulphonates, and derivatives (Liebig, A. 28, 23; Litton a. Schnedermann, A. 42, 316; Birnbaum, A. 189, 164; 162, 137; 159, 116; Dobereiner, J. pr. 15, 315; Lang, J. pr. 88, 415). (Platino-sulphites. Sulpho-platinites.) When K.PtCl., is heated with KHSO.Aq, or SQ, is passed into K.SO.Aq holding Pt(OH), in suspension, the liquid is neutralised by K.CO., and

evaporated, yellow, microscopic crystals are obtained of K_Pt(KSO_J),2H_Q. From this potassium platino-sulphonate other similar salts are obtained. These salts are better regarded as derived from platino-sulphonic acid H_Pt(HSO_J), than as double compounds of PtSO_a and K_SO_k(K_Pt(KSO_J)_i=PtSO_a,8K_SO_J]; they are analogous to the platino-chlorides M_PtCl, and the platino-nitrites M_Pt(NO_J). The ammonium, sodium, and silver salts have been isolated. Sodium-platino-oxy-sulphonic acid Na_Pt(HSO_J)_Q have also been isolated.

PLATINO - CHLOROSULPHONATES (Platino-chlorosulphites. Sulpho - chloroplatinites). Mt_Pt.Cl_1.M'SO_1. The potassium salt K_Pt.Cl_2.MSO_1 is obtained by warming K_PtCl_4 with SO_4Aq, evaporating, and adding KCl. Ammonium platino - chlorosulphonic acid Am_Pt.Cl_1.HSO_3 crystallises from a solution of Ant_Pt.Cl_3. To Am_Pt.Cl_4, in warm cone. SO_2Aq; the potassium and sodium salts of this acid are known. A complex acid, AmH.Pt.Cl.SO_*HSO_1 and the salts AmK.Pt.Cl.SO_*KSO_3 and Am_Pt.Cl.SO_*SO_3Am have been isolated.

Platino-thiosulphates. A few salts have been obtained which may be regarded as compounds of hypothetical platinous thiosulphate and sodium thiosulphate PtS₂O₃xNa₂S₂O₃.4/H₂O, where x is 3, 4, 6, and 7. They may also be looked on as derivatives of the hypothetical acid H₂Pt(S₂O₃H)₂, where H is replaced by Na (Schottländer, A. 140, 200; Jochum, C. C. 1886. 642).

M. M. P. M.

642).
PLATINUM. Pt. At. w. 194 8. Mol. w. unknown. Melts at c. 1775° (Violle, C. R. 89, 702); older determinations generally gave m.p. c. 2000° (for references v. Carnelley's Melting and Boiling Point Tables, p. 10), although Becquerel (C. R. 57, 855) gave 1460°-1480°. S.G. 2148 Och 1. 51, 630) gave 1300 1300 1300 1300 1500 150 at 17.6°, after melting in H (Deville a. Debray, C. R. 81, 839; for other values v. Clarke's Specific Gravity Tables, 2nd edit. p. 15). S.H. -03243 (Regnault); -0314 (Dulong a. Petit); -0317 + 000012t at to (Violle, P. M. [5] 4, 818). C.E. (linear at 40°) .00000899 (Fizeau, C. R. 68, 1125, for Pt that had been melted); from 0° to 100°, 00000881 (Calvert a. Johnson, B. A. 1858. for hammered Pt). T.C. (Ag = 1000) 379 (C. a. I.c.); c. 84 (Wiedemann a. Franz, J. 1855. 91). Heat of fusion c. 5276 (for 194 g.) (Violle, *Lc.*). E.C. (Ag = 100) 8.042 at 12°-18° (Becquerel, A. Ch. [3] 17,242); 10.53 at 20.7° (Matthiessen, P. 103, 428). For electrical resistance of Pt wire v. Arndtsen (P. 104, 1). Crystallines in the regular system (v. infra, Properties). For chief lines in emission-spectrum v. B. A. 1884. 436.

Occurrence.—Alloyed with Ir, Pd, Rh, Au, Cu, and Fe in the sands of many rivers, often associated with titaniferous iron and chromeiron, and in the older rocks in different parts of the world. The quantity of Pt in 'platinum ores,' varies from c. 50 to c. 90 p.c. A Canadian Ni ore was found by Clarke a. Catlett to contain from 008 to '02 p.c. Pt (Am. S. 37, 572). In 1741 Watson received some particles of a metallike substance from the gold-bearing sand of the river Pinto in New Granada; the shining silvery particles were called in the district where they occurred platina del Pisto [platina = diminuitye]

of Spanish plata = silver). Watson extracted a new metal from the substance sent him, and called it platinum (T. 1750. 585). For a short account of the history of the Pt metals, v. Noble metals, iv. 628.

Formation.-1. By decomposition of PtCl, or (NH₄).PtCl₄ by heat.—2. By heating an alloy of Pt and Pb in a current of air, whereby the Pb is oxidised and the Pt remains .- 3. By reducing many Pt salts by Zn, Fe, NaOHAq and FeSO, Aq, Na, CO, Aq and sugar, alcohol added to

an alkaline solution, &c.

Preparation.—1. The Pt ore is obtained as a fine powder by fusing with 2 or 3 times its weight of Zn, powdering the brittle alloy so formed, and removing the Zn by dilute H.SO.Aq (Descotils, G. A. 27, 231; Hess, J. pr. 40, 498). The residue is heated to redness, then warmed with HClAq (to remove portions of the baser metals), and then treated with cold aqua regia which dissolves Au. The residue is heated, in retorts, with aqua regia; the solution contains most of the Pt, along with Rh, Pd, and a little Ir; in the residue are found osm-iridium (v. vol. iii. p. 47), Ru, and a little Pt. The acid is distilled off, carrying with it most of the Os as OBO4; the concentrated solution is neutralised OSO; the concentrated solution is neutralised by Na,CO,, and the Pd is ppd. as PdCy, by HgCy,; NH,Cl is added to the filtrate, and (NH,),PtCl, is thus ppd. mixed with some (NH,),ItCl,. The Ir salt may be removed by digesting with slightly warm KCNAq until the undissolved portion is light yellow; the salt IrCl., 3NH, Cl is thus formed and dissolved, while (NH₄)₂PtCl₆ remains (Wöhler a. Mucklé, A. 104, 368). Or the NH₄.Pt and NH₄.Ir chlorides may be dissolved in hot water, and the Ir salt reduced to IrCl₂.3NH₄Cl, which dissolves, by SO₂ (cf. Iridium, vol. iii. p. 46). The residual ammonium platinichloride is then heated until all NH, and Cl are volatilised.—2. Finely-divided Pt ore is dissolved in aqua regia diluted with 2 pts. water, under increased pressure (which aids the solution); the solution is evaporated, and the residue is heated to 125°, whereby the chlorides of Pd and Ir are reduced to the lower chlorides; treatment with HClAq dissolves PtCl, which is ppd. as (NH,),PtCl, by addition of NH Cl (Heraus, v. Hotmann's Chem. Industrie auf der Wiener Weltausstellung, 2, 999; v. also Dullo, J. pr. 78, 869) .- 8. Commercial Pt is melted with 6 times its weight of Pb, the granulated alloy is treated with dilute HNO₃Aq (1:8 by volume), which dissolves most of the Pb, Cu, Pd, and Rh; the black residue is dissolved in diluted aqua regia-Ir remains undissolved—the solution is evaperated with H2SO, Aq, whereby Pb is removed as PbSO, the filtrate and washings are mixed with excess of NH,Cl and some NaCl, heated to 80°, and allowed to stand for some days; the pp. is washed repeatedly with saturated NH.ClAq, and then with very dilute HClAq; it is then dried, heated to dull redness in a Pt vessel with KHSO, and a little NH, HSO, and washed with boiling water -Rh goes into solution as Rh-K disulphate, and finely-divided Pt remains (Matthey, Pr. 28, 463). For other methods v. Deville a. Debray, A. Ch. [3] 56, 885; 61, 5.—4. Pure Pt is obtained by evaporating a solution of the ore in aqua regia with HClAq till HNO, is nearly removed, adding NaOHAq till strongly

alkaline, boiling for a long time (the alkalinity gradually disappears, owing to formation of NaClOAq), adding alcohol, and then making the turbid liquid acid by HClAq, filtering from olivegreen IrCl,, and ppg. by conc. NH, ClAq (W. von Schneider, A. Suppl. 5, 261). The Pt obtained by strongly heating the ppd. (NH₄)₂PtCl₆ should. be dissolved in diluted aqua regia, and re-ppd. by addition of NH₁Cl; on heating this pp. pure Pt remains (Seubert, A. 207, 8). For another method of obtaining pure Pt, v. Mylius a. Förster, B. 25, 665.

The finely-divided Pt obtained by the above methods may be fused into a lump by the use of the O-H flame. The metal is placed in a cavity made in a block of lime (made by strongly heating marble), which is covered by another block, through the top of which a hole is pierced to admit the flame (v. Deville a. Debray, A. Ch. [3] 56, 385; cf. PLATINUM in DICTIONARY OF APPLIED

CHEMISTRY).

Platinum black, which is extremely finelydivided Pt, is obtained by reducing solutions of some Pt salts by certain organic reducing compounds, or by Zn or Mg, &c. PtCl, Aq may be reduced by Mg (Böttger, J. pr. [2] 2, 137), zincedust or Fe in powder (Brunner, A. 109, 253), FcSO, Aq and NaOHAq (Hempel, A. 107, 97), sugar and Na₂CO₃Aq, or by alcohol. Pt black is also formed by fusing Pt with twice its weight of Zn, powdering the alloy, dissolving out Zn by H.SO, Aq, and washing with very dilute HNO, Aq (Döbereiner, A. 17, 67). Loew (B. 23, 289) recommends to dissolve 50 g. PtCl₄ in 50-60 c.c. water, to add c. 70 c.c. formic aldehyde solution of 40 to 45 p.c., to cool, and then to add gradually 50 g. NaOH in 50 c.c. water, to set aside for 12 hours, and then to filter and wash until the washings pass through black, when the washing should be stopped for some hours, and continued when the washings again pass through colourless (O is absorbed and temperature rises); the residue is washed until quite free from NaCl, and dried over H2SO4. Liebig (P. 17, 101) dissolved PtCl2 in warm conc. KOHAq, added alcohol to the hot liquid till CO, came off freely, decanted, washed the ppd. Pt, successively, with alcohol, HClAq. KOHAq, and finally, several times, with boiling water.

Crystals of platinum are obtained by heating Pt to redness, in a glass or porcelain tube, in a stream of dry Cl, for twenty-four hours (Hodgkinson a. Lowndes, C. N. 58, 158, 203; Seelheim, B. 12, 2066; Joly, N. 43, 541; cf. Troost a. Hautefeuille, C. R. 84, 94). Joly (N. 43, 541) obtained cubical crystals of Pt, about 1 mm. in length, by sprinkling some finelypowdered topaz on a ribbon of Pt, and heating to bright redness by an electric current for c. two hours. Moissan (C. R. 109, 807) obtained crystalline Pt by heating dry PtF, in a Pt tube, to bright redness. Pt that has been melted shows a crystalline structure when touched with aqua regia (cf. Koettig, J. pr. 71, 190; Nogoks, C. R. 47, 832; Kalischer, B. 15, 706; Mallet, Am. S. [2] 20, 340; Phipson, C. N. 5, 144).

Treatment of platinum residues.—Pt residues accumulated in the laboratory generally contain Pt as (NH₁)₂PtCl₂; the liquid portion usually contains alcohol. The solid part is warmed, in a water-bath, with K₂CO₂Aq, KOHAq,

er NaOHAq, and the alcoholic liquid is added little by little, or HCO₂Na is added (Duvillier, C. R. 84, 444), till the salt is reduced to Pt. The black residue is washed, dried, boiled with HClAq, and again washed and dried (Knösel, B. 6, 1159).

Properties.—Compact platinum is a white metal with a greyish tinge; it is easily polished, thereby acquiring a very high lustre. Much softer than Ag, rather softer than Cu: thin plates or wire can be cut easily with scissors. Without taste or smell. Very malleable and ductile; a wire 2 mm. diameter breaks with a weight of 124 kilos; tenacity is, therefore, c. same as Fe. Pure Pt can be drawn into very thin wire; by fusing into Ag wire, drawing out, and dissolving away the Ag, a wire of Pt 0009 mm. diameter is said to have been obtained (Gaiffe, C. R. 1877. 625). Most easily fused of Pt metals except Pd; very thin wire melts in the outer blow-pipe flame; larger masses require the O-H flame. Becomes soft and workable much below its m.p. Melts in an ordinary fire, owing to combination with C or Si (Heraeus, D. P. J. 167, 132; Deville, A. Ch. [3] 46,182; Boussingault, C. R. 82,591; Schützenberger a. Colson, C. R. 94, 1710). Crystallises in the regular system, chiefly in octahedral and dodecahedral forms (v. Scelheim, B. 12, 2066). Said to volatilise to some considerable extent when kept molten (Deville a. Debray, C. R. 44, 1101). By heating in certain gases, especially in Cl, volatile compounds are formed and again decomposed. Molten Pt absorbs O, and 'spits' when cooled rapidly.

Pt occludes H. According to Graham (P. M. [4] 36, 63), Pt foil absorbs five to six times its own volume of H at a dull-red heat; Berthelot (C. R. 94, 1383) says that Pt absorbs from 80 to 120 times its volume of H, probably with formation of definite compounds. Berliner (W. 35, 791; cf. Neumann, M. 13, 40) found that ordinary Pt foil absorbed 127 volumes of H; foil that had been quite freed from gases and cleaned absorbed 200 vols. of H and 80 vols. of O or CO. The whole of the occluded gas is removed, with difficulty, by strongly heating in vacuo; under ordinary conditions about 80 vols. of H are retained. O is also occluded by Pt foil, and the condensed O brings about oxidations, e.g. electrolytic gas (H₂+0) explodes when exposed to Pt foil at c. 180° (Berliner, l.c.). Pt is pervious to H at a bright-red heat; Graham (P. M. [4] 32, 401, 503) found that 489-2 c.c. H passed, per minute, through Pt foil 1-1 mm. thick and having a surface of 1 square metre. Gases other than H scarcely diffused through at all.

Pt is not acted on by pure HClAq, HNO,Aq, or H,SO,Aq, nor is it attacked by O; various mixtures of acids dissolve it. Pt is acted on by Cl and by substances which evolve Cl; also, at high temperatures, by molten alkalis, nitrates, KCN, a mixture of alkali carbonates with S, by P and Si, and by most of the metals.

Platinum black is a porous, heavy, very finely-divided black powder, which becomes metal-like, grey, and lustrous when rubbed; S.G. 15-8 to 17-6. Pt black absorbs large quantities of certain gases, especially 0; according to Döbereiner (A. 17, 67), from 173 to 253 vols.

O are occluded by 1 vol. Pt black. The O condensed in Pt black is able to bring about many processes of rapid oxidation: H, CO, C.H., C.H., O gas, Et.O vapour, &c., are rapidly oxidised, generally with ignition (v. von Mulder, R. T. C. 2, 44; Schönbein, J. pr. 98, 76; P. 105, 258; von Mulder a. van der Meulen; R. T. C. 1, 167); alcohol is oxidised to acetic acid, formic and oxalic acids to CO, and H.O, As.O. to As.O. (von Mulder, R. T. C. 2, 44). Pt black charged with H acts as a reducer; water is formed when the hydrogenised Pt black is brought into O (Wilm, B. 14, 878; Berthelot, C. R. 94, 1377); aqueous solutions of KClO₃, KNO₃, K.FeCy, also C.H.NO₃, &c., are reduced (Gladstone a. Tribe, C. N. 37, 245); ozone is reduced to O (von M. a. van der M., Lc.). One cause of these actions is probably the heat produced during the condensation of the gases in the porous Pt (cf. Berthelot, A. Ch. [5] 30, 519); it is not probable that an oxide of Pt is formed and then reduced (D. V. Meyer, 1, pr. [2] 14, 124; cf. Tommasi, B. 11, 811).

of Pt is formed and then reduced (p. V. Meyer, J. pr. [2] 14, 124; cf. Tommasi, B. 11, 811).

The at. w. of Pt has been determined (1) by strongly heating PtCl. (Berzelius, P. 8, 179 [1813]); (2) by determining Pt in K. PtCl., and by finding the ratio of Pt:KCl in the same salt (B., P. 13, 469 [1826]; Andrews, Chem. Gazette, 1852, 379); (3) by analyses of K,PtCl, and (NII,),PtCl, (Scubert, A. 207, 29 [1800]; Halberstadt, B. 17, 2962 [1884]; cf. Dittmar a. McArthur, E. Tr. 33, 561 [1888], and criticism thereon by Scubert, B. 21, 2179; (4) by determining S.H. of solid Pt (Violle, P. M. [5] 4, 318). As no V.D. of a Pt compound has yet been determined, the at. w. cannot be found by the direct application of the law of Avogadro. The older determinations gave 196 to 197; Seubert proved that the true value is c. 194.5, which is between the values for Ir (192.5) and Au (196.8). No compound of Pt has been gasified from which the valency of the atom of Pt in gaseous molecules can be determined. Pt is closely allied to Ir, and less closely to Os, in its chemical properties. It is distinctly metallic physically, and, on the whole, chemically also. PtO, is both basic and acidic; Pt forms numerous acids by combining with H and negative radicles such as Cl, (NO), Cl, (CN), (SCN), &c. For a fuller account of the chemical relations of Pt v. Noble metals, vol. iii. p. 628, and cf. Iron GROUP OF ELEMENTS, vol. iii. p. 67.

Ptis used for making crucibles &c. for laboratory use, and vessels for evaporating cone. oil of vitriol, &c. Apparatus is sometimes platinised by placing in hot PtCl,Aq containing KOH and some organic reducing compound.

Reactions and Combinations.—1. Is not acted on by oxygen; concerning absorption of O by Pt v. Properties.—2. Heated to redness with sulphur, in presence of borax, PtB is formed (Deville a. Debray, C. R. 89, 587).—5. Said to form a compound by leating Pt black with selenion.—4. With chlorine, bromine, and iodine Pt reacts at temperatures above c. 300° (Langer a. Meyer, Pyrochemische Untersuchungen (Braunschweig, 1885) 44, 57). Cl and Br attack Pt in presence of water.—5. Scarcely acted on by fluorine below 100° (Moissan, A. Ch. 1892, 125), 6. Hydrogen is occluded by Pt; a considerable quantity of heat is produced, and perhaps compounds are formed (v. Platinum Etdalde, p.

290).-7. Heated with arsenic, a compound! PtAs, is said to be formed (v. Gm.-K. 3, 1192-1198).—8. Phosphorus combines when heated with finely-divided Pt (Schrötter, J. 1849. 246). 9. A boride is formed by heating Pt black with amorphous boron (Descotils, A. Ch. [3] 67, 88; Deville a. Wöhler, J. 1856. 279).—10. Heated to whiteness with silicon, Pt forms several compounds; also combines with Si when heated with silica and carbon (v. PLATINUM SILICIDES, p. 291).-11. Softens when heated with carbon v. PLATINUM CARBIDE, p. 289) .- 12. Alloys with many of the more casily fusible metals (v. PLATINUM ALLOYS, infra).—13. Pt is not acted on by pure hydrochloric, nitric, or sulphuric acid (Scheurer-Kestner, C. R. 86, 1082; 91, 59). It dissolves in warm aqua regia, forming PtCl. (v. Dullo, J. pr. 78, 369). Alloying modifies the solubility in acids; alloys of Pt with small quantities of Ir or Rh are scarcely with small quantities of it of An all scales, sol. in aqua regia, while an alloy with much Ag dissolves in cone. HNO₃Aq; Pt ppd. by zane dissolves in cone, HNO₄Aq (v. Winkler, Fr. 13, 869; van Riemsdyk, B. 16, 387; Wilm, B. 13, 1198) .- 14. Conc. sulphuric acid containing a little nitrous acid dissolves small quantities of Pt (Scheurer-Kestner, C. R. 86, 1082; 91, 59). Nitric acid, containing bromine or bromhydric acid, and also hydrochloric acid, into which chlorine is passed, dissolve Pt, forming PtBr, and PtCl, respectively (Wagner, W. J. 1876. 149; Seubert, A. 207, 16).—15. Pt is acted on, at red heat, by molten alkalis, baryta, nitrates, potassium cyanide, and by a mixture of alkali carbonate and sulphur .- 16. PtCl, or PtBr, and PtI2 are formed when Pt wire is heated in iodine mono- or tri- chloride, or in chlorine mixed with iodine or iodine bromide; with phosphorus pentachloride Pt phosphide is formed; with carbon tetrachloride C, C,Cl, and Cl are produced; hydrogen chloride forms PtCl2; hydrogen fluoride produces a soluble Pt salt; and with mercurous chloride Hg and PtCl, are obtained (Hodgkinson a. Lowndes, C. N. 58, 223).

Platinum, acids of. The hydroxide Pt(OH), reacts with strong bases as an acid. Several acids have been isolated containing Pt in acids have been isolated containing Pt in combination with more or less complex negative radicles; these are II_PtCl,, H_PtCl,, H_PtBr,, H_PtL,; H_Pt(NO.),, H_Pt_iO(NO.),; H_Pt_iS, Pt(NH_), Cl.SO_H; PtCl_P(OH),. These acids are described as platino- and platini-chlorhydric acid to (IP_S) 93 and 393) victims viteward. acid, &c. (pp. 283 and 282); platino-nitrous acid, co. (p. 284); platino-cyanhydric acid, co. (vol. ii. pp. 344-5); thioplatinic acid (p. 281); platos-ammine-chloro-sulphonic acid (p. 293); platino-

chloro-phosphoric acid (p. 281).

Platinum, alloys of. Pt alloys with many metals by fusing it with them; with Sb, As, Pb, Sn, and Zn heat and light are produced. Alloys which seem to be definite compounds have been obtained with arsenic (PtAs., Gehlen, Gm.-K. 8, 1192); antimony (PtSb., Christofle); cadmium (PtCd., Deville a. Debray, A. Ch. [3] 56, 886); kad (PtPh, Bauer, B. 3, 836; 4, 449; D. a. D., C. R. 90, 1195); tin (PtSn., PtSn., and Pt.Sn., D. a. D., A. Ch. [8] 56, 885; Debray, C. R. 104, 1470); and zinc (Pt.Zn., D. a. D., l.c.). Alloys have also been formed with bismuth (Gehlen, Gm.-K. 3, 1192); copper (D. a. D., A. Ch.

1859. 611; Hélonis, B. 6, 42); gold (Dodé, B. 6, 1273); iridium (D. a. D., A. Ch. [3] 56, 385; Pelouze, C. R. 49, 896; Matthey, Pr. 28, 463; D. a. D., C. R. 81, 839; Morin, C. R. 78, 1502); iron (D. a. D., C. R. 89, 587; Daubrée, C. R. 80, 520); nickel (Hélonis, B. 6, 42); potassium (V. Meyer, B. 13, 892); silver (D. a. D., A. Ch. 1859, 611; H., l.c.); sodium (V. M., l.c.)

Analgams of platinum. According to Crafts (Bl. [2] 49, 856), Hg has no action on Pt at the ordinary temperature, but Pt dissolves to a very small extent in boiling Hg, air being excluded. When acid is present Hg alloys with Pt (Casamajor, Am. 6, 540; Skey, C. N. 22, 282; Krouchkoll, J. de Ph. [3] 3, 139). The amalgams are most easily formed by adding sodium-amalgam to PtCl, Aq; with 13.5 p.c. Pt the amalgam is a thick liquid; with 25.8 p.c. Pt it is solid; an amalgam with c. 30 p.c. Pt has also been ob-

tained (Joule, C. J. [2] 1, 378).

Platinum, antimonide of. An alloy of Pt and Sb, approximating to the composition PtSb, is obtained by melting the elements together in the ratio Pt: 2Sb; also by passing SbH, into II_PtCl,Aq, and removing ppd. Sb and PtCl, by washing with K,SAq and KCNAq mixed (Christofle, Recherches sur les Combin. de l'Antimoine.

Göttingen, 1863).

Platinum, arsenides of. An alloy PtAs, is said to be formed by heating Pt black with As (Gehlen, Gm.-K. 3, 1192). By passing AsH₄ into PtCl₄Aq, and heating the pp. in dry CO₂, Pt₄As₂ is said to be formed (Tivoli, G. 1885.

Platinum-arsenic hydroxide. According to Tivoli (G. 1885, 487) a compound PtAsOH is produced by passing AsII, containing H but no other impurity, into PtClAq (corresponding with 2 g. Pt in 60 c.c. water), and drying the black floculent pp. at 120°-130°. The compound is decomposed by washing with alcohol or water; hot conc. H₂SO₄ at once separates Pt; heating in dry CO₂ produces As₂O₃, Pt₂As₂, and H₂O. Gibbs (Am. 8, 2*9) described some compounds of Pt and As.O.

Platinum, boride of. Pt and B combine when melted together (Descotils, A. Ch. [3] 67, 88). It is best to heat Pt black and amorphous B under borax (Wöhler a. Debray, A. 101, 113). When excess of B is used, a crystalline compound containing 91.8 p.c. Pt., S.G. 17.3, is formed

(Martius, A. 109, 79).

Platinum, bromides of. Pt and Br combine when heated together to above 300° (Langer a. Meyer, Pyrochemische Untersuchungen [Braunschweig, 1885], pp. 44, 57). Two bromides are known, PtBr₂ and PtBr₄; the V.D. of neither has been determined.

PLATINUM DIBROMIDE PtBr₂ (Platinous bromide.) Formed by heating HBrAq, b.p. 126°, with Br and spongy Pt to 180° in a sealed tube—H.PtBr. TH.O is thus formed—evaporating to dryness, heating to c. 200°, and washing the residue with boiling water (Topsoe, J. 1868. 273). Pullinger (C. J. 59, 602) heats spongy Pt with Br and HBrAq in a flask with a reflux-condenser, evaporates to dryness, and heats the residue to c. 280°. PtBr, is a brown powder; decomposes slowly at c. 800° in an air-current (P., l.c.); insol. water, sol. HBrAq and KBrAq. With KBr forms K_PtBr, (v. Platino-BBOMIDES,

Combines with CO at c. 180° to form p. 282). Combines with CO at c. 180° to form PtBr. CO, a bright red, crystalline solid; melts at 177.7°; not very hygroscopic; sol. alcohol; decomposed by water (Pullinger, l.c.). This compound is called by P. carbonyl-bromoplatinite.

PLATINUM TETRABROMIDE PtBr. (Platinic bromide). Formed by heating spongy Pt with Br and HBrAq in a sealed tube to 180°—or by boiling Br, Pt, and HBrAq in flask with 1eflux-condenser (Pullinger, C. J. 59, 602) filtering, evaporating, heating residue at 180° till HBr ceases to come off; treating with boiling water, filtering from traces of PtBr, evaporating, and drying at 180° (H. Meyer a. Züblin, B. 13, 404; Halberstadt, B. 17, 2963). A dark-brown, non-hygroscopic powder; sol. aqueous alcohol, more sol. absolute alcohol or ether, v. sl. sol. water (S. at $20^{\circ} = .41$) (H. l.c.); somewhat sol. glycerin. Pt black separates when solution in alcohol, ether, or glycerin is heated. With HBr forms H2PtBr, (v. PLATINI-BROMHYDRIC ACID, p. 282). With many metallic bromides forms salts M. PtBr. (v. Platini-bromides, p. 282). When spongy Pt is heated with HBrAq and excess of HNO3, small, dark-brown, very hygroscopic crystals of platinum nitrosyl bromide, PtBr, 2NOBr, are obtained (Topsoë, J. 1868.

273).

Platinum, carbide of. Pt becomes brittle and more friable when heated to redness with charcoal. By heating the compound which PtCl, forms with acetone, Zeise (J. pr. 20, 209) obtained a black solid, to which he gave the composition PtC,

Platinum, chlorides of. Two chlorides of Pt are known, PtCl₂ and PtCl₄. When Pt black is heated in dry Cl at 240 -250°, PtCl₄ is formed, according to Schützenberger (C. R. 70, 1134, 1287). Pigeon (C. R. 108, 1009) says that at 360° PtCl, and PtCl, are formed, but the action is incomplete. Troost a. Hautefeuille (C. R. 84, 94) found that PtCl, was formed when Pt was heated in Cl to 1400°, and the tube was suddenly cooled.

PLATINUM DICHLORIDE PtCl, (Platinous chloride. Platinochloride). V.D. not determined.

Formation. -1. By heating H.PtCl, to c. 230° (Berzelius, Gm.-K. 3, 1081). - 2. By heating Pt black in Cl at 240°-250° till no more Cl is taken up (Schützenberger, C. R. 70, 1134, 1287).—

8. By decomposing Na,Pt(NaSO₃), by HClAq (Liebig, A.23, 23; for formation of Na,Pt(NaSO₃), v. Platinosulphonates, p. 285) .- 4. A solution of PtCl. is obtained by passing SO, into PtCl, Aq till

the liquid becomes red.

Preparation. -1. H2PtCl8Aq is evaporated to dryness, and the residue is heated in a bath of molten tin, i.e. at c. 230°, with constant stirring as long as Cl is given off (Berzelius, Gm.-K. 3, 1081). Or the heating is stopped before much of the solid is decomposed, the residue is dissolved in water, the dark-brown opaque liquid is evaporated, and the PtCl, which separates is dried at c. 150° (cf. Magnus, P. 14, 239). 2. H.PtCl.6H.O is heated in vacuo, in presence of molten KOH, at 100° for 2 or 3 days; the temperature is then raised to 360°, and main-C. R. 112, 1218). Shenstone a. Beck (C. J. 61, 445) say that PtCl, prepared as directed above, Vol. IV.

always contains small quantities of some basic compound; and that when the salt is strongly heated small quantities of HCl and O are obtained, as well as Cl. Shenstone (C. J. Proc. 1892 93. 38) finds that PtCl. almost free from basic compounds can be prepared by heating PtCl₄ in a stream of dry HCl; a sample prepared in this way gave only 15 p.c. of HCl and O when

decomposed by heat.

Properties and Reactions .- A brown powder; S.G. 5.87 at 11° (Bödeker). H.F. [Pt,Cl*] = 22,600 (Berthelot, C. R. 87,615). Insol. water, sol. HClAq in absence of air. Decomposed by heating to redness, giving off all Cl, and leaving Pt. According to Shenstone a. Beck (v. Preparation), the Cl thus obtained contains a little HCl and O, and H₂O is also given off. Not acted on by HNO₂Aq or dilute II₂SO₄Aq; decomposed by KOHAq, giving Pt(OII)₂; by heating with conc. H.SO, and then with water, Kane obtained a black powder to which he gave the composition PtCl₂3PtO (B. J. 24, 238).

Combinations.—PtCl, combines with many metallic chlorides; the compounds are described as platino-chlorides (p. 284). With HCl an acid H2PtCl, is formed (v. Platino-chlorhydric acid, p. 283). With CO the compounds PtCl₂.CO, PtCl₋₂.2CO, and 2PtCl₋₃.3CO are formed. These compounds are produced by passing alternate currents of Cl and CO over spongy Pt at 250° (Schützenberger, A. Ch. [4] 21, 350). Pullinger (C. J. 59, 598) found that a fourth compound is also formed -PtCl₂.2COCl₂ (or PtCl₄.2CO), Carbonyl chloroplatinite (PtCl₂.CO) combines with HCl, and with various hydrochlorides of organic bases (v. Mylius a. Förster, B. 24, 2424). PtC1, combines with PCl, to form PtCl, PCl, and PtCl_2PCl_; and from these is derived a number of complex bodies. By treating PtCl, PCl, with H₂O an acid PtCl, P(OH), is ob-By treating tained, from which various salt-like compounds are derived; similarly PtCl2.2PCl3 yields an acid PtCl_P2(OH), and this gives many salt-like derivatives (Schützenberger, A. Ch. [4] 15, 100; 21, 350; Baudrimont, C. R. 53, 637: cf. PLATINO-GHIOROPHOSPHARES, P. 284). By heating PtCl, PCl, with PtCl, Colchin (O. R. 86, 1402) obtained 2PtCl, PCl, For ammoniacal derivations of the PtCl, Colchin (O. R. 86, 1402) tives of the platino-phosphorus chlorides v. Colchin (l.c.) and Quesneville (M.S. [3] 6, 659), also Schützenberger (Bl. [2] 14, 97; 17, 482; 18, 101, 148).

PLATINUM TETRACHLORIDE PtCl. (Platinic chloride. Platinichloride). V.D. not determined.

Formation.—1. By heating Pt in Cl to c. 1700° (Langer a. Meyer, l.c. 44, 57); if a thin wire of Pt is heated by an electric current nearly to melting, in a stream of Cl, PtCl, is formed (Hodgkinson a. Lowndes, C. N. 58, 158, 228).-2. By allowing H_PtCl_s.6H_O to remain over 2. By allowing H₂PtCl₂GH₂O to remain over KOH, when it loses 4H₂O, and then heating in Cl to c. 350° (Pigeon, C. R. 110, 77).—3. By heating Pt and Se, mixed with AsCl₃, in Cl (v. Preparation).—4. PtCl₂SH₂O is obtained by adding AgNO₂Aq to H₂PtCl₂Aq in the ratio of H₂PtCl₂(2AgNO₃, heating, filtering from AgCl₃ and evaporating finally over H₂SO₄ (Norton, J. pr. [2] 2, 469; 5, 365; Engel, Bl. [2] 50, 100; Quesneville, M. S. [8] 6, 659).

Preparation.—1. Support Pt is mixed with

Preparation.—1. Spongy Pt is mixed with rather less than its own weight of Se, the mix-

ture is placed in a tube of hard glass filled to one-third with AsCl, and heated in a stream of Cl till the mass liqueties and boils, when the tube is sealed and heated for some hours at 250°; on cooling, the colourless crystals are separated from the pale-yellow crystals and the yellow liquid, and are heated in vacuo at 110°, whereby PtCl, and SeCl, remain; this residuo is then heated at 360° in a stream of Cl, when SeCl, sublimes and PtCl, remains (Pigeon, C. R. 108, 1009). -- 2. Dry H,PtCl, is placed in a porcelain boat which is heated, in a tube of hard glass, to 165° for about 15 hours in a stream of dry HCl (Pullinger, C. J. 61, 422).

Properties and Reactions. - H.F. [Pt,Cl] = 59,800; [Pt,Cl',Aq] = 79,400 (Pigeon, C. R. 110, 77; 112, 791). A brown solid, said by Pigeon to be deliquescent; described by Pullinger as very soluble in water, but not deliquescent. The hydrate (v. Fornation, No. 4) forms large, red, monoclinic crystals; according to Norton this compound has 5H.O. according to Engel 4H,O ; all H.O except one molecule is removed at 100°, but the last molecule is not removable without decomposition. Decomposed by heating to dull redness (Pigeon, C. R. 110, 77); in presence of Cl, may be heated to c. 360°; in dry HCl slight decomposition occurs at c. 200° (Pullinger, Le.). HClAq produces H.PtCl., Aq; NH,Cl. ppts. (NH,).PtCl. AgNO, Aq ppts. Ag,PtCl., from cold PtCl, Aq, but on heating AgCl is formed and PtCl, goes into solution (Jörgensen, J. pr. [2] 16, 345). Piggon (C. R. 119, 761). 112, 791) gives [Ag²PtCl⁴,Aq] = 12,160, to form PtCl,Aq and 2AgCl; PtCl,Aq is decomposed by light, for some measurements v. Fousscreau (C. R. 103, 248).

Combinations .- 1. With water (v. Formation. No. 4, and Properties). — 2. With hydrogen chloride to form H.PtCl_v-6H.O; the compound HPtCl, 2H, O was obtained by Pigeon by heating H.PtCl. 6H,O in vacuo at 100° (v. PLATINIоньовнурко асто, р. 282). Pigeon (С. R. 110, 77) gives [PtCl⁴,2HClAq] = 24,800. — 3. With many metallic chlorides to form platini-chlorides (q. v., p. 282).—4. A compound with phosphorous chloride PtCl, PCl, is formed by treating PtCl, PCl, with Cl (Schützenberger, Bl. [2] 14, 97; 17, 482; 18, 101, 148; cf. Baudrimont, C. R. 53, 637) .- 5. A compound with nitrosyl chloride, PtCl, 2NOCl.H.O, is one of the products of the action of fuming HNO, on the products of the action of luming fino, on H.PtCl₂Aq (Weber, P. 131, 441).—6. Combines with alcohol, and with ethyl sulphide, to form PtCl₂.2C₂H₂O and PtCl₂.2(Et)₂S respectively (Sohützenberger, C. R. 70, 1134; Blomstrand, J. pr. [2] 17, 189).—7. Compounds with various organic bases and metallic chlorides, EtNH, &c., are described by Jörgensen (J. pr. [2] 33,

409).
Platinum, chloro-iodides of; v. Platinum IODOCHLORIDES, infra.

Platinum, cyanides of: and derivatives: v. vol. ii. p. 343.

Platinum, fluoride of. Only one fluoride of Pt has been isolated, PtF. Prepared by heating Pt wire in F, in a Pt or fluorspar tube, to c. 500°; if HF is mixed with the F combination occurs at the ordinary temperature (Moissan, C. R. 109, 807). Small buff-coloured crystals, or fused masses of a deep red colour. Dissolves in a little water, forming fawn-coloured solution, which almost at once decomposes, with rise of temperature and production of PtO, xH,O and HFAq. Heated to bright redness in Pt tube, PtF, is decomposed to F, and Pt which separated in crystals. A compound with PF, viz. PtF, 2PF, is formed by passing PF, over spongy Pt heated to dull redness (M., Bl. [3] 5, 454). The decomposing action of H.O on PtF, explains the failure of former attempts to prepare a fluoride of Pt in the wet way.

Platinum-iridium, or platin-iridium. An alloy of Pt and Ir which remains, mixed with osm-iridium, when many samples of Pt ore are heated with aqua regia (cf. IRIDIUM, vol. iii. p. 46).

Platinum, hydride of. Pt black absorbs considerable quantities of H. According to Berthelot (A. Ch. [5] 30, 519), the relative weights of Pt and H are approximately 15:1 and 10:1; a considerable quantity of heat is produced. No certain evidence of the formation of hydrides has been obtained; but Thoma's result (Z. P. C. 3, 69), that the excess of II, above a definite quantity, absorbed by Pt when Pt is the negative electrode during the electrolysis of dilute sulphuric acid, is not easily given up, indicates the probable existence of a compound or

compounds (cf. Palladium, vol. ii. p. 720).

Platinum, hydroxides of; v. Platinum,

OXIDES AND HYDROXIDES OF, p. 291.

Platinum, iodides of. Pt and I combine directly to form PtI,; the lower iodide PtI, has also been obtained, but not pure.

PLATINUM DI-IODIDE PtI, (Platinous iodide. Platino-iodide). This compound is described as a black, heavy powder, insol. water, alcohol, and acids; giving Pt and I at 300°-350°; decomposed by NaOHAq to PtO,H₂. It is produced by boiling PtCl₂ with fairly conc. KIAq (Lassaigne, A. Ch. [2] 51, 113); but it has not been obtained pure (Clementi, J. 1858, 420; Topsoë, Ar. Sc. 38, 297). The compound PtI. CO, carbonyl iodoplatinite, is described by Mylius a. Förster (B. 24, 2424).

PLATINUM TETRA-IODIDE PtI, (Platinic iodide. Platini-iodide). V.D. not determined. Prepared by heating PtO₂ with HIAq (Clementi, J. 1855. 420); also by the action of cold HIAq on H.PtCl₂.6H₂O (Topsoë, Ar. Sc. 38, 297), and evaporating. Pullinger (C. J. 59, 602) obtained PtI, by dissolving spongy Pt in a hot solution of I in HIAq, evaporating to dryness, heating to 180°, and washing with water. A brown-black amorphous powder, insol. water; sol. HIAq and metallic iodide solutions (Topsoë, l.c.); not wholly decomposed by heating with Na,CO, to the m.p. of the carbonate (Pullinger, l.c.). Combines with HI to form H2PtI8.9H2O (v. PLATINI-IODHYDRIG ACID, p. 283), and with metallic iodides to form salts (v. Platini-iodides, p. 283).

Platinum, iodochlorides of. A compound PtI₂Cl₂ is said to be formed, in large red plates, by dissolving Pt and I in aqua regia and evaporating at 100° (Kämmerer, A. 148, 329). Another compound PtI₂Cl was obtained by Mather, as a black powder, by evaporating H₂PtCl₂ with a small excess of HIAq, and heating the residue to 150° (Am. S. 27, 257).

Platinum-nitrosyl bromide and Platinum-

nitrosyl chloride, v. PLATINUM TETRABROMIDE.

p. 299; and Platinum Tetrachloride, Combinations, No. 5, p. 290.

Platinum, oxides and hydroxides of. Three oxides have been isolated; PtO, Pt₃O,, and PtO₂; hydrates of all are known. PtO forms a few salts; it also dissolves in molten KOH and NaOH. PtO₂ forms corresponding salts, and also combines with alkaline oxides to form platinates (q. v. p. 281).

PLATINUM MONOXIDE PtO (Platinous oxide). Obtained as a violet powder, by strongly heating the pp. formed by CaOAq acting on H2PtCl,Aq in sunlight, and washing with water and then with HNO₃Aq (Döbereiner, P. 28, 181). Also by carefully heating PtO2H2. Reduced to Pt at red heat, also by action of reducers such as Dissolves in molten KOH and HCO, HAq. NaOH, but the compounds thus formed have not been examined. A compound which is perhaps Pto.CO is described by Mylius a. Förster (B.

24, 2440). PLATINOUS HYDROXIDE Pto.H., was obtained by Thomsen (J. pr. [2] 15, 294) by adding NaOHAq to K_PkCl₄Aq (1:12) in the ratio 2NaOH:K_PkCl₄, and heating to boiling. A black powder, sol. HClAq, HBrAq, and SO2Aq, forming corresponding salts. Freshly ppd. Pto.H. dis-

solves in excess of NaOlIAq.

TRI-PLATINUM TETROXIDE Pt.O. (Platinoplatinic oxide). A black powder, insol. acids; obtained by heating dehydrated Na, PtCl, with 4 parts dry Na CO, till fusion begins, boiling with water, then with dilute HNO, Aq, and finally with aqua regia (Jörgensen, J. pr. [2] 16, 344). Loses its O at red heat; easily reduced to Pt by H or coal-gas, even without heating. Prost (Bl. [2] 46, 156) describes a hydrate Pt,O4.9H2O.

PLATINUM DIOXIDE PIO, (Platinic oxide). A black powder, obtained by gently, heating PtO, H., PtO, is insol. acids, but saits of this

oxide are formed from the hydroxide.

PLATINIC HYDROXIDE PtO, H,. Formed by boiling PtCl,Aq for a considerable time with a large excess of NaOHAq, acidifying by acetic acid, drying the white flocculent pp. in the air, and heating the yellow hydrate, PtO,H, 2H,O to 100° (Topsoë, B. 3, 462; Fremy, A. Ch. [3] 31, 478). Also obtained by evaporating H.PtCl.Aq with excess of Na,CO3, rubbing up the residue in water, and treating with acetic acid (Döbereiner, P. 28, 181; Topsoë, l.c.; cf. Wittstein, R. P. 74, 43). A hydrate PtO,II, II,O was obtained by Prost (Bl. [2] 46, 156) by adding water to a solution of PtO,II, in conc. HNO, Aq. A reddish-brown powder; dehydrated by heating gently; at a higher temperature gives Pt and O. Heated in H gives Pt. Sol. NaOHAq, HClAq, HNO,Aq, and H,SO,Aq. With acids forms platinic salts, PtX., where X = \(\frac{1}{2} \text{SO}_1, \frac{1}{2} \text{CO}_1, \frac{1}{2} \text{CO}_1, \frac{1}{2} \text{CO}_2, \frac{1}{2} \text{CO}_2, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_4, \frac{1}{2} \text{CO}_3, \frac{1}{2} \text{CO}_4, \frac{1} \text{CO}_4, \frac{1}{2} \text{CO}_4, \frac{1}{2} \text{CO}_4, NO, &c.; with strongly basic oxides forms platinates, PtO...xMO (v. Platinates, p. 281). Compounds with SnO and SnO, are described by Delachanel a. Mermet (C. R. 81, 370), Schneider (P. 136, 105), Lévy a. Bourgeois (C. R. 94, 1365), and Schützenberger (C. R. 98, 985). Pto,H, dissolves in solutions of certain molybdates and tungstates, forming platini molybdates and platini-tungstates (q. v. p. 283).

Platinum, oxychlorides of. When AgNO, Aq

together in the ratio H.PtCl,:4AgNO, a pp. is obtained which has the empirical composition PtCl2(OH)2.2AgCl; this substance may be regarded as a compound of the hydrated oxy-chloride PtOCl. H.O (Jörgensen, J. pr. [2] 16, 345). The pps. formed by CaOAq and BaOAq in PtCl Aq are supposed to contain oxychlorides of Pt (v. Johannsen, A. 155, 204).

Platinum, oxysulphide of, 2PtOS.H.O. PtS. slowly oxidises by exposure to air; by washing the product (to dissolve H.SO, and SO,) and drying in a stream of CO, a black powder is obtained having the composition 2PtOS.H₂O (perhaps HO.PtS.O.SPt.OH). This substance is an energetic oxidiser; H, CO, H,S, SO, take fire when brought into contact with it; NH, is absorbed and oxidised to HNO, and HNO, (E. von Meyer, J. pr. [2] 15, 1).

Platinum, phosphides of. Pt and P combine when strongly heated together. Schrötter obtained a grey metal-like mass, S.G. 8-77, to which he gave the composition PtP, by heating Pt black in vapour of P (J. 1879, 240). By heating by the property of th ing Pt and P to white heat, Clarke a. Joslin (Am. 5, 231) obtained Pt₂P₅; and by heating in a mufile they got Pt₂P, sol. aqua reqia but changed

to insoluble PtP.

Platinum, salts of. But few salts, excepting the halides, are known wherein Pt replaces the H of acids; Pt more frequently enters into the acid radicle, than the positive radicle, of salts.

Platinum, selenide of. By heating Pt and Se, Berzelius obtained a grey, infusible powder;

perhaps PtSe (Gm.-K. 3, 1081).

Platinum, selenocyanides of; for a double salt v. vol. ii. p. 348.

Platinum, silicides of. A white, crystalline, brittle solid, Pt, Si, was obtained by Guyard (Bl. [2] 25, 510) by heating together equal parts of Pt black and powdered crystalline Si (cf. Winkler, J. pr. 91, 203). According to Miles (Am. 8, 428), the conditions favourable to the formation of compounds of Pt and Si are a high temperature, the presence of a reducer such as CO, a basic substance such as MgO, and SiF, in contact with Pt (v. also Brown, Am. 7, 173).

Platinum, sulphides of. Pt and S combine

when heated together. Two sulphides have been isolated, PtS and PtS2; there is also evidence

of the existence of Pt.S.

PLATINUM MONOSULPHIDE PtS (Platinous sulphide). Obtained by heating Pt black and S. and volatilising excess of S, in absence of air; also by heating (NH,) PtCl, with S, out of contact with air, till NH,Cl and excess of S are volatilised; also by passing H2S into PtCl.Aq (Berzelius). Prepared in crystals by heating to redness a mixture of 1 pt. Pt, 1 pt. borax, and 10 pts. pyrites (Deville a. Debray, A. Ch. [2] 55, 215). A grey, lustrous solid; S.G. 6·2. PtS prepared in the wet way is a black powder. Unpared in the wet way is a black powder. changed in air, even when moist; unacted on by hoiling acids; loses S when heated in air, leaving Pt; reduction in II begins at 19°. A compound with CO—PtS.CO—was obtained by Mylius a. Förster (B. 24, 2438) by the action of H.S on PtCl,.CO.

PLATINUM DISULPHIDE PtS, (Platinic sul-Platinum, oxychlorides of. When AgNO,Aq phide). Obtained by passing H,S into is added to PtCl,Aq in the ratio PtCl,2AgNO, Na,PtCl,Aq, or by dropping H,PtCl,Aq into solution when AgNO,Aq and H,PtCl,Aq are heated tion of an alkali hydrosulphide. Also formed

by digesting, in a strong closed flask, 1 pt. PtCl4, 4 pts. alcohol, and 5 pts. CS, (Böttger, J. pr. 3, 274); and by decolourising H.PtCl.Aq by SO, and then heating in a scaled tube at 200° (Geitner, A. 129, 358). PtS. is also a product of the action of HClAq in air on Na Pt S or H₂Pt₄S_e (v. Thioplatinates, p. 281). Colloidal soluble PtS₂ was obtained by Winssinger (Bl. [2] 49, 452) by passing H2S into very dilute PiCl, Aq, and dialysing. A black solid; as obtained from Na,Pt,S, forms steel-grey needles, S.G. 5.27. PtS, prepared by one of the wet methods must be dried in absence of air, else it is partially decomposed. Heated out of air forms PtS, and Pt and S. Oxidised to sulphate by strong oxidisers, such as aqua regia, Cl, fuming HNO, molten KClO₃ or KNO₃. Freshly ppd. PtS₂ dissolves in alkali sulphide solutions forming thioplatinates (q. v.), from which solutions it is reppd. by acids. Clässon (J. pr. [2] 15, 193) describes a compound with EtSH.

PLATINUM SESQUISULPHIDE, Pt2S3. This compound is said to be formed, as a steel-grey, metal-like solid, S.G. 5.52, by the oxidation in air of H.Pt.S. (Schneider, P. 136, 105; 138, 604; 139, 661; 141, 519; 148, 633; 149, 381). Schneider also describes a compound 4PtS.PtS.

= Pt,S,.

Platinum, sulphocyanides of; v. vol. ii. p. 357; v. also Guareschi, Giorn. della R. Accad. di Med. 1891. No. 5; abstract in B. 25, Ref. 7.

Platinum, thiocarbide of. Pt₂CS₂. compound is described by Schützenberger (C. R. 111, 391). It is a black powder; obtained by passing a stream of N, or H, charged with CS, over spongy Pt heated to 400°-450°.

M. M. P. M. PLATINUM - AMMONIUM COMPOUNDS (Ammonio-platinum compounds. Ammoniacal platinum bases. Platinammines). When a solution of PtCl2 in HClAq reacts with NII3, more than one compound of the form PtCl, 2NH, is obtained. These compounds react with acids, oxidisers, &c., to form many derivatives containing Pt, N, H, and negative radicles, in which the reactions of Pt and NH, are more or less modified.

The platin-ammonium compounds may be regarded as salts of bases derived from two or more NH, groups, in which part of the H is replaced by Pt; thus PtCl. 2NII, may be called platoso-diammonium chloride, and formulated as NgH Pt.Cl. Similarly PtCl24NH3 may be

regarded as Pt<\(NH_2(NH_4)Cl\), and called ammo-

nium platoso-diammonium chloride. The compounds derived from PtCl, are regarded, in this scheme, as platini-ammonium compounds; thus, PtCl., 2NH, is Cl.Pt.NH_NII, Cl₂ (v. Hofmann, T. 1851. [2] 357; Weltzien, 4. 97, 19; Kolbe, J. pr. [2] 2, 217; Grimm, 4. 99, 67).

This view of the constitution of the compounds in question was opposed by Claus (J. pr. 63, 99), Blomstrand (B. 4, 40, 639, 673; 6, 1469), Jörgensen (J. pr. [2] 33, 489), and others. Jörgensen found that pyridine, N.C.H., forms a compound with platinous chloride similar to PtCl,4NH,; in this pyridine compound, which has the composition PtCl,4NC,H, the atoms of hydrogen cannot be in direct union with N; for the constitution of pyridine is known to be

HC. CH Now if the ammoniacal platinum HC CH

bases are all to be derived from NH, by substituting H by NH, groups, it is evident that the substituted H atoms must always be directly bound to N atoms. But the existence of the pyridine compound shows that this is not necessary. Hence PtCl₂4NII₃ may be regarded as Pt</ri>
NH₃NH₃Cl
NH₃NH₃Cl

The classification and nomenclature of the platin-ammonium compounds proposed by Blomstrand (Chemie der Jetztzeit, Heidelberg, 1869; B. 2, 202; 4, 40, 639, 673; 6, 1469) is now usually adopted. In the following formulæ R stands for a monovalent negative radicle. Blomstrand uses the term annine to distinguish these compounds from the amines, which contain the group NH...

Class I. PLATO- OF PLATOSO- COMPOUNDS. Series 1. Platosemiammines, RPtNH3R.

2. Platosammines, Pt(NH,R).

3. Platodiammines, Pt(NH3 NH3R)2. 4. Platosemidiammines,

Pt(NH3.NH3R)R.

5. Platomonodiummines. Pt(NH3.NH3R)(NH3R).

Series 2 and 4 are isomeric. Cleve has isolated two distinct aniline compounds, Pt(NH₃)₂·(C₆H₄NH₂)₂·R₂ (cf. Jörgensen, J. pr. [2] 33, 489).

Class II. PLATINI- OF PLATIN- COMPOUNDS. Series 1. Platinammines, R.Pt(NH.R).

2. Platinidiammines. R2Pt(NH3.NH3R)2.

3. Platinisemidiammines, R.Pt(NH, NH,R)R.

4. Platinimonodiammines R.Pt(NH3.NH3)R(NH3R).

5. Platinitriammines R2Pt(NH3.NH3.NH3R),

Series 1 and 3 are isomeric.

The prefixes mono, di, &c., are used to denote the number of NH, groups in direct union with one another, and not the number of NH, groups in union with the atom of Pt. As the compounds in Series 3 contain one diammine chain, (NH, NH,), they are called semidiammines; and as those in Series 4 contain a diammine and a monammine chain, they are called monodiammines.

Class III. DIPLATINUM COMPOUNDS. These contain 2 Pt atoms; the group Pt, may be divalent, tetravalent, or hexavalent.

Series 1.

Pt(NH,.NH,R) Diplatodiammines, Pt(NH..NH.R)

Series 2.

RPt(NH,.NH,R) Diplatosindiammines,

RPt(NH,.NH,R) Pt(NH,.NH,R) B.Pt(NH.NH.B) Series 3.

Diplatinammines.

RPt(NH.B). RPt(NH.R).

Series 4.

RPt(NH,NH,R), Diplatinidiammines, RPt(NH,NH,R)2

Iodides of platinum bases with 4 and 8 atoms Pt are also known; I,Pt,8NH,I, and I.Pta.16NH3.I16.

Many organic bases, such as aniline, pyridene. &c., can take the place of NH3 in these compounds, and the N of NH, is often replaceable by P or As.

Class I. Plato- or Platoso- compounds.

Series 1. Platosemiammines, RPtNH₄R. None of these has been isolated, but Cossa (B. 23, 2503) has obtained a compound which the bably contains platosemiammine chloride; the compound is 2PtNH₂Cl₂.Pt(NH₂),Cl₂.

Platosammines, Pt(NH₂),...

Pt(NH₂R)₂.

These compounds are generally obtained by heating the corresponding platodiammines, Pt(NH₂,NH₂R)₂, which thus lose 2NH₃; by heating with NH, Aq, platodiammines are re-formed; with oxidisers, platini- compounds are obtained.

PLATOSAMMINE CHLORIDE Pt.NH, Cl.NH, Cl. (Peyrone, A. 51, 1; 55, 205; 61, 178). Obtained heating Pt(NII3),Cl2 (plato-diammine chloride) to 250°, or by evaporating that compound with HClAq at 100° and dissolving out AmC in water; also by evaporating with HCl the solution of the corresponding nitrate or sulphate. Microscopic, sulphur-yellow crystals. S. 022 at 0°, '77 at 100'. Sol. NH, Aq, forming Pt(NH, NH, Cl), (platodiammine chloride); in aqua regia forms Cl2Pt(NH3Cl)2 (platinammine chloride). With AgNO Aq, in the ratio 2Pt(NH₂Cl)₂:AgNO₂, one half of the chloride remains unchanged and one half gives Pt(NH₃,NO₃)₂. Heated to 270°, the chloride is decomposed thus:

 $3Pt(NII_3Cl)_2 = 3Pt + 4NH_4Cl + 2HCl + N_2$

Platosemidiammine chloride

Pt(NH₂,NH₂Cl)Cl, and platodiammine chloride platinous chloride Pt(NH₂,NH₂Cl)₂, PtCl₂(Magnus' green salt), are isomeric or polymeric with platosammine chloride. Other compounds, perhaps also isomeric, were obtained by Peyrone (l.c.) and by Cossa (B. 23, 2503)

Grimm (A. 99, 67) obtained a double compound with AmCl; Pt(NH3Cl)22AmCl. Jörgensen (J. pr. [2] 33, 489) obtained the pyridine compound Pt(NC,H,Cl)₂; and also the mixed compound PtNC₂H₁Cl.NH₂Cl (v. also Hedin, Dissertation, Lund; B. 20, Ref. 108).

PLATOSAMMINE HYDROXIDE

Pt.NH3OH.NH3OH. Said to be obtained, as a the sulphate, Pt(NH,NH₃)SO, by BaOAq (Odling, C. N. 21, 269, 289). The compound thus formed may have been the isomeric platosemi-diammine hydroxide, OH.Pt(NH₂,NH₃OH). solution of Odling's hydroxide reacts strongly alkaline, absorbs CO₂ from the air, neutralises acids, decomposes salts of NH, giving off NH₂, and ppts. many metallic hydroxides from salts of the metals.

PLATOSAMMINE ONIDE Pt(NH_NH_)O.

grey solid, insol. water or NH, Aq; heated in a retort to 195° gives N, NH,, H,O and Pt. Obtained by heating platodiammine hydroxide (Pt[NH,NH,OH],) to 110° (Reiset, A. Ch. [3] 11, 417).

PLATOSAMMINE SULPHONATES and CHLORO-PHONATES Pt.NH, SO, M.NH, SO, M and SULPHONATES Pt.NH,Cl.NII,SO,M. Ammonium platosammine reaction of excess of Am, SO, Aq on Pt(NH, SO), (Peyrone, A. 51, 1; 55, 205; 61, 178). The salts of Ba, Co, Cu, Pb, Mu, Ni, Ag, Na, UO2, and Zn have been obtained. Ammonium platosammine chlorosulphonate, Pt.NIIsCl.NH3SO,Am.H2O, is obtained, in colourless rhombic tablets, by leading SO, into a boiling solution of Pt(NH,Cl), and neutralising with NH, Aq. If the neutralisation is omitted, platosammine chlorosulphonic acid, Pt.NH₂Cl.NH₂SO₂H, is obtained (Peyrone,

The other salts of the platosammine series which have been isolated are the following; wisch have been isolated are the following; M=Pt(NH₂):—bromide, MBr₂ (Jörgensen, J. pr. [2] 33, 521, 531, 535); cyanide, MCy₂ (Buckton, A. 92, 280); iodide, ML₂ (Cleve, Bl. [2] 7, 12; 17, 482; Reiset, A. Ch. [3] 11, 417); nitrate and nitrite, M(NO₃)₂, and M(NO₂)₂ (Cleve, l.c.); sulphate and sulphite, MSO₄, H₂O and MSO₄, H₂O (Cleve, L. 1); contact the contact of the cont l.c.); and sulphocyanide, M(CyS), (Buckton, l.c.). Substituted derivatives of the bromide, of the form Pt(NH2RBr)2 and Pt.NH3Br.NH2RBr, where R = Et, Me, or Pr, have been obtained (Jörgensen,

Series 3.—Platodiammines Pt(NII₃.NII₃R)₂. Formed by action of NH₃Aq on platinous salts, platosammine or platosemidia.nmine compounds. Easily lose NH, on heating, giving platosammine compounds. Give platinidiammine compounds by action of oxidisers.

PLATODIAMMINE CHLORIDE

Pt(NH₃.NH₃Cl)₂.H₂O (Reiset, A. Ch. [8] 11, 417). Sometimes called Reiset's first chloride. tained by the prolonged action of boiling NH3Aq on PtCl., Magnus's green salt (v. infra), platos-ammine chloride Pt(NH₃Cl), or platosemidiam-mine chloride Pt(NH₃NH₃Cl)Cl, precipitation by alcohol, and crystallisation from water. Also formed by reduction of platinidiammine chloride $Cl_2Pt(NH_3 NH_3Cl)_2$, by H_2S (Thomsen, J. 1868. 278). Large, colourless, tetragonal crystals; S. 25 at 16.50, more sol. hot water; insol. absolute alcohol and ether. Addition of H₂SO₄Aq, IINO₄Aq, or H₂C₂O₄Aq ppts. the corresponding sulphate, nitrate, or oxalate. By gently warming with IINO, Aq the salt (NO₃), Pt(NH₂, NH₂Cl), is formed; Cl, Br, and FcCl, Aq react similarly. At 240°-270° NH, is given off, and Pt(NH,Cl), is formed (v. Platosammine chloride, supra). Combines with PtCl., and PtCl., to form M.PtCl. and M.PtCl. respectively [M=Pt(NH4.NH4.Cl.)].
Compounds are known in which NH4.is wholly or partly replaced by pyridine, also by alkyl radicles (Jörgensen, J. pr. [2] 33, 489), and also by PEt, (Cahours a. Gal, C. R. 70, 1381).

Double compounds. Combines various metallic chlorides to form compounds of the form $M.XCl_2$, where $M = Pt(NH_1.NH_2Cl)_2$, and X=Pt, Cu, Pb, Hg, Sn, and Zn (v. Thomsen, J. 1868. 278; Buckton, C. J. 5, 213; Millon a.

Commaille, C. R. 57, 822).

The most important of these compounds is PLATODIAMMINE CHLORIDE PLATINOUS CHLORIDE, known as Magnus's green salt,

Pt(NH_NH_Cl)__PtCl__. This salt is obtained by the action of NH_Aq on PtCl_2 in HClAq, or on PtCl_1 in HClAq after passing in SO_2 till AmCl ceases to give a pp. (Magnus, P. 14, 242; Gros, A. 27, 241). Also by adding Pt(NH_1NH_Cl)_2 to PtCl_2 in HClAq. It is best prepared by making Am_PtCl_1, from PtCl_4 in HClAq treated with SO_2 and crystallised from AmClAq, and heating this with HClAq and NH_AQ (Claus, A'. 107, 138). Green, microscopic prisms or needles; insolwater, alcohol, and dilute HClAq. Digestion with hot NH_AQ forms Pt(NH_1,NII_5Cl)_2; Cl, Br, or HNO_AQ produces platinidiammines (Gros, Lo.; Raewsky, A. Ch. [3] 22, 278). Boiling with AgNO_AQ produces PtCl_2 and Pt(NH_1,NI_1,NO_2)_2. If the empirical formula nPt(NH_1)_cl_2 is given

AgNO₂Aq produces PtCl₂ and Pt(NH₂,NH₂NO₂)₂. If the empirical formula Pt(NH₃)₂(l₂ is given to Magnus's green salt, it is seen to be isomeric, or polymeric, with platosammine chloride Pt(NH₂Cl)₂, platosemidiammine chloride Cl₂Pt.NH₂NH₃Cl, platomonodiammine chloride platinous chloride 2[Pt(NH₂,Cl)(NH₂,NH₂Cl)]. PtCl₂,diplatosindiammine chloride Cl₂Pt₂(NH₂,NH₂Cl)₂, and with a double salt obtained by Cossa (B. 23, 2503), 2[Pt.NH₂,Cl₂]. Pt(NH₂,Cl₂).

PLATODIAMMINE HYDROXIDE Pt(NH₃,NH₃OH)... Sometimes called Reiset's first base (Reiset, A. Ch. [8] 11, 417). White, crystalline, deliquescent needles; by decomposing the sulphate by the proper quantity of BaOAq, filtering, and evaporating in vacuo. Solution in water is strongly alkaline, absorbs CO, from the air, and drives out NH₃ from NH₄ salts. NH₃ is not given off when an aqueous solution is boiled alone or with potash. Molts at c. 110°; at a higher temperature gives off NH₄ and H₂O and leaves platosammine oxide Pt(NH₃).20 (q. v. p. 293).

The other chief compounds of the platodiammine series are the following; M = Pt(NI_A); — carbonates, MCO, 4aq and M(CO₃H)₂ (Peyrone, A. 51, 14; Reiset, A. Ch. [3] 11, 417); chromates MCrO, and MCr₂O; bromide, MB₁, 3aq (Cleve); nitrate and nitrite, M(NO₄), and M(NO₂), 2aq (Feyrone, b.c.); phosphate, MHPO, aq (Cleve, Bl. [2] 7, 12; 17, 482); sulphate and sulphites, MSO₄, MSO. M(SO. H), 3aq (Cleve, Le.).

MSO., M(SO.H). 2aq (Cleve, l.c.).
Series 4 Platosemidiammines,
Pt(NH, NH, R)R. Generally formed from the
chloride by double decomposition: the chloride
is a product of the action of NH, Aq or
(NH,). 2Co, Aq on PtCl... Prolonged treatment of
the platosemidiammines with NH, Aq produces
diammine compounds. Jörgensen (J. pr. [2] 33,
489) has replaced NH, in these compounds by
alkyl radioles and by pyridine.

PLATOGEMIDIANMINE CHLORIDE Pt. Cl.

Sometimes called Peyrone's chloride. PtCl, is formed by the action of SO₂ on PtCl, in HClAq, and the solution is heated to boiling with excess of (NH₂).CO₂ until the red solution has become light-yellow and a greenish-brown pp. forms, when the liquid is rapidly filtered. The chloride separates as the liquid cools; it must be filtered off at once (else it may re-dissolve), and crystallised from boiling water (Peyrone, A. 51, 14; 55,

209; v. also Thomsen, Gm. K. 8, 1115; Cleve, Bl. [2] 7, 12, 17, 462). Small yellow crystals. S. 26 at 0°, 3°6 at 100°. Decomposes at 270°, giving off NH, and HCl. Boiling NH, Aq forms platodiammine chloride, Pt(NH, NH, Cl); Cl, Br, I, and some other oxidisers produce platinisemidiammine compounds, R, Pt(NH, NH, NH, R) With AgNO, and Ag, SO,, the corresponding nitrate and sulphate are formed.

It is doubtful whether the hydroxide Pt(NH,NH,OH)OH has been prepared; the compound obtained by Odling (C. N. 21, 269, 289) was this or the isomeric platosammine hydroxide, Pt(NH,OH), (v. Platosammine hydroxide, Pt(NH,OH), (v. Platosammine hydroxide, Pt(NH,OH), (v. Platosammine hydroxide, Pt(NH,OH), (v. Platosammine hydroxide, Pt(NH,NH,:-bromide, MBr.; chlorosulphonic acid, MCl.SO₂H (Cleve. L.c.); codide, MI.; nitrate and nitrite, M(NO₂); and M(NO₂); sulphate, MSO₃; double sulphites, MSO₃; 2X₂SO₃, X₂=2NH, Ba. Co, Ag₇; these may be regarded as compounds of sulphites with salts of the hypothetical platosemiammine sulphonic acid Pt(NH₃,NH₃,SO₃H)SO₃H.

Series 5. Platomonodiummines
Pt(NH_NH_1k)(NH_1k). Most of the salts of this
series are prepared from the double salt of the
chloride with PtCl...

PLATOMONODIAMMINE CHIORIDE PLATINOUS CHLORIDE 2Pt NH₃NH₃Cl. PtCl₂. This compound is one product of the action of NH₃Aq on PtCl₂ in HClAq; it is prepared by neutralising PtCl₂ in HClAq by (NH₄)₂CO₃Aq, heating to boiling, and adding (NH₁)₂CO₃Aq drop by drop, when it separates in small red tablets (Peyrone, A. 55, 209). Fairly sol. cold water, more sol. hot water. Boiled with NH₃Aq forms Magnus's green salt, Pt(NH₂,NH₃Cl)₂PtCl₂. Isomeric, or polymeric, with Magnus's green salt, platosammine chloride, and platosemidiammine

PLATOMONODIAMMINE CHLORIDE

Pt<\s\NI_s\NI_sCl \tag{NI_strong colourless} Obtained, in lustrous colourless crystals, by adding HClAq to an ice-cold solution of the nitrate.

PLATOMONODIAMMINE NITRATE

Pt<NH, NH, NO. Formed by decomposing the chloride in solution by AgNO, Aq, filtering, and evaporating. The sulphate

Pt $\langle {}_{NH_3}^{NH_3}NH_3 \rangle$ SO₄.H₂O is also known (v. Cleve, l.c.; Blomstrand, B. 4, 40, 639, 673; 6, 1469).

Class II. Platini or Platin- compounds. Series I. Platinammines, R.pt(NH,R). These compounds are formed by the addition of Cl, Br, or I to platosammines, or by the action of such oxidisers as HNO₂Aq on platosammines; they are generally changed to platinidiammines by heating with NH,Aq, and are reduced to platosammines by SO.Aq. The radicles in direct union with Pt are replaced with more difficulty than those in union with NH. The nomenclature is arranged to indicate, first, the nature of the radicles in direct union with Pt, and then those in direct union with NH.

those in direct union with NH₂.

I. Chloro: compounds Cl.Pt(NH₂R),
Ohloroplatinamming chloride Cl.Pt(NH₂Cl),
Formed by suspending platosamreine chloride

Pt(NH,Cl), in boiling water, and passing in Cl until the original citron-yellow particles are changed to microscopic yellow octahedra (Gerhardt a. Laurent, C. R. 30, 273), or until the liquid, which is yellow at first, begins to turn reddish. Aqua regia, or KMnO, Aq and HClAq, may be used instead of Cl (Odling, C. N. 21, 269, 289). A heavy, yellow, crystalline powder. S. 1 at 0°; 3 at 100°. Unacted on by boiling conc. HNO₃ or H₂SO₄; sol. boiling KOHAq without evolution of NH₃; sol. NH₃Aq, with formation of chloroplatinidiammine chloride, Cl.Pt(NH, NH, Cl.)2. The Cl is ppd. as AgCl only after long boiling with AgNO, Aq (Grimm, A. 99, 67).

CHLOROPLATINAMMINE NITRITE

Cl.Pt(NH3.NO)2. Ppd. in colourless rhombic plates by addition of excess of HClAq to solution of the nitrato-nitrite, (NO3) Pt(NH4, NO2)2, which is formed by boiling platosammine nitrite, Pt(NH3.NO), with HNO3Aq.

CHLOROPLATINAMMINE CHLORONITRITE Cl₂Pt(NH₄Cl)(NH₃.NO₂), is produced by the re-action of K,PtCl₄ and (NO₃)₂Pt(NH₃NO₂)₂.

II. Hydroxyl compounds

(OH), Pt(NH,R),.

HYDROXYL PLATINAMMINE HYDROXIDE (OII) Pt(NH₂,OII)₂. Yellow, lustrous crystals; by adding excess of NII₄Aq to a boiling solution of the nitrato-nitrate (NO3),Pt(NH3,NO3), and allowing to cool. Scarcely sol. water; easily sol. dilute acids. Boiling KOHAq does not evolve NH₃; decomposes above 130°, giving off NH₃ and H₂O, and leaving Pt (Gerhardt a. Laurent, C.R. 30, 273).

HYDROXYL PLATINAMMINE NITRATE (OH)₂Pt(NH₂NO₃)₂, 2aq. Crystalline pp. by decomposing Cl₂Pt(NH₂Cl)₂ by AgNO₂Aq. Not acted on by cold HClAq; evaporation with HNO₂Aq produces (NO₂)₂Pt(NH₂,NO₂)₂(G. a. L., l.c.; Cleve, Bl. [2] 7, 12; 17, 482).

HYDROXYL PLATINAMMINE SULPHATE

(OII)2Pt(NH3)2SO, aq. Formed as a pale-yellow, hard crust of needle-shaped crystals, by decomposing Cl_Pt(NH_2Cl)₂ by Ag_SO₄Aq. Evaporation with H_3O₁Aq produces the sulphate-sulphate, SO₄Pt(NH₂)₂SO₄ and Cl_Pt(NH₂Cl)₂ are produced (Cl_Pt(NH₂)₂SO₄ and Cl_Pt(NH₂Cl)₂ are produced (Cl_Pt(NH₂Cl)₂). produced (Cleve, l.c.).

The following salts of this series have also been The following satisfy this series have also been isolated: Bromo-bromide, Br.,Pt(NH,Br), (Cleve, l.c.); bromo-nitrite, Br.,Pt(NH,NO,), (Cleve, l.c.); iodo-iodide, I,Pt(NH,I), (Cleve, l.c.); nitrato-nitrate, (NO,),Pt(NH,NO,), nitrato-nitrite, (NO,),Pt(NH,NO,), nitrato-chloro-nitrite, NO,Cl.Pt(NH,NO,), (Cleve, l.c.); sulplato-sulphate, BO,Pt(NH,)2SO,3aq (Cleve, l.c.)

Lc.).
Series 2. Platinidiammines,
Generally form R₂Pt(NH₃NH₃R)₂. Generally formed by action of Cl. Br. I, and other oxidisers on platodiammines. A large number of these compounds is known. R attached directly to Pt may be the same as, or different from, R united directly to NH. The nomenclature is similar to that of the platinammine series. The radicles in direct union with Pt are removed with more difficulty than those united with NH,.

I. Chloro-compounds CIR.Pt(NH, NH, R)(NH, NH, R); the R's may be the same or different.

CHLOROPLATINIDIAMMINE CHLORIDE

Cl_Pt(NH_NH_Cl)₂. By passing Cl into a fairly conc. boiling solution of platediammine chloride, Pt(NH_NH_Cl)₂, till the liquid begins to turn red (Raewsky, A. Ch. [3] 22, 278); also by dissolving chloroplatinammine chloride, Cl.PP(NH,Cl),, in NH,Aq (Gerhardt a. Laurent, C. R. 30, 273). Pale-yellow, crystalline powder; scarcely sol. cold water, sl. sol. boiling water. HNO, Aq produces the chloro-nitrats Cl.Pt(NII, NII, NO,),; a little AgNO, Aq produces the chloro-hydroxyl-nitrate

Cl(OH)Pt(NH3.NH3.NO3)2; long boiling with CHOHJEU(NH₂,NH₂,NO₂)₂; long boiling with AgNO₂Aq is needed to remove all Cl as AgCl. Reduced by H.S, or action of Ag, to Pt(NH₂,NH₂Cl)₂ (Thomsen, J. 1868, 278; Jörgensen, J. pr. [2] 33, 489). Forms double compounds with PtCl₂ and PtCl₄ (Reiset, A. Ch. [3] 11, 417; G. a. L., L.c.; Cleve, Bl. [2] 7, 12; 17, 482).

The other chloro- compounds which are known are the following: Chloro-nitrate, Cl.Pt(NII, NH, NO₃)₂ (Gros, A. Ch. [2] 69, 204; Raewsky, A. Ch. [3] 92, 278; Hadow, C. J. [2] 4, 345); chloro-chloro-nitrite, Cl.Pt(NII, NII, NO₂)(NII, NII, Cl); chloro-hydroxyl-chloride, Cl(OII)Pt(NII, NII, Cl), (Cleve, Chloride, Cl(OII)Pt(NII, NIII, Cl), (Cleve, Chloride, Cl(OII)Pt(NIII, NIII, Cl), (Cleve, Chloride, Cl(OII)Pt(NIIII, Cl), (Cleve, Chloride, Cl(OII)Pt(NIIII)Pt(NIIII)Pt(NIIII)Pt(NIIII)Pt(NIIII)Pt(NIIIII)Pt(NIIIIIII)Pt(NIIII)Pt(NIIIII)Pt(NIIIII)Pt(NIIIII)Pt(NIII l.c.; Hadow, l.c.); chloro-hydroxyl-carbonate, Cl(OH)Pt(NH₃,NH₃)₂CO₃.H₂O (Raewsky, l.c.; Gros, l.c.); chloro-hydroxyl-chromate and di-chromate, Cl(OH)Pt(NH₃,NH₃)₂CrO₄ and chromate, Cl(OH)Pt(NH₂,NH₃)₂CrO₄ and Cl(OH)Pt(NH₂,NH₃)₂Cr₂O₂ (Cleve, l.c.); chlorohydroxyl-nitrate, Cl(OH)Pt(NH₃,NH₃,NO₃)₂, (Raewsky, l.c.; G. a. L., l.c.; Cleve, l.c.); chlorochromate and dichromate, and chloro-sulphate, MCrO₄, MCr₂O₇, and MSO₄, where Cl₂Pt(NH₂,NH₃)₂ (Cleve, l.c.).

II. Bromo-compounds. The following members of this class have been isolated (Cleve, l.c.); bromo-bromide, MBr₁; bromo-chloride, MCl₂; bromo-dichromate, MCr₂O₁; bromo-nitrate, M(NO₃)₂; bromo-phosphate,

M(PO,H.), 2aq (in these formulæ

M=Br.Pt(NH,NII,)); bromo-chloro-chloride,
BrClPt(NH,NH,Cl); bromo-hydrocyl-chloride
and nitrate, MCl, and M(NO₂), where and nitrate, MCl₂ an M = Br(OH)Pt(NH₄.NH₃)₂. and M(NO₂)₂,

III. Hydroxyl compounds. Hydroxylnitrate and sulphate, M(NO₂)2 and MSO₄, where

 $\mathbf{M} = (\mathbf{OH})_2 \mathbf{Pt}(\mathbf{NH_3.NH_3})_2.$

IV. Iodo-compounds. Iodo-iodide, MI2; iodo-nitrate, M(NO3)2; iodo-sulphate, MSO4; where M = LPt(NH3, NH4)2.

IV. Carbonato-compounds. Carbonatobromo - carbonate, carbonato - chloro - carbonate, and carbonato - nitrato - carbonate, Br. (CO,)R, and caronnais nations of some strong of the caronnais and (NO₃),CO₃R, where R = 2[Pt(NH_x,NH_y)₂).(CO₃)_x.

V. Nitrato-compounds (Cleve, l.o.; Ger-

V. Nitrato-compounds (Chardt a. Laurent, C. R. 30, 273); (NO₃).Pt(NH₂,NH₂Cl)₂.2aq; (NO₃).Pt(NH₂,NH₂Cl)₄; (NO₃).Pt(NH₂,NH₂CrO₄; (NO₃).Pt(NH₂,NH₂).CrO₅; (OH(NO₃)Pt(NH₂,NH₂).SO₂.aq; Cl(NO₃)Pt(NH₂,NH₂,NO₃)₂; VI. Nitrato-compounds

VI. Nitrito- compounds (Cleve, la.

Hadow, C. J. [2] 4, 345): (NO₂), Pt(NH₂, NH₂, NO₂); I(NO2)Pt(NH2.NH2.NO2)

VII. Sulphato-compounds (Cleve, Lc.): (SO₄)Pt(NH₂,NH₄)₂SO₄,aq; OH.Pt(NH₂,NH₂)₂Cl.2aq;

OH(SO,)Pt(NH,,NH,)2SO,.8aq; Br2(SO,)Pt(NH,.NH,),(SO,),2aq. Series 3. Platiniscinidiammines,

R.Pt(NH, NH, R)R. These compounds are isomeric with the platinammines, R,Pt(NH,R). They are generally formed by oxidising the platosemidiammines, Pt(NH3.NH2R)R.

CHLOROPLATINISEMIDIAMMINE CHLORIDE Cl.Pt(NH, NH, Cl)Cl. By chlorinating plato-semidiammine chloride, Pt(NH, NH, Cl)Cl, by Cl or aqua regia (Cleve, l.c.). Orange, crystalline powder; S. 33 at 0°, 1.52 at 100°. Not acted on by cone. H.SO, or alkali solutions.

The following salts of this series are known

(Cleve, l.c.):

bromo-bromide, Br₂Pt(NH₃,NH₃Br)Br; bromo-nitrite, Br₂Pt(NH₃,NH₃,NO₂)NO₂; chloro-nitrite, Cl_Pt(NH₃,NH₃,NO₂)NO₂; chloro-hydroxyl-nitro-nitrite, Cl(OH)Pt(NH₂,NH₃,NO₂)NO₂; trihydroxyl-nitrate, (OH)2Pt(NH3.NH3.NO3)OH; hydrocyl-sulphate, (OH), PtNH, NH, SO,

Series 4. Platinimonodiammines, R2Pt(NH3.NH3R)(NH3R). Of this series the following have been isolated (Cleve, l.c.): bromo-nitrate, Br.Pt(NH, NH, NO,)(NH, NO,); bromo-sulphate, Br.Pt(NH, NH, SO, NII,) aq; chloro-chloride, Cl.Pt(NH, NH, Cl)(NH, Cl); hydroxylnitrate. (OH), Pt(NH3.NH3.NO3)(NH3.NO3).aq; hydroxyl-bromo-nitrate,

(OH)BrPt(NH3.NH3.NO3)(NH3.NO3).aq; bromide, I.Pt(NH3.NH3Br)(NH3Br).

Series 5. Platinitriammines, R.Pt(NH₃,NH₂,NH₃R). This co This constitution is probably to be given to salts formed by electrolysing ammonium carbamate or carbonate solution, using electrodes of Pt (Drechsel, J. pr. [2] 20, 378; 26, 277; Gerdes, J. pr. [2] 26, 257). The salt formed as described is probably carbonato-platinitriammine carbonate. (CO₂).Pt NH, NH, NH, CO₃. By the action of HNO, H.SO, and HCl, respectively, on

this compound are obtained the nitratonitrate, sulphato-sulphate, and chloro-chloride, (NO₂₎₂, M.(NO₃)₂, SO₁, M.SO₂, aq, and Cl₂, M.Cl₂, where M = Pt(NH₁, NH₂, NH₃)₂,

Class III. Diplatinum compounds.

Pt(NH,.NH,R)

Series 1. Diplatodiammines, | Pt(NH₂.NH₄R) (Blomstrand, J. pr. [2] 3, 207). Cleve (l.c.) gives to these compounds the formula

Pt2(NH3)2(NH2)2R2 The following members of this series are known: chloride, MCl₂; hydroxide, M(OH)₂; mitrate, M(NO₃); and sulphate, MSO₄; where M = Pt₂(NH₃).

Series 2. Diplatosindiammines.

RPt(NH, NH,R)

The only compound of this RPt(NH..NH.R)

series is the chloride Cl2Pt2(NH2), Cl2 RPt(NH,R),

Series 8. Diplatinammines, BPt(NH.B), The only compound of this series is the iodide LPt₂(NH₃)₄I₄ (Cleve, l.c.); by treatment with HIAq, the compound Pt₄I₁₀(NH₃)₈ and Pt_sI₁₃(NH_s)₁₆ are produced. Series 4. Diplatinidiammines,

RPt(NH, NH, R)2

(Cleve, l.c.). The iodo-nitrate,

RPt(NH3.NH3R)2 I.Pt.(NH3),(NO3), is formed by reacting on I₂Pt(NH₃)₄(NO₃)₂ with NH₃Aq and treating the product with HNO₃Aq; most of the other compounds of the series are formed from the iodonitrate. Various classes of compounds of this series are formed by varying the composition of the radicles, R; the nomenclature is similar to that used for the platinidiammines. The compounds which have been isolated are bromonitrate, bromo-anhydronitrate, and bromosul-phate, $M(NO_3)_a$, $M(NO_3)_a$, and $M(SO_4)_x$ 2aq, where $M = Br_*Pt_*(NH_3)_s$; hydroxyl-chloride, di-Chromate, plosphate, and sulphate, MCl, aq, M(Cr,O,),, M(HPO,), and M(SO,), 2aq, where M = (OH), Pt₂(NH₃), iodo-iodide, anhydro-iodide, M = (OH)₂Pb₂[N n₃]s; vous-voucae, uningaro-voucae, nitrate, anhydronitrate, phosphate, and sulphute, M₁, M₂O, M(NO₃),4aq, M(NO₃)₂O, M(HPO₁)₂, and M(SO₄)₂, where M = I₂Pt₂(NH₃)₈; nitrato-nitrate, (NO₃)₂Pt₂(NH₃)₈(NO₈)₄·4aq. M. M. P. M.

PLATINUMS, FULMINATING. Various compounds of Pt, N, Cl, O, and H, all of which Various explode when heated, are formed by the action of KOHAq on (NH₄) PtCl₆, or by ppg. Pt(SO₄), with NH₂Aq and boiling the pp. with KOHAq (Proust, Gehlen's J. 1, 348; Döbereiner, G. A. 72, 194; Fourcroy a. Vauquelin, Gehlen's J. 1, 348; Davy, S. 19, 91). These compounds are classed together as fulminating platinums. E. von Meyer (J. pr. [2] 18, 305) classifies according to the quantities of Cl they contain; all contain Pt and N in the ratio of equal numbers of atoms: tetrachloro- compound Pt,N,Cl,Q,H₂₄, trichloro-oxy-Pt,N,Cl,(OH)Q,H₂₁₁,dichloro-Pt,N,Cl,Q,I₁,H₂₁, chloroxy- Pt,N,Cl(OH)Q₁₂H₂₂. Tetrachloro-ful-minating platinum is formed by adding KOHAq drop by drop to Am, PtCl, in the ratio 40KOH: Am.PtCl., and washing the pp. by repeatedly boiling with acetic acid solution and then with water. At 150° 4H.O is given off; explosion occurs at a higher temperature. Dilute H₂SO₄Aq produces H₂C₂O₄ and evolves CO₂. By treatment with KOHAq, or NH₂Aq, Cl, is easily removed, a third Cl is removed with difficulty, but the fourth Cl remains unattacked. M. M. P. M.

PLUMBAGO. A name sometimes given to graphite; v. Carbon, vol. i. p. 686.

PLUMBATES. Salts wherein PbO2 acts as acidic radicle, v. vol. iii, p. 132.

PLUMBITES. Salts wherein PhO acts as

PLUMERICS. Sames wherein the access ac acidic radicle, v. vol. iii. p. 129.

PLUMERIC ACID 0, H, O. (139°). Occurs as calcium salt in the milky juice of Plumeria acutifolia (Oudemans, A. 181, 154). Minute crystals (from water), v. sol. alcohol and ether, sl. sol. cold water. Yields salicylic acid on sl. sol. cold water. Yields salicylic acid on fusion with KOH. Reduced by sodium amalgam to crystalline 'hydroplumeria' acid C₁₉H₁₂O₄.—
K₄A'' 8aq. — Ca(H₂A''), 4aq. S. '5 at 20°. —
CaH₂A'' 5aq. S. '25 at 20°.—Ca₂(HA''), 8aq.—
Ag.H₂A'' aq. — Ag.HA'' 1¹/₂aq: needles (from water).

PODOCARPIC ACID C17H22O, i.e. C_1H_{1b} . C_0H_2 Me(OH). CO_2 H. Mol. w. 274. [188°]. [α]_p = 136°. Constitutes at least 90 p.c. of the resin found by de Vrij in the trunk of an old tree, Podocarpus cupressina, var. imbricata (Oudemans, A. 170, 213). Plates (from dilute alcohol), insol. water, v. sl. sol. benzene, v. e. sol. alcohol and ether. Dextrorotatory. Resolved at 300° into water and anhydride C34H aO, Yields methanthrene C15 II12 on distillation with zinc-dust. The Ca salt on distillation yields p-cresol, hydrocarpol, carpono C₀H₁₁, and methanthrol C₁₂H₁₂O. Br added to its alcoholic solution forms C₁₁H₂₂BrEtO₄(EtOH) [above 80°], which gives off alcohol when heated for some time, leaving C17, H20BrEtO3 [158°].

mne, reaving U₁H₂₀BTELO₂ [158*]. Salts.—NaA' 7aq. S. 33 at 21°. Needles.—
KA' 3aq.—KA' 4aq.—(NH₄)HA'₂ aq.—BaA'₂ 3aq.
—BaA'₄ 8aq. — BaA'₂ 9aq. — BaA'₄ 15aq. —
BaO₄H₂₀O₃ 8aq. — CaA'₂5aq. — PbA'₄ 4aq., —
PbC₄H₂₀O₃ aq. — PbH₂A'₄ 10aq. — CuA'₂ 10aq.—
AgA' 2 aq.

Matheliatics MA'₂ [1712]. Continu

Methyl ether MeA'. [174°]. Grains. Ethyl ether EtA'. [146°]. Needles.

Acetyl derivative C., H., AcO. Small needles (from dilute alcohol).

Nitropodocarpic acid $C_{12}H_{21}(NO_2)O_3$. [205]. Formed, as well as the di-nitro-acids, by the action of HNO₃ (S.G. 1³4). Small crystals, insol. water, m. sol. hot alcohol. May be reduced to unstable amido-podocarpic acid, which forms

C1, H2NO HCl laq.

Salts.—(NH₀)₂C₁,H₁₀NO₃4aq.—

K₂C₁,H₁₀NO₃5 baq. Red needles with green lustre, v. sol. water.—Na₂C₁,H₁₀NO₃9aq. Scarlet Plates. — BaC., H₁₀NO₃ 7aq. Red needles. — BaC., H₁₀NO₃ 3aq. — Rad v. 4aq : yellow needles, sl. sol. water. — CaC., H₁₀NO₃ 4aq : orange needles.

Di-nitro-podocarpic acid C1, H2 (NO2)2O3. [203°]. Pale-yellow crystals, insol. water, m. sol. alcohol. -- Salts: K2C17H18N2O, 5aq. Crimson needles, with green reflex. BaC1, H18N2O, 4aq. -Ag2C1,H18N2O, 4aq: orange pp.

Sulpho-podocarpic acid C1,H (SO1H)O18aq. Got by warming with H.SO.. Amorphous mass. Salts: Na,A" 7aq: easily soluble rosettes.—Ba(HA"), 6aq. — BaA" 8aq: white laminæ. — CaA" 7aq: thin lamine.

Hydrocarpol $C_{1a}H_{20}O$. (220° in vacuo). A product of the distillation of calcium podocarpate. Viscid oil, v. sol. alcohol and ether. Yields p-cresol, carpene, and methanthrol $C_{15}H_{12}O$ [122°] when distilled. Methanthrol is crystalline, sol. KOHAq.

PODOPHYLLIN. The resin extracted from the root of Podophyllum pellatum (Guareschi, B. 12, 683; G. 10, 16; Busch, Ph. [3] 8, 443; Senier a. Lowe, Ph. [3] 8, 445). It contains bitter and physiologically active 'picropodophyllin' crystallising in needles [200°-210°], and several resins, e.g. 'podophyllo- quercetin' [247°-250°] and 'podophyllic acid' (Podwissotzky, Ph. [3] 12, 1011).

POLYCHROÏTE v. SAFFRON.

POLYMERISM; a term generally applied to the phenomens of the existence of more than one substance having the same composition, and related in properties, but with different molecular weights; v. Isomerism, vol. iii. pp. 79-81. M. M. P. M.

POLYPORIC ACID C, H, O,. [above 800°]. Occurs in a fungus belonging to the genus Polyporus, which grows on the bark of diseased or dead oaks. The fungus is yellow, but is turned violet by ammonia (Stahlschmidt, A. 187, 177; 195, 365). Bronzed tables (from alcohol), insol. water, ether, benzene, CS2, and HOAc, sl. sol. chloroform and alcohol. Alkalis form purple solutions, decolourised by zine-dust. Yields a tetrahydride when boiled with conc. KOHAq. Wields benzene on distillation with zino-dust. Conc. HNO, forms C_1 , H_1 , (NO.), O_4 , [230°]. KClO, and HCl give C_1 , H_1 , C, O_4 , [108°] and C_1 , H_2 , C, O_4 [110°].

Salts .- K, A" 2aq: purple monoclinic crys. tals.—Na Λ'' 2aq : violet needles. — $(NH_4)_2\Lambda''$ 2aq.—Ba Λ'' 4aq.—Ba Λ'' 2aq.—Sr Λ'' 4aq.—Sr Λ'' aq. -CaA" 3aq: pale-violet needles. MgA" 3aq.-Ag A": insoluble pp.

Methylether McA". [187°]. Ethylether Et,A". [134°]. Needles. Diacetyl derivative C, H, 2Ac,O. [205°]. Yellow needles, sl. sol. alcohol

Hydride C₁₈H₁₈O₄. [163°]. Formed, together with the acid C₂₀H₁₈O₂ [156°] which [163°] yields Ag,A", by boiling polyporic acid with cone. KOHAq. White crystalline powder (from hot water), sol. alcohol.—Na,A" 4a,—BaA".—MaM", 6aq.—Ag,A": crystalline pp.
POPPY OIL. The oil expressed from the

seeds of Papaver somniferum contains glycerides of linoleic, stearic, and palmitic acids (Oudemans, J. 1858. 304; 1863. 333; cf. Mulder, J. 1865, 323).

POPULIN is the Benzoyl derivative of SALICIN. PORPHYRINE C₂₁H₂₂N₃O₂. [97°]. Occurs, together with alstonine and alstonidine, in the bark of Alstonia constricta (Hesse, A. 205, 366). White amorphous substance, sol. alcohol, ether, and chloroform. Conc. H.SO, gives a purple solution. Its acid solutions exhibit blue fluorescence. -B'2H2PtCl, 4aq.

POTASH. Potassium hydroxide, q. v., p.

POTASSIUM. K. At. w. 39-04. Mol. w. probably 39·04 (Bansay, C. J. 55, 521; v. infra). M.P. 58° (Quinoke, P. 135, 642); 62·5° (Bunsen, A. 125, 368). B.P. 719° -731° (Carnelley a. Williams, C. J. 35, 563); 667° (Perman, C. J. 55, 326). S.G. 865 at 15° (Gay-Lussac a. Thánard); 875 at 13° (Baumhauer, B. 6, 655). V.D. not known with certainty; v. infra, molecular weight. S.H. from -78° to +10° 166 (Regnault, A. Ch. [3] 26, 286). C.E. (linear, 0'-50') 00008415 (Hagen, Verhandl. d. physikal. Ges. su Berlin, 1882. No. 13). Volume at to vol. at 0° 1882. No. 13). $(1 + .00023935t + .00000020925t^2)$ for interval 10° to 95° (Hagen, l.c.). E.C. at 0° (Hg at 0° -1) 11.23; at 100° (liquid) 5.586 (Matthiessen, P. 100, 177). Refraction-equiv 7.51 (Kanonnikoff, J. R. 1884 (1), 119). The emission-spectrum is characterised by a line K, in the extreme red, and a line Ks in the violet; for measurements of all the chief lines v. B. A. 1884. 436; for the absorption-spectrum v. Roscoe a. Schuster, C. N. 29, 268. H.C. [K²,O] = 66,050 (Woods, P. M. [4] 2, 268).

Occurrence. - Compounds of K are widely distributed in large quantities. Felspar, mica, &c., contain silicates of this metal; carnallite, sylvine, &c., contain KCl; alum-stone and other

minerals contain K₂SO₄; saltpetre is chiefly partly filled with mineral naphtha, and having KNO₂. Sea-water contains c. 5 to 7 g. KCl an opening through which an iron rod may be per litre. Potassium salts, e.g. acid tartrate and passed to clear the tube which carries the K oralate, are found in plants. Animals contain salts of K, chiefly phosphate and chloride.

Marcska. A. Ch. [3] 35, 147). Castner C. N.

Historical.—Polash was decomposed by Davy (T. 1808. [1] 5) in 1807, by passing the electric current from a Volta-pile of 200 plates, through a piece of potash placed in a Pt basin. Gay-Lussac a. Thénard, in 1808, reduced potash and obtained the metal, by heating it to whiteness with iron filings (A. Ch. 65, 325). In the same year Curaudan (A. Ch. 66, 97) showed that charcoal could be used instead of iron. Brunner (S. 38, 517) made this process applicable on the large scale, and B.'s method was modified by several workers, especially by Donny a. Mareska

(A. Ch. [3] 35, 147).

Formation.—1. By electrolysing KOH. The most effective method is to place a little cone. KOHAq, with pieces of solid KOH in it, in a Pt basin, to connect this with the negative pole of a powerful battery, to pour a little Hg into the basin, and place therein the wire from the positive pole. The K which is thus formed amalgamates with the Hg; the amalgam, after drying, is heated in a small retort, along with a little mineral oil, which drives out the air, and the K remains when the Hg has been distilled off .- 2. By electrolysing a molten mixture of KCl and CaCl2 in the ratio 2KCl: CaCl2. Temperature is arranged so that a solid crust remains on the surface of the molten mixture. Electrodes of gas-coke are used. After electrolysis the mixture is allowed to cool for twenty minutes, and the contents of the crucible are scraped out under petroleum (Matthiessen). Linnemann electrolyses molten KCN (J. pr. 73, 415).—3. By heating KOH to redness with iron filings or charcoal.-4. By heating an intimate mixture of K,CO, and C, or a mixture of K,CO, or KOH, C, and very finely-divided iron (Castner, C. N. 54, 218).-5. By heating sulphide of K with iron filings (Dolbear, C. N. 26, 33).-6. By heating potash with sodium under petroleum to c. 170' (Williams, C. N. 3, 21).-7. By the action of Na on dry molten K acetate (Wanklyn, C. N. 3, 66).

Preparation. -- An intimate mixture of K.CO. and C is formed by heating cream of tartar (K-H tartrate) in a closed crucible. The mixture is then strongly heated in an iron bottle, connected with a flat receiver about 30 centim. long, 12 centims. wide, and 6 centims. from the inner surface of one side to that of the other; this receiver is made of two pieces of sheet iron (about 4 mm. thick) screwed together, and has an opening at the end farthest from the retort, to allow the escape of CO. The reaction may be represented thus: $K_2CO_3 + 2C = 2K + 3CO$. The K distils over and condenses in the receiver; when full the receiver is removed, plunged under mineral oil and there opened, and the K is removed by a chisel. K combines with CO at a red heat to form a black, very explosive substance; the more rapidly the distilled K is cooled the less of this explosive compound is formed. The distilled metal is purified by wrapping it, when under oil, in a piece of linen, heating the oil to c. 65°, and pressing the molten K through the linen; the metal is then redistilled, from an iron bottle, into a copper tube

partly filled with mineral naphtha, and having an opening through which an iron rod may be passed to clear the tube which carries the K from the bottle into the receiver (Donny a. Marceka, A. Ch. [3] 35, 147). Castner (C. N. 54, 218) uses as reducer a mixture of C and a metallic carbide, or a mixture of very finely-divided metal and C (conveniently prepared by heating a mixture of $Fe_{\chi}O_{\chi}$ and tar in a covered vessel), and heats in an iron crucible with an exit-tube passing through the lid. The reaction, using KOH, Fe_{χ} and C, may be formulated as $3KOH + Fe_{\chi} + 2C = 3K + Fe + CO + CO_{\chi} + 3H$.

Properties. - A silver-white, lustrous metal. As soft as wax at ordinary temperatures, brittle at 0°, melts at c. 60°. Boils when heated in a stream of H to c. 700°, and forms a brightgreen vapour. A sublimate, in a very thin film on glass, shows a rich purple colour in transmitted light (Dudley, C. N. 66, 163; Newth, N. 47, 55). Crystallises in quadratic octahedra, which have a greenish-blue sheen. These crystals are obtained by melting K in a glass tube, narrowed at one place, and filled with coal-gas, and allowing the semi-solidified metal to flow slowly through the constricted part of the tube (Long, C. J. 13, 122). Sol. liquid NII, forming a blue liquid, from which the metal is obtained by allowing the NH, to evaporate (Seeley, C. N. 23, 169; v. Potassammonium, p. 299). Combines very rapidly with O; on exposing a freshly-cut surface to air, oxidation occurs at once. composes cold water rapidly. K must be kept under a liquid free from O, such as mineral naphtha or rock-oil.

The atomic weight of K was determined by Berzelius, Penny, Marignac, Pelouze, Millon, Faget, and Maumené, from 1813 to 1846, by reducing KClo₃, KClO₄, and KIO₅ to KCl and KI, and by converting KCl, KBr, and KI to AgCl, AgBr, and AgI. The researches of Stas, in 1860 and 1865, have determined the at. w. with great accuracy. Stas heated KClO₅, thus getting KCl, decomposed KClO₅ by HClAq, determined the ratio of KCl and KBr to Ag required for complete ppn., converted KCl into KNO₅ and KBr into AgBr, and determined the ratio of KBr to AgNO₇ required for ppn. (Stas, Rech. 69, 70, 91,

118; Nouv. R. 244, 303).

The molecular weight of K is not known with certainty. Dewar a. Dittmar (C. N. 27, 121) and Dewar a. Scott (Pr. 29, 206, 490) determined the V.D. of K at c. 1000°; the earlier results pointed to a mol. w. of c. 90, and the later numbers to a value c. 45. V. Meyer (B. 13, 391) showed that the results were untrustworthy, as vapour of K attacks glass vessels. It has also been shown that vessels of Cu, Ag, Pt, or Fe cannot be used (Ricth, B. 4, 807; Meyer, Lc.). Ramsay (C. J. 55, 521) attempted to find mol. w. of K by dissolving in Hg, and finding the decrease of the vapour-pressure of Hg thereby produced. Assuming the mol. w. of liquid Hg to be 200, and also assuming that equal vols. of dilute solutions contain equal numbers of molecules, the results gave mol. w. of K as 29:1 and 30°2; it seems probable that the mol. of K is monatomic.

The only compound of K whose V.D. has been determined is KI; in this molecule the atom of K is monovalent.

K is a very strongly positive element. In all

its compounds it reacts as a metal, and does not enter into the composition of any negative radicles. K forms very few basic salts, and no oxyhaloid compounds; its halide compounds are very stable towards heat. K is closely related to Cs, Li, Na, and Rb (v. Alealis, METALS OF THE, vol. i. p. 114).

Reactions .- 1. Heated in dry air or oxygen, K₂O and K₂O₄ are formed (v. Oxides, p. 304).—2. At about 300° K absorbs hydrogen readily, probably forming K₂H (v. Hydride, p. 301).— 3. Combines with chlorine, bromine, and iodine when heated (v. Chlorides, bromides, iodides, pp. 299, 300, 302) .- 4. Forms compounds with sulphur, selenion, and tellurium when heated (v. Sulphides, selenides, tellurides, pp. 305, 306).-5. Combines with phosphorus (v. Phosphide, p. 305) .- 6. Alloys with several metals (v. Alloys, infra). -7. Reacts rapidly with water, forming KOHAq and H .- 8. Heated with hydrogen sulphide forms KHS (v. Hydrosulphide, p. 302). — 9. Dissolves in liquid ammonia (Seeley, C. N. 23, 169; v. infra, Potassammonium). Heated in dry ammonia gas, KNII, is formed (v. Amide, infra). - 10. Combines with carbon monoxide to form KCO (v. Carbonyl compound, p. 300). At red heat decomposes CO with separation of C.— 11. Decomposes carbon dioxide, and nitrous and nitric oxide, when strongly heated with these compounds. - 12. Reacts with moist carbon dioxide to form K2CO3 and HCO2K (Kolbe a. Schmitt, A. 119, 251).-13. Decomposes silica and boric acid, when heated with these compounds, probably forming silicide and boride (q. v., pp. 299, 305).

Potassium, alloys of. Alloys of K with most metals are known; K alloys easily with the The alloys generally more fusible metals. oxidise in air, and decompose cold water. K forms amalgams with Hg; according to Joannis (C. R. 113, 795), Hg₁₈K is formed by letting potassammonium (q. v.) in liquid NH, drop on to Hg. For polarisation of K amalgam in KCIAq against Zn amalgam v. Le Blanc, Z. P. C. 5, 467. For supposed alloy with NH., v. infra, POTASSAMMONIUM.

Potassium, aluminate of; v. vol. i. p. 141.

Potassium amide, KNH₂. Gay-Lussac a. Thénard (G. A. 29, 135; 32, 23) obtained dark olive-green crystals by heating K in dry NH3. Baumert a. Landolt (A. 111, 1) confirmed G. a. T.'s formula KNH₂. The compound is formed by passing dry NH₃ into a flask of c. 50 c.c. capacity, fitted with a cork carrying an inlet and exit tube, quickly throwing in pieces of K, continuing the passage of NH,, and heating very gently till the metal just ceases to dissolve in the greenish-blue liquid that is formed; on cooling, a yellowish-brown solid is obtained. KNH, is a non-conductor of electricity. Melts at a little over 100°, at a higher temperature NH, is given off, along with H and N, and K,N remains (v. Potassium nitride, p. 304). Burns when heated in O, or heated to redness in air, giving N and KOH; decomposes in moist air to KOH and NH.; must, therefore, be kept under rock oil. Reacts energetically with water, giving NH, and KOHAq.

Potassium-ammonium or Potassammonium. By evolving dry NH, from AgCl.xNH, in a

Faraday tube containing K in the other end, Weyl (P. 121, 697) obtained a substance which he regarded as an alloy, or compound, of K and NH. Seeley (C. N. 23, 169) regarded the blue liquid formed by dissolving K in liquid NH, as a solution, inasmuch as K was obtained again when the NH, was allowed to evaporate. Joannis (C. R. 109, 900, 965; 110, 238) examined the vapour-pressures of a solution of K in liquid NH, and also the thermal phenomena attending the formation of the solution. He found the vapour-préssure to decrease till a certain value was reached, when it became constant, provided temperature was not changed; on removal of more NH, a copper-red solid separated, and thereafter NII, was given off at constant pressure, till only K remained. This last part of the process was regarded by J. as a dissociation of NHaK; analysis showed this ratio (NHaK) to be always at ained when the final part of the change commenced. The heat of formation of NH₃K is given by J. as 6,300 when NH₄ is gas and K solid, and as 1,900 when NH, is liquid and K solid. Joannis (C. R. 113, 795) found that NII, K in liquid NH, is decomposed by Sb, Pb, and Hg, but not by Al, Cu, Ag, or Zn; by dropping the liquid on to Hg, and washing the product with liquid NH, he obtained a crystalline amalgam Hg, K.

By measuring the depression of the vapourpressure of liquid NH, by solution of K therein, J. concludes that the mol. formula of potassammonium is N.II.K. (C. R. 115, 820).

Potassium, antimonide of. Probably SbK, A greyish-white, lustrous solid; decomposes water, giving KOH, Sb, and H. Formed by heating the elements together, or by fusing Sb,O, with K,CO, and C.

Potassium, antimonates of; v. vol. i. p. 286. Potassium, arsenates of; v. vol. i. p. 309.

Potassium, arsenites of; v. vol. i. p. 306.

Potassium, auricyanide of; v. vol. ii. p. 332. Potassium, borates of; v. vol. i. p. 529.

Potassium, boride of. The brown solid

formed when boric acid is reduced by heating K may contain a compound of B and K.

Potassium, borofluoride of; v. vol. i. p. 526. Potassium, boronitride of. By very strongly heating a mixture of 7 parts B₂O₃ with 20 parts KCN, Balmain (J. pr. 27, 422) obtained a white, infusible solid; insol, water or KOHAq; decomposed by boiling aqua regia, leaving BN (vol. i. p. 527); heated in steam gave off NH, and left KOH and boric acid.

Potassium, bromide of, KBr. Formula probably molecular, from analogy of KI. Melts at 699° (Carnelley, C. J. 33, 279). S.G. 2.695 to 2.72 at 4° (Schröder, P. 106, 226); 2.712 at 12.7° (Clarke's Tables of Spec. Gravities, 2nd ed., 31); 2·199 fused (Quincke, P. 138, 141); v. also Spring (B. 16, 2724). S.H. (16° to 98°) 11322 (Regnault, A. Ch. [3] 1, 129). Vol. at 40° - vol. at 0° (1+00012602) (Fizeau, C. R. 64, 814). 8. 53·48 at 0°, 64·6 at 20°, 74·62 at 40°, 84·74 at 60°, 93·46 at 80°, 102·04 at 100° (Kremers, P. 25, 119); Coppet (A. Ch. [5] 30, 411) gives S. 54.43 + 5128t where t varies from - 18.4° to 110°. Gerlach (Fr. 8, 285) calculated the following from Kremer's data:

	8.G.	KBrAq	
б р.с.	1.037	30 p.c.	1.256
10 ,,	1.075	35 ,,	1.309
15 ,,	1.116	40 ,,	1.366
20 ,,	1.159	45 ,,	1.430
25 "	1.207] "	
T TO 1727	D=1 = 05 910 ·	[IZ Br A a] - 0	0 0 3 0 17

production of much heat (v. Balard, Merz, a. Weith, B. 6, 1518) .- 2. By treating BrAq with weith, B. 6, 1016).—2. By treating Braq with iron filings and ppg. with K.CO.3.—3. By neutralising HBrAq by KOHAq or K.CO.3Aq, and evaporating.—4. By decomposing CaBr.Aq by K, SO, filtering after 12 hours, adding K, CO as long as turbidity is produced, filtering, and evaporating (Klein, A. 128, 237).

Preparation.- A moderately conc. solution of KOH, free from K₂CO₂, is prepared from pure K₂CO₂ and pure CaO (v. Potassyum hydroxide, p. 302); to this solution Br is added, little by little, till the liquid is slightly yellow; very finely-powdered charcoal, equal to about one-tenth of the quantity of Br used, is added, and the liquid is evaporated to dryness (6KOHAq + 3Br₂ = 5KBrAq + KBrO₃Aq + 3H₂O); the dry residue is well powdered, and heated to dull redness in a closed crucible for some time $(2KBrO_3 + 3C = 2KBr + 3CO_2)$; the residue is extracted with warm water, the solution is filtered, and evaporated to the crystallising point.

Properties and Reactions. - KBr crystallises in very lustrous, white cubes, sometimes elongated to prisms or flattened to plates; it has a strongly saline taste. Easily sol. water, with considerable lowering of temperature; [KBr,Aq] consideration towering of temperature; [ABF,Aq] = -5,080 (Th. 3, 235). Chlorine reacts with KBrAq to give KClAq and Br; Br is not set free by H₂SO₄ containing N₂O₃, nor by KNO₂Aq + dil. H₂SO₄Aq. KBr heated with possible the containing the containing N₂O₃. tassium chromate and sulphuric acid gives off Br; KCl under similar conditions gives CrO2Cl2. Conc. sulphuric acid produces HBr, Br, and SO.: the amount of HBr (the primary product of the reaction) thus decomposed varies very nearly in proportion to the quantity of IL₂SO₄ used; if the H₂SO₄ is in such large excess that the water formed in the reaction causes no sensible dilution, only SO, and Br are produced; by using dil. H.SO.Aq (c. 30 p.c.) a mere trace of Br is obtained, the products being almost wholly KHSO, Aq and HBrAq (v. Addyman, C. J. 61, 94). Hypochlorous acid solution produces KClAq and KBrO, Aq, with evolution of Br and Cl. Potassium permanganate solution has no action even when boiled; but Br is set free if a little H,SO, is added, even without warming, the decomposition being soon completed (Hempel, A. 107, 160). Fusion with potassium chlorate produces KBrO.

Combinations .--With many bromides of less positive metals to form double salts; some of these are best regarded as K salts of acids containing Br and a metal less positive than K, e.g. AuBr, KBr is best looked on as KAuBr, (v. the various metallic bromides). Also with iodina bromide, to form KBr.IBr (Wells a. Wheeler, Am. S. [3] 48, 475). Also with some metallic chlorides; thus SbCl, forms SbCl, 3KBr identical with SbBr. 3KCl, and therefore to be regarded as SbK,Cl,Br, (Atkinson, C. J. 48, 290). Feit

(J. pr. [2] 39, 373) describes MgBr. KBr. 6aq, analogous to carnallite (MgCl. KCl.6aq). Schiff (A. 228, 72) describes a compound with arsenious

Potassium tribromide KBr., According to Berthelot (A. Ch. [5] 21, 370), orange crystals of this composition are formed by adding Br to KBrAq; no analyses are given. The substance KBrAq; no analyses are given. The substance decomposes rapidly. B. gives [KBr,Br²] = 2940.

Potassium, carbonyl compound of. (Carbonic oxide potassium.) The black solid formed in the preparation of K was thought by Berzelius (P. 4, 31) to be a carbide; Liebig (A. 11, 182) found that the same compound was formed by passing CO over K heated just to melting; Brodie (C. J. 12, 269) confirmed Liebig's result, and determined that one molecule CO is absorbed for each atom K; hence the empirical formula is probably KCO. This substance is extremely explosive; many serious accidents have occurred with it. If the CO used is quite dry, and the substance is washed rapidly in alcohol as soon as it is prepared, the residue is not nearly so explosive (Nietzki a. Benckiser, B. 18, 1833, where details of the method of preparation are given); probably the alcohol dissolves out unchanged K. Potassium carbonyl is a greyish solid; on standing in air it becomes yellowish and very explosive; it dissolves in water, with evolution of much gas (according to E. Davy [A. 23, 144] this gas contains C.H., and generally with combustion or explosion; heated to redness it is resolved into K and CO. By exposure to moist air, or by other processes of oxidation, a series of organic compounds is obtained (v. CROCONIC ACID, vol. ii. p. 275; HEXA-OXY-BENZENE, vol. iii. p. 678; Tetra-oxy-quinone, vol. iii. p. 771; RHODIZONIC ACID, this vol.).

Potassium, chloride of, KCl. Formula probably molecular, from analogy of KI. Melts at (Carnelley, C. J. 33, 279). S.G. 1 9775 at 4º (Playfair a. Joule, C. S. Mem. 2, 401); 1.9453 at 15° (Stolba, J. pr. 97, 503); 1.612 at M.P. (Braun, C. J. [2] 13, 31); 1.87 fused (Quincke, P. 135, 642); v. also Spring (B. 16, 2721). S.H. 14° to 99 17295 (Regnault, A. Ch. [3] 1, 129; v. also Kopp, T. 155 [1] 71). Vol. at $40^{\circ} = \text{vol}$. 2. at 80 Appp, F. 155 [1] 71). Vol. at 40° = Vol. at 0° (1 + 00011408) (Fizeau, C. R. 64, 314). S. 32 at 10°, 334 at 15°, 34·7 at 20°, 37·4 at 30°, 40·1 at 40°, 42·8 at 50°, 45·5 at 60°, 48·3 at 70°, 51° at 80°, 53·8 at 90°, 56·6 at 100° (Mulder, Scheikund, Verl. 1864. 39); Coppet (A. Ch. [5] 30, 411) gives S. $28.51 + .2837t^{\circ}$, where t° varies from -11° to 109° . S. at 0° in alcohol is given in following table (Gerardin, A. Ch. [4] 5, 139); where S.G. of alcohol is at 0°, and $S+t^\circ$ is solubility at t° (cf. Schiff, A. 126, 167):

Alcohol S.G.	s.	t°	Alcohol S.G.	S.	to
.9904	$23 \cdot 2$.27	9573	7.1	.162
.9848	19.4	.255	.9390	4.2	·125
.9793	15.7	.233	8767	1.89	.061
.9726	11.9	.205	1		_

Gerlach (Fr. 8, 281) gives the following data:

			8.G.	KCLAq			
1	per	cent.	1.0065	20	per	cent.	1.1861
5	٠,,	19	1.0325	20 24 24-9	٠,,	**	1.1657
10	**	99	1.0658	24-9	19	20	1.1728
15			1.1004				

H.F. [K,Cl] = 105,610; [K,Cl,Aq] 101,170 (Th. 3, 285). 30 parts KCl dissolved in 100 parts water at 18.2° lower the temperature to '6°, i.e. through 12.6° (Rüdorff, B. 2, 68). Solution of 1 g. KCl in 100 g. water freezes at - 446°; saturated solution freezes at -10.9° (Rüdorff, P. 114, 63: 122, 337). Saturated solution boils at 108°.

Occurrence. - In small quantities in sea-water, and in some mineral springs. As chloride in sulvine; as double chloride, especially as carnallite KCl.MgCl..6aq. In crude pearl ash, in plant ash, and in kelp.

Formation .- 1. By the direct union of the elements; K burns in Cl at the ordinary temperature. - 2. By heating K in HCl gas. - 3. By passing Cl over KOH or KI heated to redness. -4. By the action of HClAq on KOH or K,CO,.-5. By decomposing various metallic chlorides by fusion with K.

Preparation.-1. Commercial KCl is prepared chiefly from carnallite. The mineral is dissolved in warm water, heated by steam to c. 120°, and allowed to cool; at 60°-70°, MgSO, aq, CaSO, and NaCl separate, and on further cooling c. 70 p.c. of the KCl is obtained; the crystals of KCl are washed with a little cold water, to remove NaCl and MgCl,, and a product containing c. 95 p.c. KCl is thus obtained (for details v. Dic-TIONARY OF APPLIED CHEMISTRY) .- 2. Pure KCl is prepared by neutralising pure HClAq by pure KOH or K,CO,, evaporating to the crystallising point, and recrystallising from water.

Properties.—White salt, crystallising in cubes.
Saline taste. Unchanged in air. Decrepitates when heated; melts at c. 740°, and volatilises at a higher temperature. Fairly sol, water or aque. ous alcohol; insol. absolute alcohol, or conc. HClAq; sol. in 20 p.c. KC₂H₂O₂Aq.

Reactions. -1. With acids, KCl generally

gives K salt of the acid used and HCl .- 2. Said to combine with sulphuric anhydride, and chromic anhydride, probably forming SO. Cl.OK and CrO, Cl.OK respectively (H. Rose, P. 38, 117) .- 3. Fused with potassium, in H, a blue substance is formed, supposed by H. Rose to be a subchloride (P. 120, 15). What is probably the same substance is formed during electrolysis of molten KCl (Bunsen a. Kirchoff, P. 113, 344). 4. For action of water and oxygen, in presence and absence of acids, v. Schulze, J. pr. [2] 21,

Combinations. - 1. With sulphuric and chromic anhydrides, v. Reactions, No. 2 .- 2. With most metallic chlorides; some of the compounds are best regarded as K salts of metal-containing acids, e.g. KAuCl, (v. the different metallic chlor-- 3. With iodine trichloride, to form KCl.ICl,; prepared by mixing KClAq and ICl, Aq, by passing Cl into warm KIAq containing HCl, or by dissolving 1 part KIO₄ in 8 parts HClAq of S.G. 1·176, at 40°-50°. Forms lustrous yellow prisms, smelling of Cl; on heating gives Cl, KCl, and ICl; with water forms KIO₄; ether dissolves out ICl₄ (Filhol, J. Ph. 25, 435, 506).— 4. With iodine monochloride, to form KCl.ICl (Wells a. Wheeler, Am. S. [3] 43, 475).

Potassium, eyanide of; v. vol. ii. p. 346. Potassium, chromicyanide of; chromisulphoeyanide of; and chromocyanide of; v. vol. ii. p.

Potassium, cobalti- and cobalto-cyanide of: v. vol. ii. p. 330.

Potassium, ferrate and ferrite of; v. vol. ii. p. 547.

Potassium, ferri- and ferro-cyanide of; v. vol. ii. pp. 339, 336.

Potassium, fluorides of. Two fluorides are known, KF, and KHF, or KF.HF.

Potassium fluoride KF. Formula probably molecular, from analogy of KI. Prepared by neutralising fIFAq by K.CO, in a dish of Ag or Pt, evaporating to dryness, and heating till HF ceases to be given off. According to Berzelius (P. 2, 218), KF is obtained in crystals by slowly evaporating an aqueous solution at 35°-40° in a very shallow dish. Deliquescent; fusible; solution has alkaline reaction to litmus, and etches glass. Guntz (A. Ch. [6] 3, 5) says KFAq is neutral, but the salt is decomposed in solution and becomes alkaline. Evaporation of a very cone. solution gives KF.2H.O, according to H. Rose. S.G. 2.454 (Bödeker); 2.096 at 21.5° (Clarke, Am. S. [3] 13, 291). Combines with HF to form KF.HF (v. infra); with BF, to form KBF, (v. Potassium borofluoride, vol. i. p. 526); with SiF, to form K2SiF, (v. p. 305); with B2O, to form 2KF.B.O., obtained by dissolving B.O. in molten KF (Schiff, A. 228, 72); with TeF, to form KF.TeF, by evaporating TeO, in HFAq with addition of K.CO. (Högborn, Bl. [2] 35, 60); and with many metallic fluorides.

POTASSIUM-HYDROGEN FLUORIDE KHIF. KF.HF. Prepared by dividing a quantity of HFAq into two equal parts, neutralising one, adding the other, and evaporating; also by evaporating KF in acetic acid. White cubes or four-sided tables; c. sol. water, almost insol. dil. HFAq. When heated gives HF, leaving KF. By electrolysis of HF containing KHF2, F is obtained (v. Fluoring, vol. ii. p. 561). Moissan (C. R. 106, 547) says that two other compounds of KF and HF are obtained by dissolving dry KF in liquid HF, and cooling; to these compounds he gives the formula KF.2HF and KF.3HF. Guntz (A. Ch. [6] 3, 5) gives [HF,KF] = 21,100.

Potassium, haloid compounds of. The compounds KF, KCl, KBr, and KI are the chief halides of K; as KI has been gasified and the molecular weight corresponds with the simplest formula, it is probable that KX expresses the molecular composition of these halides. also exists, but is decomposed by heat; and there are indications of the existence of KBr. KF combines with HF to form KHF, and, according to Moissan, also KF.2HF and KF.3HF.

Potassium, hydride of, K.H. The absorption of H by heated K was observed by Gay-Lussac a. Thénard (A. Ch. 74, 203), and was confirmed by Jacquelain. Troost a. Hautefeuille (A. Ch. [5] 2, 273) found that the absorption of H by K begins at c. 200' and becomes rapid at 350-400°; if the action continues for some time 126 vols. H are absorbed by 1 vol. K. The product is brittle, and much resembles Ag amalgam; it is fusible without change in H or in vacuo; takes fire in contact with air; heated in vacuo, dissociation begins at 200° (for vapourpressures of H given off, v. Dissociation, vol. ii, p. 398). The formula K,H requires 124.6 vols H to 1 vol. K.

Potassium, hydrosulphide of, KHS (Potassium sulphydrate). Gay-Lussac a. Thénard (A. Ch. 115, 165) obtained this compound by heating K in dry H₂S gas; it is more readily formed by heating K₂CO₂ to redness in H₂S (H₂O and CO₂ are given off) (Berzelius, P. 6, 438). By saturating KOHAq with H₂S, and CO₂ are given off) (Columbia) evaporating the conc. solution over CaO or CaCl., in vacuo, Schöne (P. 131, 380) obtained lustrous, rhombohedral crystals of 2KHS.H₂O; and by dehydrating this in a stream of dry H.S. Sabatier (A. Ch. [5] 22, 5) obtained KHS as a yellow, amorphous solid. Prepared in the dry way, KHS appears reddish-black when molten. and white when cold; it crystallises in prisms; is very deliquescent, and reacts strongly alkaline; easily sol. in alcohol. Thomsen (Th. 3, 235) gives [K,S,H,Aq] = 65,140. KHSAq gives off H,S at 70°, according to Drechsel (J. pr. [2] 4, 20). When a current of an ixert gas is passed through KHSAq, H₂S is given off, and K₂SAq remains (Gernez, C. R. 64, 606). Electrolysis produces H and KOH at the negative pole, and H.B at the positive (Bunge, B. 3, 911). KIISAq dissolves S with evolution of H2S; it ppts. MnS, or PbS, from a neutral solution of a Mn or Pb salt, at the same time giving off H2S. These reactions distinguish KHSAq from K2SAq; the · latter does not give off H.S while dissolving S or ppg. MnS or PbS. KHSAq dissolves several sulphides of the less positive metals, e.g. Sb, As, So, forming K thiosalts.

Potassium, hydroxide of, KOH (Caustic potash. Potassium, or potassic, hydrate). S.G. 21 (Dalton); 2044 (Filhol, A. Ch. [3] 21, 415). H.F. [K,O,H] = 103,170; [K,O,H,Aq] = 116,460 (Th. 8, 235).

Konnation.—1. By the reaction between K and H₂O, or K₂O and H₂O, followed by evaporation.—2. By boiling K₂CO₂Aq with CaO.—8. By adding powdered K₂SO₄ to warm conc. BaOAq, evaporating, filtering, and again evaporating (Schubert, J. pr. 26, 117).—4. By heating KNO, with 2-8 parts thin copper turnings, to redness, in an iron, or copper, crucible, extracting with water when cold, filtering from CuO and Ou₂O₄ and evaporating (Wöhler, A. 87, 373).—5. By heating I part KNO₃ with 1 part Fe₂O₃, in a closed crucible of Cu, H being passed in; treating with water, and drawing off the clear liquid, and evaporating it (Schulze, Z. 1861. 109). Evaporation of KOHAq should be performed in vessels of polished iron, or, better, of silver.

Preparation.—1. A solution of pure K_CO₂ in 10-12 parts water is boiled, in a dish of silver or polished iron, with milk of lime, added little by little, till a portion of the clear supernatant liquid gives no effervescence with an acid; rather more than half as much CaO is required as the weight of K_CO₂ taken; large excess of CaO should be avoided; water should be added as the boiling proceeds, because if the quantity of water is less than c. 10 times the quantity of K_CO₂ used the KOHAq begins to decompose the CaCO₂ formed, and the change of K_CO₂ to KOH stops (Liebig, A. 1, 124). When the change is completed, the vessel is closed, and, after a few hours, the clear liquid is drawn off by a syphon; the liquid is then rapidly evaporated in an iron vessel, allowed to stand for an hour or two, the vessel being closed, syphoned off from anypp, that has formed.

evaporated in a silver dish till the oily liquid thus produced begins to volatilise in white clouds, and cooled in an exsiccator. Impure KOH may be freed from all impurities, except KCl and traces of K₂CO₂ and KC₂H₁O₂, by dissolving in absolute alcohol, allowing to settle, draining off, and evaporating, at first on a water-bath, in a silver dish; the resinous matter which is produced is removed from the warm evaporated semi-solid mass, by a silver spatula, and the KOH is then poured out on to a plate of polished iron, or, better, of silver.

Graeger (J. pr. 96, 188) recommends to heat the K₂CO₂Aq used with Ag₂CO₃, to filter from AgCl and excess of Ag₂CO₃, to boil, in a silver dish, with pure CaO made by strongly heating pure CaCO₃, to filter the solution of KOH through pounded marble which has been washed with water till free from very fine particles, and to evaporate in a silver dish.—2. Water and benzene are placed in a silver dish, and small pieces of K, cut from the inside of a lump, are thrown in one by one; the K remains near the surface of separation of the two liquids, and reacts fairly slowly with the water. The benzene is removed by warming, and the aqueous solution of KOH is then evaporated to dryness.

Properties .- After fusion, KOH is a white. hard, brittle solid, often showing a fibrous texture. Melts below red heat, and volatilises at full redness in white pungent vapour. Very deliquescent; sol. water with production of much heat, [KOH,Aq] = 13,290 (Th. 3, 235). Easily sol. alcohol. Skey (C. N. 36, 48) says KOH is very sl. sol. ether. Absorbs CO, rapidly from the air, forming KHCO₃. KOH has a slight, but nauseous, odour, a strongly acrid taste, and acts as a powerful cautery towards both animal and vegetable matter. KOHAq should be kept in glass vessels free from Pb, as it corrodes lead-glass; it attacks vessels of glass or porcelain when heated in them. To keep KOHAq free from carbonate, it is advisable to store it in bottles fitted with corks carrying a syphon-tube, and a rather wide tube filled with a mixture c. equal parts CaO and Na2SO4, well rubbed together, dried over a flame, and passed through a sieve to remove fine powder; the air which enters through this mirture is quite free from

KOHAq is strongly alkaline; the affinity of KOH in solution is large, about equal to that of NaOH and LiOH, and about 50 times greater than NH₃Aq (Ostwald). KOH saponifies ethereal salts, and ppts. most of the heavier metals as oxides or hydroxides from solutions of their

The table on next page, given by Lunge, shows the composition of KOHAq of different S.G.

Expansion occurs when conc. KOHAq is diluted; Frankenheim (J. 1847-8. 69) gives $V=1+\cdot 000415t+\cdot 000000577t^2$ as representing the volume of KOHAq S.G. 1-2738 at 0°, between 18° and 100°.

Reactions.—1. According to Deville (C. R. 45, 857), KOH is decomposed to K. Q. and H. by heating to white heat.—2. Strongly heated with non-volatile acidic anhydrides, water and potassium, laits are formed,—8. Heated with potassium, K.O and H. are formed; heated with sodium under a liquid free from Q, an alloy of K and Na

	_						
8.G. KOHAq	Baumé	Twadde	100 pts. by weight contain			l cub. metre contains Kilos	
, m			K,0	коп	K,0	коп	
1.007	1	1.4	0.7	0.9	7	9	
1.014	2	2.8	1.4	1.7			
1.022	3	4.4	2.2	2.6			
1.029	4	5.8	2.9	3.5	30	36	
1.037	5	7.4	3.8	4.5	39	46	
1.045	6	9.0	4.7	5.6		58	
1.052	7	10.4	5.4	6.4	57	67	
1.060	8	12.0	6.2	7.4	66	78	
1.067	9	13.4	6.9	8.2		88	
1.075	10	15.0	7.7	9.2	83	99	
1.083	11	16.6	8.5	10.1	29	109	
1·091 1·100	12	18.2	9.2	10.9	100	119	
1.108	14	20·0 21·6	10.1	12.0		132	
1.116	15	23.2	10.8	12.9	119	143	
1.125	16	25.0	12.4	13·8 14·8	129	153	
1.134	17	26.8	13.2	15.7	140 150	167 178	
1.142	18	28.4	13.9	16.5	159	188	
1.152	19	30.4	118	17.6	170	203	
1.162	20	32.4	15.6	18.6	181	216	
1.171	21	34.2	16.4	19.5	193	228	
1.180	22	36.0	17.2	20.5	203	212	
1.190	23	38.0	18.0	21.4	211	255	
1.200	24	40.0	18.8	22.4	226	269	
1.210	25	42.0	19.6	23.3	237	232	
1.220	26	44.0	20.3	21.2	218	295	
1.231	27	46.2	21.1	25.1	260	309	
1.241	28	48.2	21.9	26.1	272	324	
1.252	29	50.4	22.7	27.0	284	338	
1.263	30	52.6	23.5	28.0	237	353	
1.274	31	54.8	24.2	28.9	308	368	
1.285	32	57.0	25.0	29.8	321	385	
1.297	33	59.4	25.8	30.7	335	398	
1·308 1·320	31	61.6	26.7	41.8	3 F)	416	
1.332	36	64.0	27.5	32.7	363	432	
1.345	37	66.4	28·3 29·3	33.7	377	449 469	
1.357	38	71.4	30.2	35.9	410	487	
1.370	39	74.0	31.0	36.9	425	506	
1.383	40	76.6	31.8	37.8	440	522	
1.397	41	79.4	32.7	38.9	457	543	
1.410	42	82.0	33.5	39.9	472	563	
1.424	43	84.8	31.4	40.9	490	582	
1.438	44	87.6	35.4	42.1	509	605	
1.453	45	90.6	36.5	43.4	530	631	
1.468	46	93.6	37.5	416	549	655	
1.483	47	96.6	38.5	45.8	571	679	
1·498 1·514	48 49	99.6 102.8	39.6	47.1	593	706	
1.530	50	102.8	40.6	48.3	615	731	
1.540	51	100.0	42.5	49·4 50·6	635 655	756 779	
1.563	52	112.6	43.6	51.9	681	811	
1.580	53	116.0	44.7	53.2	706	810	
1.597	54	119.4	45.8	54.5	731	870	
1.615	55	123.0	47.0	55.9	759	905	
1.634	56	126.8	48.3	57.5	789	940	
		1	!				
						1	

Is said to be formed (Williams, Rep. Chim. pure, evaporatir 3,177).—4. Iron decomposes KOH at white heat, and evaporating Fe₂O₂, H, and K.—5. Molten KOH acts formed by generally as an oxidiser: e.g. Fe, As, Sb, Pt, &c. is decompored form ferrate, arsenate, antimonate, and platinate of K; Or,O₂ forms K,OrO,, &c. Salts are generally decomposed by molten KOH, giving 121, 225).

K salts, and setting free the bases.—6. KOHAq neutralises acids, forming salts.—7. KOHAq decomposes most metallic salts in solution, ppg. oxides or hydroxides of the metals.—8. According to Schöne (A. 193, 241), addition of hydrogen peroxide to KOHAq produces K₂O₄ (v. Potassium tetroxide, p. 305).

Combinations.—1. With carbon dioxide, to form KHCO₂.—2. With water, to form hydrates.

TETROXIDE, p. 305).

Combinations.—1. With carbon dioxide, to form KHCO,—2. With water, to form hydrates. Pickering (C. J. 63, 890) obtained KOH.H.O freezing at 143°, KOH.2H.O freezing at 35.5°, and KOH.4H.O freezing —32.7° (cf. Walter, P. 39, 192; Schöne, P. 131, 147). P. (l.c.) gives full data for freezing points of KOHAq. Göttig (B. 20, 1094) described two hydrates, 2KOH.9H.O and 2KOH.5H.O, obtained from an alcoholic solution of KOH containing some water; but in a later paper (B. 20, 1907) G. says that these hydrates contained alcohol besides water.

3. With methyl alcohol, to form 3KOH.5MeOH (Göttig, B. 20, 1832). 4. With ethylic alcohol, to form KOH.2EtOH (Engel, C. R. 103, 155); decomposed by heating to EtOK, EtOH, and 11.O.

Patassium, iddides of Two icidias are

Potassium, iodides of. Two iodides are known, KI and KI.

Potassium ionne, Kl. Mol. w. 165-57. Melts at 634° (Carnelley, C. J. 33, 279). S.G. 3-659 (Playfair a. Joule, C. S. Mon. 2, 401); 3-077 to 3-081 (Schröder, P. 106, 226); fused 2-497 (Quincke, P. 138, 141); v. also Spring (B. 16, 2724). V.D. 91-5 (Dewar a. Scott, Pr. 29, 206); 84-6 at above 1300°, in N (Mensching a. Meyer, Z. P. C. 1, 157). S.H. (20° to 99°) -08191 (Regnault, A. Ch. [3] J. 129). Vol. at 40° evol. at 0° (1 + 20012796) (Fizeau, C. R. 64, 314). S. 132-1 at 5°, 136-1 at 10°, 140-2 at 15°, 144-2 at 20°, 152-3 at 39°, 169 at 40°, 168 at 50°, 176 at 60°, 184 at 70°, 193 at 80°, 201 at 90°, 209 at 100°, 218 at 110° (Mulder, Scheikund. Verhandel, Rotterdam, 1864.162). Coppet (A. Ch. [5] 30, 411) gives S. at t° = 126-23 + 8088t, where t varies from -5°9° to 120°. S. in aqueous alcohol is given in following table. (Gerardin, A. Ch. [4] 5, 139); the values hold for 0° to 18°;

S.G. alcohol	S.	S.O. alcohol	8.
·9904	130.5	9528 •	76.9
9851	119.4	-9390	66.4
•9726	100.1	.9088	48.2
•9665	89.9	·8464	11.4
		-8322	6.2

H.F. [K,I] = 80,130; $[K,I,\Lambda q] = 75,020$ (Th. 3, 235).

Formation.—1. By the direct union of K and I.—2. By neutralising HIAq by K₂CO₃, and evaporating.—3. I is added to water and iron fillings till the iron is almost wholly dissolved, the solution is filtered, and K₂CO₃ added so long as FeCO₃ ppts.; the liquid is filtered (if alkaline it is neutralised by Hi Aq) and evaporated, any FeO₃ which separates being filtered off (Baup, J. Ph. 9, 37, 122).—4. By adding I to KOHAq, evaporating, heating with C, dissolving, filtering, and evaporating (v. Preparation).—5. Bal, Aq is formed by the action of I and water on BaS, and is decomposed by K,SO₄; BaSO₄ is filtered off, and the liquid is evaporated. Liebig (A. 121, 222) used Cal₂ in place of Bal₄ (cf. Pettenkoler, A. 121, 225).

Preparation. -- Moderately, but not too, conc. KOHAq, quite free from K,CO,, is prepared from K.CO.Aq and CaO (v. Potassium Hydroxide, Preparation, p. 802); I is added, little by little, to the slightly warm liquid till a slight yellow colour is produced; very finely powdered charcoal is now added, equal to c. $\frac{1}{10}$ of the weight of I used, the liquid is evaporated quite to dryness, the residue is powdered, and heated, in a closed crucible, to dull redness for some time $(6KOHAq + 6I = 5KIAq + KIO_3Aq + 3H_2O)$; $KIO_s + 3C = KI + 3CO$). The contents of the crucible, when cold, are extracted with water, the liquid is filtered, neutralised by HIAq if alkaline, and crystallised. Morse a. Burton (Am. 10, 321) recommend to remove traces of KIO, by boiling for some time with Zn amalgam and water, filtering, and crystallising; neither Zn nor Hg is found in the filtrate. The Zn amalgam is made by agitating zinc-dust with Hg in presence of tartaric acid solution, and washing with water.

Properties .- White cubes; non-deliquescent. Has a sharp taste. Solution in water is attended with fall of temperature; 140 pts. in 100 pts. water at 10.8° produce a fall to -11.7° (Rüdorff,

P. 136, 276).

Reactions .- 1. Unchanged in dry air, but decomposed in ordinary air when exposed to sunlight (v. Downes a. Blunt, Pr. 29, 319; Loew. Fr. 1870. 251). Air containing ozone also decomposes KI (Houzeau, J. 1858, 60), -2, Heated in air to 230°, some KIOa is formed. -3. Heated in steam, I is evolved (Petterson, Fr. 1870. 362) and HIAq formed (Schindler, Mag. Pharm. 31, 33) .- 4. Decomposed, with separation of I, and formation of KOH, by heating with lead dioxide, manganese dioxide, arsenic oxide, antimonic oxide, chromium trioxide, hydrogen peroxide, &o. (v. Weltzien, A. 138, 134).—5. Chlorine decomposes hot KI to KCl and I. KIAq with ClAq gives KClAq, and I; with excess of Cl, ICl, is formed and remains in solution, or combines with the KCl and separates as KCl.ICl₃, according to the quantity of water present. Bromine acts similarly to Cl.—6. Nitrous acid solution sets I free; KNO, and dil. HClAq act in the same way (v. Price, C. J. 4, 155) .- 7. Conc. sulphuric acid, or nitric acid, decomposes KI when heated with it, giving sulphate or nitrate of K, and I; with H.SO, SO, and H.S are also formed. Addition of cone. H.SO, to KIAq, or evaporation with HNO, Aq, sets I free. If KIAq contains KIO, a few drops of a dilute acid suffice to give free I (5H1Aq + HIO, Aq = 3I2 + 3H.O). Aqua regia sets I free from KIAq (for the delicacy of this reaction v. Harting, J. pr. 22, 46).—8. Heated with sulphuric anhydride, K,SO,, SO2, and I are formed (H. Rose, 38, 121).—9. Manganese dioxide and sulphuric acid produce I, MnSO,, and K₂SO, when heated with KI.—10. KI fused with potassium-hydrogen sulphate gives K,SO, and I.—11. Fusion with potassium chlorate produces KIO,—12. Heating with barium mitrate forms KIO, and BaO, (Henry, J. Ph. 18, 845) .- 13. By heating with ammonium chloride, I, AmI, and KCl are formed.-14. Conc. potassium ferricyanide solution gives I and K.FeCy, Aq; on dilution the action is reversed (Mohr, A. 105, 57).—15. Heated with potassium borate, KIO, and a polyborate (? probably K.B.O. are formed (Schiff, A. 228, 72).

Combinations .- 1. With most iodiles of less positive metals (v. various metallic iodides). Several of the compounds produced are best regarded as K salts of metal-containing acids (v. Remsen, Am. 11, No. 5).—2. With arsenious oxide to form KI.As.O. (Schiff, A. 228, 72).—3. With potassium ferricyanide, to form a very unstable compound, KI.K, FeCy, (Preuss, A. 29, 323; Mohr, A. 105, 57; Blomstrand, J. pr. [2] 3, 207; Kern, C. N. 33, 184).

Potassium trit-iodide KI, Dark-blue, lustrous needles; almost black by reflected light; melts at 45°; S.G. 3 498 at c. 15°; by saturating KIAq with I, and evaporating over H₂SO₄ (Johnson, C. J. 31, 249). Very deliquescent; in a little water some I is deposited; sol. alcohol, in a very small quantity water, and in saturated solution of I in KIAq. Agitation with CS, of conc. KIAq saturated with I abstracts the dissolved I (Baudrimont, C. R. 51, 827). Jörgensen (J. pr., [2] 2, 317) found, however, that CS₂ did not remove the I from an alcoholic solution of KI containing excess of I in ratio KI:2I, and that alcoholic KI completely decolourised solutions of I in CS...

Potassium di-fodide ?KI. A solution of 3 pts. I in 4 pts. KI in water is said by Guyard (Bl. [2] 31, 297) to contain an unstable compound of this composition; with Pb(NO₃) Aq or Pb(C2H,O2) Aq, this solution gives an almost

black pp., said by G. to be PbI,

Potassium, iodobromide of. The compound KBr.IBr may be called iodobromide of potassium: v. Potassium bromide, Combinations, p. 300.

Potassium, iodochlorides of. The compounds KCl.ICl, and KCl.ICl may be called iodochlorides of potassium; v. Potassium chloride, Combinations Nos. 3 and 4, p. 301.

Potassium, iridicyanide of; v. vol. ii. p.

Potassium mangani- and mangano-cyanide of; v. vol. ii. p. 342.

Potassium, nitride of, K.N. Formed by heating to redness KNH₂ (v. Potassium amide, p. 209) in absence of O. A dark-grey, almost black, solid. Sublimes partially at white heat. Takes fire in air, with evolution of N; reacts with water to give KOHAq and NH. K, N is a conductor of electricity. Combines with S and P (Gay-Lussac a. Thénard, A. Ch. 65, 325).

Potassium, nitroprusside of; v. vol. ii. p.

Potassium, osmocyanide of; v. vol. ii. p.

Potassium, oxides of. Two oxides have been certainly isolated, K2O and K2O4; there are indications of the existence of others.

POTASSIUM OXIDE K₂O (Potassium monoxide). A mixture of K₂O and K₂O₁ is formed by burning K in air; when K is burnt in a stream of dry O only K₂O, is produced, but on strongly heating this product O is given off, and K.O remains (Davy, T. 1808 [1] 5). K.O is also formed by heating KOH and K in the ratio KOH: K; according to Beketoff (Bl. [2] 87, 491), K and KOH do not react. B. says that K₂O may be prepared by heating a mixture of K₂O, and K in a silver dish. To prepare pure K₂O Kühnemann (C. C. 1864. 491) recommends to lead air, freed from CO, over K heated just to fusion; the K spreads out into a thin layer

lustrous solid; S.G. 2.656 (Karsten, S. 65, 894); melts at full red-heat, and volatilises at a very high temperature. Thomsen (Th. 8, 235) gives [K', 0, Aq] = 165,460. K.O reacts with water to form KOHAq, with production of much heat. Von Schaffgotsch (A. 43, 17) says that K.O.Fe.O, is obtained, but not pure, by heating Fe,O, with K,CO,.

POTASSIUM TETROXIDE K2O4 (Potassium peroxide). The formation of this compound by heating K in dry air or O was observed by Gay-Lussac a. Thénard (A. Ch. 65, 325). The preparation and properties of the compound were examined by Vernon Harcourt (C. J. 14, 267). Prepared by heating K till it melts, in a hard glass flask filled with N, then sending in a slow stream of dry air, and continuing to heat in the air-stream until the metal is completely changed to a yellowish amorphous solid, and heating this for some time in dry O. It is also formed by throwing small pieces of K into molten KNO, (Bolton, C. N. 52, 289). A mixture of K.O. with KOH.H.O is said to be formed by mixing equivalents of KOH and H.O. in Aq, and evaporating in vacuo (Schöne, A. 193, 241). K.O. is an amorphous powder, having the colour of PbCrO. It begins to soften at 280°, and melts at red heat to a black liquid, which crystallises in leaflets on cooling. At white heat gives off O and leaves K.O. Deliquesces in moist air, giving off O. In water forms KOHAq and H.O.Aq, and evolves O. Heated in H produces KOH and H₂O. K₂O, oxidises P, S, C, &c., and many metals to their highest oxides. Reacts with CO, when heated, giving K₂CO₃ and O. No action with N₂O; with NO forms KNO₂ and KNO, and gives off N oxides.

Oxides of Potassium other than K.O and K2O4. Harcourt (l.c.) asserted the existence of K₂O₂, obtained by exidation of K. Lupton (C. J. 1876, [2] 565) thought that the exides K₂O₃, K₄O₃, and K₀O, are formed by the action of air on K at c. 65°; these oxides may be regarded, according to L., as 3K2O.K2O2, K2O.K2O2, and 2K2O.K2O2 respectively. The substance described as a suboxide, K,O, is said by L. to be a mixture of K and K_2O . Schöne (A. 193, 241) obtained $K_2H_1O_4$, probably $K_2O_2:2\Pi_2O_2$, by evaporating, in vacuo, at -10° , a mixture of 1 equiv. KOH and 2 equivs. H.O. in Aq.

Potassium, phosphide of. K and P combine when heated under rock-oil, or in N, forming a dark-yellow solid (Magnus, P. 17, 517; Vigier, A. 122, 831). A compound, or compounds, of K and P seems also to be formed when K is heated in PH, and also when K is heated in P in a stream of H (H. Rose, P. 12, 547). The compound prepared by Rose was a crystalline, red-dish, lustrous solid; decomposed by water, giving KH₂PO₂Aq and PH₃, and when heated in air, to K phosphate. burning,

Potassium, platinocyanide of, and allied salts; v. vol. ii. pp. 844-5.

Potassium, salts of. Compounds formed by replacing H of acids by K. The chief salts of K, besides the halides and sulphides, are carbonates, chlorate and perchlorate, chromate and derivatives, iodate and periodates, nitrate and nitrite, phosphates and derivatives, silicates, Vol. IV, sulphates and derivatives, sulphite, thiosulphate (v. Carbonates, Phosphates, &c.).

Potassium, selenides of. Berzelius (Lehr-buch, 5th ed. 2, 222) investigated the conditions of combination of K and Se, without isolating and analysing any definite compounds. Se and K combine when melted together: a steel-grey solid sublimes, which dissolves in water with formation of a red liquid that decomposes in air with separation of Se, and gives off H.Se with acids. . Compounds of Se and K are also formed by reducing K.SeO, or K.SeO, by C or H at red heat (Wöhler a. Dean, A. 97, 5; Rathke, A. 152, 211). Mixtures of selenate and selenides of K are formed by fusing KOH or K, CO, with Se. Boiling KOHAq dissolves So, forming a brown liquid, from which a brown powder separates on evaporation, and which gives Se when heated with acids, or when diluted and allowed to stand in air.

Fabre (C. R. 102, 613) obtained K. Se. xH. O. x = 9, 14, and 19, by passing a rapid current of H2Se into KOHAq of different concentrations these hydrates of potassium monoselenide are all very easily decomposed. Fabre (C. R. 102, 703) gives the following thermal data: [K*,Se] = 98,340 from solid elements; [2KOHAq,H_SeAq] = 7,520; $[2KOHAq, H_2Se] = 16,920$; [K'Se, Aq] = 8,540.

Potassium, selenocyanide of, v. vol. ii. p. 848. Potassium, selenostannate of, K.SuSe, Saq. Yellow, unstable crystals; by saturating K. SeAq with SnSe, and evaporating in vacuo (Ditte. C. R. 95, 641).

Potassium, selenothiostannate of.

K.SnSe,S 3aq. Yellow, octahedral crystals; by boiling K,SAq with Sn and Sc, and evaporating in vacuo. Sol. water, with red colour. Both solid and solution in water very readily undergo decomposition, with separation of Se (Ditte, l.c.).

Potassium, silicide of. By reducing S.O. by K, Berzelius obtained a brown solid, which reacted with water to give H, KOHAq, and SiO,

(Lehrbuch, 5th ed. 2, 84).

Potassium, silicofluoride of, K,SiF. Prepared by adding H2SiF4Aq to a fairly conc. solution of a K salt, washing, and drying. Small tesseral white crystals. Preis (Listy Chem. 13, 150; abstract in C. J. 58, 694) found hexagonal, and also regular, crystals of this salt, along with CaSO,, in a basin wherein phosphoric acid had been prepared from phosphorite. K.SiF. is isodimorphous with the ammonium salt. 2.665 at 17.5° (Stolba, J. pr. 97, 503). Easily sol. hot water, very sl. sol. cold water. Melts at low red heat, giving off SiF, and leaving KF (v. Bothe, Hofman's Ber. über die Entwick. der Chem. Industric, 1, 318). Decomposed by conc. H.SO., giving off SiF, and HF. Decomposed by boiling (not cold) solutions of alkali hydroxides or carbonates, with separation of gelatinous silicic acid and formation of KF.

Potassium, siliconitride of. The white, infusible solid, obtained by heating SiO₂ with KCN, is probably a compound of K, Si, and N

(Balmain, P. M. October 1842).

Potassium, sulphides of. K and S combine when heated together, the K burning brilliantly. Five compounds of K and S are known: K,S, K₂S₂, K₂S₃, K₄S₄, and K₂S₅. They are all sol. water, the polysulphides also in alcohol. K₂SAq is colourless; solutions of the others are coloured

yellowish brown, the colour being deeper the greater the proportion of S. Solutions are decomposed by acids; K,SAq with evolution of H,S, the other solutions also with ppn. of S. Solusale other solutions also with plin. of S. Solutions decompose in air; K.SAq to K.S.Q.Aq and KOHAq, K.S.Aq to K.S.Q.Aq, and the others to K.S.Q.Aq with separation of S. Solutions of the polysulphides react with K2SO, Aq to form K2SAq and K,S,O,Aq; these solutions are reduced to K,SAq by shaking with Hg. With EtI or EtBr they form Et, S,, which dissolves the S set free; these solutions dialyse unchanged (Spring a. Demarteau, Bl. [3] 1, 311).

POTASSIUM MONOSULPHIDE K2S. Formed by reducing dry K2SO4; by heating in H (Berzelius, P. 6, 438); by heating with C (Berthier, A. Ch. 22, 233; Bauer, J. pr. 75, 246; Wittstock, P. 55, 536). Not obtained free from polysulphides by these methods; if vessels of glass or porcelain are used the product contains SiO2, as K.S acts on silicates. The product of the foregoing reactions is a brown, crystalline, deliquescent solid; sol. in water, with production of much heat and formation of KSHAq and KOHAq; Thomsen (Th. 3, 235) gives [K*,S,Aq] = 113,300.
Sabatier (A. Ch. [5] 22, 5) says that K.S has never been obtained pure. An aqueous solution of K2S is prepared by saturating KOHAq with H2S, and adding an equal quantity of the same KOHAq. By evaporating this solution in vacuo at a low temperature, the pentahydrate K,S.5H,O is obtained in orthorhombic crystals, which lose 3H,O by heating to 150°, out of air (Schöne, P. 181, 380; cf. Sabatier, l.c.). K2SAq is colourless out of contact with air; it is very alkaline and caustic; in air it becomes yellow, H₂S is given off, and K₂CO₂Aq and K₂S₂O₃Aq are formed. K₂SAq dissolves S, forming polysulphides: it

dissolves Fe or Fe₂O₃, forming a green liquid.

Porassium disclination K₂S₂. Formed by allowing an alcoholic solution of K₂S to stand in air till the surface is covered with a film of K2S2O2, then pouring off, and evaporating in racuo (Berzelius, l.c.). Also by heating 2 equiva-lents KHSO, with 7 or more equivalents C (Geiger). Berzelius obtained K₂S₂ by heating 4 equivalents K2CO3 with rather less than 7 equivalents S. A yellowish red, deliquescent solid; K₂S₂Aq is yellow; in air it oxidises to K₂S₂O₂Aq without separation of S; acids give off H₂S and cause ppn. of S.

POTASSIUM TRISULPHIDE K,S. Formed by Potassium Trisurphide A.S., Formed by passing CS, over K.CO, heated to redness (Berzelius, Lc.; cf. Schöne, Lc.). Also by heating 100 parts K.CO, with 58-22 parts S to dull redness, till CO, ceases to be given off; the product contains some K.SO,. Also, with some S, by passing H.S over strongly-heated K.SO. By heating K.S. to over 800°. A yellowish-brown solid, black when molten; not decomposed at 900°, gives off S at white heat (B.). Easily sol. water and alcohol; K,S,Aq in air gives K,S,O,Aq with separation of S; decomposed by acids, S separating and H.S being evolved.

POTASSIUM TETRASULPHIDE K₂S₄. Formed by passing CS₂ over strongly-heated K₂SO₄ so long as CO, is produced. Also by melting K.CO, with 1 to 2 parts S, heating till excess of S is removed, and then reducing K₂SO, formed by heating in H₂S. A red-brown, crystalline solid (B., Lc.; S., Lc.). Decomposed at 600°-900° to K₂S₂ and S.

The dihydrate K.S., 2H.O is obtained by bound K,SAq with the proper quantity of S, and evapo rating in vacuo (S., l.c.). Sabatier (A. Ch. [5] 22, 53) obtained the octahydrate, K.S., SH.O. by adding 90 p.c. alcohol to K,S,Aq, separating the brown oily liquid, and letting it crystallise.

POTASSIUM PENTASULPHIDE K.S. Formed by heating any of the lower sulphides with S until the excess is removed; Schöne (L.c.) says temperature should not exceed 600° (p. B., Lc.). A solution of K.S., containing also K.S.O., is formed by heating K.CO.Aq with S (Fordos a. Gélis, C. R. 23, 211); or by digesting a solution of a lower sulphide with S (B., l.c.). A red, fusible solid; decomposed by heating in steam, giving K,SO, and H.S (Drechsel, J. pr. [2] 4, 20). Very sol. water, also in alcohol; K,SA, 4 slowly decomposes in air, giving K,SO,AA, K,CO,AA, and S; acids evolve H,S and separate S.

Liver of sulphur. This name is given to the brown solid obtained by heating S with K₂CO₃ in a closed vessel; it contains various sulphides of K, along with K₂SO₄, and generally some K, CO,.

Potassium, sulphydrate of: v. Potassium нудковицениры, р. 302.

Potassium, sulphocyanide of; v. vol. ii. pp.

Potassium, telluride of. Probably K.Te. By heating together K and To in H; also by heating a mixture of 100 pts. H,TeO₃, 20 pts. KOH, and 10 pts. C. A brittle, crystalline, copper-coloured solid. Easily sol. water; exposed to air Te separates from the solution. HClAq evolves H₂Te (Davy; v. also Berzelius, Lehrbuch (5th ed.) 2, 247).

Potassium, tellurofluoride of, KF.TeF.; v. POTASSIUM FLUORIDE, p. 301.

Potassium, thio-arsenates and thio-arsenites

of; v. vol. i. pp. 317, 316.

Potassium, thiocarbonate of; v. vol. i. p. M. M. P. M.

PRASEODYMIUM. The constituent of didymium which yields green-coloured salts; v. DIDYMIUM, vol. ii. p. 383.

PREHNITENE v. c-DURENE.

PREHNITIC ACID C, H,O, i.e. C_aH₂(CO₂H)₄[1:2:8:4]. Mol. w. 254. [237°-250°]. Formed by heating either of the tetrahydrides of pyromellitic acid with H₂SO₄ (Baeyer, A. 166, 325), and by the oxidation of c-durene and of c-tetra-ethyl-benzene (Töhl, B. 21, 907; Galle, B. 16, 1746; Jacobsen, B. 17, 2518). Crystallises from water in large prisms (containing 2aq) resembling the mineral prehnite. Converted by fusion into an anhydride C₁₀H₄O, [239°]. May be reduced to a viscid hydride. - KH, A'raq. -BaH,A,' 3aq. -BaH,A' aq: needles. -Pb,A': small needles, insol. water.

Methyl ether Me, A'v. [104°-108°]. PREHNITOL v. c-DurenoL.

PREHNOMALIC ACID C, H,O, i.e.

C.H.,(OH)(CO.H)₄. Oxy-prehnitic acid dihydride. [210°]. A product of the action of H.SO, on the tetrahydrides of mellitic acid (Baeyer, A. 166, 325; B. 4, 275). Needles, readily converted by heat into an anhydride CaH, O1, [210°]. heating with H₂SO₂, or by treatment with B_r, it is converted into prehnitic acid.—Ag, A^r.

PRIMULA CAMPHOR O₁₁H₁₇O₂. [49°].

(above 200°). Contained in the root of Primula

veris (Mutschler, A. 185, 222). Six-sided plates, v. sl. sol. water, v. sol. alcohol and ether. Smells like anise. FeCl, colours its aqueous solution violet. Fields salicylic acid on oxidation.

PRIMULINE BASE $C_{:s}H_{1s}N_{1}S_{1}$ i.e. $-C_{s}H_{1s}N_{s}S_{2}$ O.O. $H_{s}N_{s}S_{s}$ O.O. $H_{s}N_{s}S_{s}$

Prepared by heating p-toluidine (2 mols.) with sulphur (4 or 5 atoms), H.S being evolved (Green, C. J. 55, 234). Yellowish powder, nearly insol. all solvents. Not decomposed at 400°. Its salts are decomposed by water. The Na salt of its sulphonic acid (primuline), is taken up by unmordanted cotton. KOH at 260° yields amidotolyl-mercaptan and p-amido-benzoic acid (Gattermann, B. 22, 425, 1066).

Dehydrothiotoluidine C1, H12SN2 i.e.

 $C_eH_aMe < S C.C_eH_4.NH_2.$ [191°]. (434° at 766 mm.) (Pfitzinger a. Gattermann, B. 22, 1066). An intermediate body in the preparation of primuline. Formed, together with primuline base, by heating p-toluidine with S (Dahl & Co., G. P. 35790; Green, C. J. 55, 230). Got also by the action of HI and P upon primuline (Jacobsen, B. 22, 330). Yellowish iridescent needles (from isoamyl alcohol), v. sol. HOAc, sl. sol. hot alcohol, v. sl. sol. benzene, almost insol. boiling water. Its alcoholic solutions have violet-blue fluorescence. Ppd. by adding water to its solution in HClAq.

Reactions.—1. Yields p-toluidine on distilla-

tion with zinc-dust. - 2. Yields primuline on heating with S. - 3. Converted by diazotisation in

boiling alcoholic solution into $C_uH_xMe < \frac{N}{S} > CPh$

[123°] .- 4. When diazotised and boiled with water it gives C, H, (OH)N, S [256°], which gives C, H, (OAc)N, S [132°], -5. Furning H, SO, (containing 70 p.c. SO,) forms, below 50°, a sulphonic acid C14H11(SO3H)SN2, which crystallises in yellow needles (containing aq), or orange plates (containing 2aq), sl. sol. hot water, and forms NH, A'aq, sl. sol, hot water, CuA', 2nq, a reddishbrown pp., and AgA', a white pp.—6. MeI yields C, H₁₀(NMe₂)NS [197°] (434°), and C_{1.}H₁₀(NMe,I)NS, a bright-yellow powder, v. sol. water. MeOH and HCl at 150°-200° give O₁₄H₁₀(NMe,Cl)NS, a yellow powder which forms (C₁,H₁₀NS,NMe,Cl),PtCl₄ [234°].

Acetyl derivative C, H, AcN, S. [227°]. White plates or prisms, sl. sol. HOAc.

PROPACONIC ACID v. Lactone of Oxy-BUTYLMALEÏC ACID.

PROPANE C3H8 i.e. CH3.CH2.CH3. Mol. w. 44. (-17°). S. (alcohol) 6. H.F.p. 35,110. H.F.v. 33,870 (Thomsen, Th. 4, 52). Occurs in the gases given off from the petroleum springs of the United States (Ronalds, C. J. 18,54; Lefevre, Z. [2] 5, 185). Formed by the action of HI on propyl iodide, allyl iodide, isopropyl iodide, acetone, and glycerin (Berthelot, Bl. 7, 60; 9, 18, 184). Prepared by heating n-propyl iodide (9.6 pts.) with AlCl. (2.5 pts.) at 140° (Köhnlein, B. 16, 560), or by heating isopropyl iodide with zinc and HClAq (Schorlemmer, A. 150, 209). Gas. On compression with water at a low temperature it yields a hydrate, dissociating at 8.5° (Villard, C. R. 111, 302).

References, DI-BROMO-, BROMO-10DO-, BROMO-

MITBO-, CHLORO-, CHLORO-IODO-, DI-GHLORO-MITRO-, Dr. 1000, and NITRO- PROPANE.

PROPANE CARBOXYLIC ACID v. BUTTER ACID.

Propane dicarboxylic acid v. GLUTARIC-PYROTARIARIC, and ETHYL-MALONIC ACIDS.

Propane tricarboxylic acid CaH,Os i.e CH,CH(CO,H).CH(CO,H), (Bischoff, B. 18, 2164; 14, 614; 15, 1107; 17, 2783; 22, 8180; A. 214, 53). [146°]. Formed by saponitying the ether with dilute alcoholic potash. Crystalline mass, v. e. sol. water, alcohol, and ether. Splits up when heated alone, or with dilute HClAq, into CO2 and pyrotartaric acid. Bromina forms bromopyrotartaric and bromocrotonic acids.—Ba, A"; bulky pp. $ds.-Ba_aA'''_a$: bulky pp. $Methyl\cdot di\cdot ethyl$ is ther MeEt,A'''. (266°).

S.G. 4 1.078. Formed from methyl a-chloro-

propionate and sodium malonic ether. $Ethyl \ eth \ r \ Et, A'''$. (270·3° cor.). S.G. 2° 1·0698. $\mu_D = 1.4288$ at 20°. Formed from sodium malonic other and a-bromo-propionic ether. Oil, miscible with alsohol and ether. NaOEt yields C,H,Na(CO,Na)(CO,Et).

Propane tricarboxylic acid

CH, C(CO,H), CH, CO,H.

Methyl ether Me₂A'''. Oil (Barthe). Ethyl ether Et, A'''. (273.5° oor.). S.G. Ψ 1 077. $\mu_D = 1.4311$ at 20°. Formed from sodium

methyl-malonic ether and hloro-acetic ether, and also from sodium ethane tricarboxylic ether and MeI or MeCl (Bischoff a. Von Kuhlberg, B. 23, 635). Yields on saponification pyrotartaric and a little succinic acid.

and a little succinic acid.

Methyl ether of the mono-nitrile
CH_xC(CN)(CO_xMe).CH_xCO_xMe. Formed from
metnyl cyanosuccinate, MeOH, and MeI
at 70° (Barthe, Bl. [3] 1, 303; C. R. 108,
297; 112, 1013). Oil. The corresponding
CII_xC(CN)(CO_xEt).CH_xCO_xEt is also an oil (185°
at 35 mu. at 35 mm.).

Propane tricarboxylic acid

CO.H.CH.CH.CH(CO.H)... Ethylether Et.A". (161° at 13 mm.). S.G. 20 1.0808. Formed from sodium malonic ether and \$\beta\$-bromo-propionic ether (Emery, \$B\$. 24, 282). The free acid splits up into CO, and

glutaric acid on boiling with HClAq. Isomeride v. TRICARBALLYLIC ACID. Propane tetracarboxylic acid

CO.H.CH...CH(CO.H).CH(CO.H). Ethylether Et.A. (204° at 18 mm.). S.G. ²⁰ 1·1184. Formed from sodium malonic ether and chloro-succinic ether (Emery, B. 28, 8759).
Oil, v. sol. alcohol and ether. The free acid splits up into CO, and tricarballylic acid.

Propane tetracarboxylic acid (CO,H),CH.CH,CH(CO,H)2. Dicarboxy-glutaric acid. [170°]. An acid formed by the action of sodium amalgam on dicarboxyglutaconic ether C.H.Et.O. in alkaline solution (Conrad a. Guthzeit, A. 222, 257). One of the products of the action of chloro-di-methyl oxide on sod um malonic ether (Kleber, A. 246, 106). Got also by boiling its ether with dilute alcoholic potash (Guthzeit a. Dressel, B. 21, 2234; 22, 1423; A. 256, 174). Crystalline powder (from ether), v. e. sol. water. At 180° it splits up into CO, and glutaric acid [98°].—Ba,A'' 2aq.—Ca,A'' 2aq.—Pb,A'' 2aq.

Ethyl ether Et.A'r. (235° at 80 mm.).

Control (Extraversion Courts)

8.G. 22 1-116. Formed from sodium malonio ether by treatment with CH_cCl₂ or CH_cI₃, and got also by reducing dicarboxy-glutaconic ether with zinc-dust and HOAo (W. H. Perkin, jun., C. J. 59, 993). Oil, with very bitter taste. NaOEt forms a di-sodium derivative, which reacts with EtI forming oily C₁,H₂₈O₈ (c. 248° in sacuo).

Propyl-tri-ethyl ether Et, PrA'. (195°-202° at 15 mm.). Formed from propyl triethyl dicarboxy-glutaconate, zinc-dust, and HOAc.

Colourless oil.

Propane tetracarboxylic acid

CO.H.CH. C(CO.H).r.CH. CO.H. [151°]. Got by saponifying its ether with alcoholic potash. Prisms (from water), v. sol. water, alcohol, and ether. At 170° it splits up into CO. and tricarballylic acid.—K.,HA!" 2½ aq (at 100°).—Zn.A!" 3aq (dried at 100°).—Pb.A!" aq.—Ag.A": include pp. Ethyl ether Et.A!". (295° uncor.). S.G.

Ethyl ether Et.A'. (295° uncor.). S.G. 44 1-102. Formed from malonic ether, alcoholic NaOEt, and chforo-acetic ether, followed by a second dose of NaOEt and chloro-acetic ether (Bischoff, B. 13, 2163; A. 214, 61). Oil.

Ethyl ether of the mono-nitrile CO_Et.CH_.C(CN)(CO_Et).CH_.CO_Et. [41°]. (200°-215° at 10 mm.). Formed from sodium cyano-succinic ether and chloro-acetic ether (Haller a. Barthe C. R. 106, 1413). White crystals, sol. alcohol and ether.

Methyl ether of the mono-nitrile CO₂Me.CH₂C(CN)(CO₂Me).CH₂CO₃Me. [47°]. Prepared in like manner (Barthe, C. R. 111, 344). Prisms, insol. water and alkalis.

Propane pentacarboxylic acid

CH(CO₂H)₂C(CO₂H)₂CH₂CO₂H. [151°]. Got by saponifying its ether. Spherical aggregates (from ether).—K₄A^{*} 4aq.—Ba₂A^{*}₂ 4aq: orystalline pp.

Ethyl ether Et,A. (275°-280° at 188 mm.). S.G. ¹⁵/₁₅ 1·121 (Bischoff, B. 15, 1107; 21, 2118). Formed from sodium-malonic ether and CCl(CO,Et),CH,CO,Et. Formed also from sodium ethane tricarboxylic ether and chloroscetic ether. Oil.

Reference.—OXYPROPANE TRICARBOXYLIC ACID.

PROPANE PHOSPHONIC ACID

C₁H₁.PO(OH)₂. [60°-70°]. Prepared by oxidation of propyl-phosphine with fuming HNO₂ (Hofmann, B. 6, 304). Wax-like mass, sol. water.

PROPANE SULPHONIC ACID

CH₂·CH₂·CO₄·

Propane sulphonic acid (CH₃)₂:CH.SO₃H. (below 100°). Formed by oxidising isopropyl mercaptan with HNO₃. Obtained also from acetone by successive treatment with P₂S₃ and HNO₄ (Claus, B. 5, 660; 8, 533; Spring, Bl. [2] 40, 66). Crystalline. Its salts are v. e. sol. water.

Propane disulphonic acid
CH₄(SO₂H).CH₂,CH₂(SO₂H). Formed by boiling
trimethylene bromide with a saturated solution
of ammonium sulphite (Monari, B. 18, 1345).
Deliquescent needles, v. sol. water and aloohol.—
Na,A'' 4\$q.—BaA'' 2aq: very soluble needles.

Propane disulphonic acid
OH.-CH(SO₃H).CH₂(SO₂H). Formed in like
manner from propylene bromide (M.).—Na₂A"aq.
—BaA": sparingly soluble crystals.

Propane disulphonic acid C₂H₂(SO₂H)₂. Got from butyramide and fuming H₂SO₄ (Buckton a. Hofmann, A. 100, 153), and also by heating butyric acid with ClSO₃H at 140° (Baumstark, A. 140, 83).—BaA".—PbA": crystalline.

Propane trisulphonic acid

CH.(SO₃H).CH(SO₃H).CH₂(SO₃H). Got by boiling s-tri-chloro-propane with aqueous K₂SO₃ (Schäuffelin, 4. 148, 117).—Ba₂A'''₂: crystalline powder, sl. sol. water.

References.—CHLORO- and OXY-PROPANE SUL-

PHONIC ACID.

DIPROPARGYL C.H. i.e.

CH:C.CH., CH., CiCH. Hexmene. (86°). S.G. 12 · 81. H.F.p. - 96,040. H.F.v. - 97,200 (Thomsen, Th.). Formed by distilling diallyl tetrabromide with solid KOH, and boiling the resulting dibromo-diallyl with alcoholic potash (Henry, B. 6,956; 7,21; 14,399; 17,1132). Limpid, highly refractive oil, v. sol. ether. Burns with smoky flame. Combines with explosive violence with bromine, forming C,H,Br, a thick liquid S.G. 12 · 2·464, from which, by further action of Br, crystalline C,H,Br, (14¹) can be obtained. Iodine in KI forms dipropargyl tetraiodide C,H,I, [113°] crystallising from CS, in prisms. Dipropargyl gives with ammoniacal cuprous chloride a yellow pp. Cu,C,H, 2aq, which explodes below 100°. Dipropargyl is very easily polymerised, forming a resin.

PROPARGYL ALCOHOL C₂H₁O i.e.
CH:C.CH₂OH. Mol. w. 56. (115°). V.D. 1:88
(calo. 1:93). S.G. ²⁰ :9715. μ_B = 1:437. R_∞
= 24:01 (Brühl). H.F.p. = 3,500. H.F.v. = 4,370
(Thomsen, Th.). Formed by boiling bromoallyl alcohol with KOHAq (Henry, B. 5, 274,
449, 569; 6, 728; 7, 20, 761). Formed also
from propargylamine oxalate, NaNO_a and HCl
(Paal a. Hempel, B. 24, 3039). Colourless
liquid of peculiar odour, sol. water.

Reactions.—I. Ammoniacal Cu_.Cl₂ ppts. canary-yellow Cu_.(C₂H_.O)₂ which explodes when heated, and is decomposed by dilute acids with reproduction of propargyl alcohol.—2. Ammoniacal AgNO₃ ppts. white AgC₂H_.O,—3. Anhydrous BaO forms Ba(C_.H_.O)_.C₂H_.O, crystallising in small plates.—4. On heating with solid KOH it yields formic acid and acctylene.—5. HBr forms bromo-allyl alcohol.—6. HNO₃ yields CO₂

Acetyl derivative C.H., OAc. (125°). S.G. 9 1.0052. $\mu_{\beta} = 1.427$. $R_{\infty} = 39.71$ (Brühl). Got from the alcohol and AcCl.

and oxalic acid.

Methyl ether C.H.OMe. (62°). S.G. 125°83. H.F.p. -10,910. H.F.v. -12,360 (Thomsen, Th.). Formed by boiling s-tri-bromo-propane with KOH dissolved in MeOH (Liebermann, A. 135, 287) and by boiling the dibromide of methyl allyl oxide with alcoholic potash (Henry). Ammoniacal AgNO, ppts. lemon-yellow C.H.Ag.OMe, whence I in KI forms oily C.H.LOME [127].

Ethyl ether C.H., OEt. (81°-85°). S.G. 2°-8326. μ₈-1·4096. R_∞ = 39·5 (Brühl). This body is formed by the action of alcoholic potash on CH₂Br. CHBr. CHBr. on CH₄·CBr₂·CH₂Br₄

on dichluropropylene, or on ethyl bromo-allyl oxide (Liebermann, A. 135, 278; 158, 230; Henry, B. 5, 274; Baeyer, A. 138, 196). Mobile liquid, with penetrating odour, v. sl. sol. water, miscible with alcohol. Combines with Br, forming C, H, Br, OEt. Boiling very dilute (1 p.c.) H.SO, splits it up into alcohol and propargyl alcohol. Sodium forms C.H.NaOEt. Alcoholic silver nitrate forms crystalline (C₃H₂Ag.OEt)₂AgNO₃ converted by ammonia into amorphous C₃H₂AgOEt, whence I in KI forms crystalline C.H.IOEt and oily C.H.I.OEt. An ammoniacal solution of AgCl added to an alcoholic solution of C,H,OEt ppts. white (C₃H₂AgOEt) AgCl. Ammoniacal Cu₂Cl₂ gives yellow amorphous C₃H₂CuOEt.

Isoamyl ether C₂H₃OC₃H₄. (140°-145°). PROPARGYLAMINE C₂H₃NH₄. Formed by the action of NaOEt on bronno-allyl-amine and on di-bromo-propyl-amine (Paul a. Hermann, B. 22, 3080). The free base has not been isolated. -B'H₂C₂O₄. [143°]. Large tables (from water), al. sol. alcohol. Gives a white pp. with ammoniacal AgNO₃.—B'C₃H₁(NO₃), OH. [189°]. Large red plates or tables.—B'HCl.—B'HBr. [130°-171°].—B'HI. [205°]. White plates, v.

e. sol. water.

PROPARGYL-ISOAMYL-AMINE C.H., N i.c. C3H2NHC5H11. Formed from di-bromo-isoamylamine and NaOEt (Paal a. Hermann, B. 22, 3084). Liquid.—B'H.C.O. aq. [204]. White needles (from water).—B'HBr. [186°]. Pearly plates.

PROPARGYL BROMIDE CH; C.CH.Br. (89°). S.G. M 1-59. Formed from propargyl alcohol and PBr_s (Henry, B. 6, 728). Liquid.

Propargyl tribromide v. Tat-bromo-propyl-

PROPARGYL-ISOBUTYL-AMINE C.H., N i.e. CH;C.CH, NH.CH, Pr. (135"). Formed from di-bromo-propyl-isobutyl-amine and NaOEt (Paal a. Heupel, B. 24, 3045). Liquid, miscible with water.—B'HCl. [148°].—B'H,PtCl., [210°]. Needles and plates, m. sol. cold water.

PROPARGYL CHLORIDE C.H.Cl. S.G. 1 1045. Formed from propargyl alcohol and PCl₂ (Henry, B. 8, 398). Mobile oil. PROPARGYLIC ACID is PROPIOLIC ACID

PROPARGYL IODIDE CH:C.CH,I. (c. 115°). S.G. 2 2 018. Formed from propargyl bromide and NaI in alcohol (Henry, B. 17, 1132). Yellowish liquid. Iodine forms CHI:CI.CH,I. [41°].

PROPARGYL-PROPYL-AMINE C.H., N i.e. C,H,NH.C,H, The salt B'HBr [180°] is got from propyl bromide and propargylamine (Paal s. Hermann, B. 22, 3084)

PROPARGYL SULPHOCYANIDE C.H.SCN. Formed from propargyl bromide and potassium sulphocyanide (Henry, B. 6, 729). Oil, smelling like mustard. Decomposed by heat.

PROPARGYL-DI-THIO-CARBAMIC ACID CH:C.CH, NH.CS, H. [115°]. Formed by boiling propargylamine with CS, and alcohol (Paal a. Heupel, B. 24, 3041). Needles (from dilute alcohol) or plates (from benzene-ligroin).
PROPENYL-o-AMIDO-PHENOL

OXYLIC ETHER C.H. < O > CMe.CH. CO.Et. [108°]. Formed by heating a mixture of o-amidophenol and acetoscetic ether (Hantzsch, B. 16, from the fruit of Cucumis prophetarum, split up

1948). Flat prisms, readily resolved into the parent substances by dilute acids, alkalis, or even boiling water.

PROPENYL-o-AMIDO-PHENYL MERCAP. TAN C.H., NS i.e. C.H. < N > CEt. (252°). Formed by heating o-amido-phenyl mercaptan with propionyl chloride at 160° (Hofmann, B. 13, 21). Heavy oil.—B'2H2PtCla: large prisms.

PROPENYLAMINE CH., CH; CH.NH. Formed by the action of baryta on β-bromo-propylamine (Hirsch, B. 23, 968). Does not propylamine (Hirsch, B. 23, 968). Does not decolourise bromine water.—B',H,I,2BiI,: sixsided plates.

PROPENYL-BENZENE SULPHONIC ACID CH.: CMe.C.H..SO.H. The salts of this acid are formed by heating the dry salts of the acid CMe, (OH). C, H, SO, H (R. Meyer, A. 219, 802).

Amide C, H, SO, NH, [1520].

o-PROPENYL-BENZOIC ACID CH₂:CMc.C₆H₄.CO₂H. [61°]. Formed from dimethyl-phthalide and KCy at 260° (Wislicenus, A. 248, 64). Needles (from water).

p-Propenyl benzoic acid CH₂CMe.C₆H₄.CO.H. [161°]. Formed by heating (CH₂)₂.C(OH).C₆H₄.CO₂H with dilute HCl on a water bath (R. Meyer a. J. Rosicki, B. 11, 1791; A. 219, 270). White satiny plates (from 1 pt. alcohol and 1 pt. water) or slender needles (from water). Sl. sol. hot water, v. e. sol. alcohol and other. Sodium amalgam reduces it to cuminic acid.

Salts. - NH,A'. - BaA', aq. - CuA', 7aq. -AgA': amorphous pp.

Methyl cther. MeA' [53°]. (254° cor.).

V.D. 6.09. Insol. water.

Isopropenyl-benzoic acid C,H,.C,H,.CO,H [255°-260°]. By boiling oxy-propyl-benzoic acid (CH₂)_C(OII).C₂II₂.C₂H with fuming HCl (B. Meyer, B. 12, 1076; A. 219, 281). Minute needles grouped in stars (from alcohol). Insol. water. Does not decolourise bromine, and is not reduced by sodium amalgam, but is converted by HI into cuminic acid. Hence it would appear to be a polymeride of propenyl-benzoic acid, not containing a C:C group.

Salts.—NH, A' aq. Sl. sol. water.—BaA'₂ aq. CaA'₂ 1½aq.—CuA'₂—AgA': pp., insol. water.

Methyl ether MeA'. [83']. Decomposed by heat.

References .- AMIDO., NITRO., and OXY- PRO-

PENYL-BENZOIC ACID. PROPENYL BROMIDE v. BROMO-PROPYLENE. PROPENYL CARBINOL v. BUTENYL ALCOHOL. PROPENYL-TRICARBOXYLIC ACID v. Pro-PANETRICARBOXYLIC ACID

PROPENYL CHLORIDE v. CHLORO-PROPYL-

PROPENYL-PHENOL. Methul derivative v.

PROPENYL-ISOPROPYL BENZENE C, H, i.e. Pr.C.H., CH.CHMe. (230°). S.G. 13. 890. Got by boiling Pr.C.H., CH., CBrMe.CO.H with Na.CO.Aq (Perkin, C. J. 1877, ii. 660). Dibromide C., H., Br. [59°]. PROPENYL-SALICYLIC ACID v. OXY-FRO

PENYL-BENZOIC ACID.

PROPERTONE v. PROTEÏDS.

PROPHETIN CasHasO,. A bitter resin got

by boiling dilute HClAq into glucose and prophetein C. H. O. (Walz, J. 1859, 566).
PROPINENE v. ALLYLENE.

PROPINENE DIPHTHALIDE C, H12O, i.e. O.CO C.H. Formed by -Ç:CMe.CH:Ç-C.H. < CO. ò

heating phthalic anhydride (3 pts.) with pyrotartaric acid (3 pts.) and sodium acctate (1 pt.) at 240°-290° (Roser, B. 17, 2776). Fine yellow needles, not melted at 280°.

PROPIO-GUANAMINE C.H.N. CH,Me.C:N.C(NH) NH. Got by heating guanidine propionate at 230° for an hour (Haaf, J. pr. [2] 43, 78). Granules (from NaOHAq) or dimetric prisms (from water).

PROPIO-HOMO-FERULIC ACID v. DI-OXY-

PHENYL-CROTONIC ACID

PROPIOLIC ACID C.H.O., i.e. CH:C.CO.H. Propargylic acid. [6°]. (c. 144°). Formed by boiling the acid K salt of acetylene dicarboxylic acid with water (Bandrowski, B. 13, 2340). Liquid, solidifying at about 4°. Smells like acetic acid. Turns brown in air. Sol. water, alcohol, and ether. Reduces HgCl₂, AgNO,, and

Reactions. - 1. Ammoniacal AgNO, gives a white crystalline explosive pp.-2. Ammoniacal Cu, Cl, gives a green amorphous explosive pp., turning brown. - 3. Sodium-amalgam reduces it to propionic acid .- 4. Combines with HCl, forming \$-chloro-acrylic acid. HBr and HI act in like manner .- 5. Br forms di-bromo-acrylic acid [85°]. - 6. I forms CHI:CI.CO.H [104°] (Bruck, B. 24, 4120).

Salt .- KA' aq. Transparent prisms, v. sol.

water, deflagrating at 105°.

Ethul ether Eth'. (119°). V.D. 3.47. Liquid, smelling like horse-radish. Oxidised by alkaline K.FeCy, to diacetylene dicarboxylic acid (Baeyer, B. 18, 677, 2269).

Reference. - BROMO- and IODO- PROPIOLIC

PROPIONAMIDE v. Amide of PROPIONIC

PROPIONAMIDINE C.H.N. i.e.

CEt(NH).NH. The hydrochloride is formed by leading HCl into a solution of propionitrile in isobutyl alcohol, and heating the product with alcoholic NH, (Pinner a. Klein, B. 11, 1484; 17, alcohold Nr., (Pinier a. Riell, B. 1, 1494; 17, 176; 18, 2845). Very unstable oil, sl. sol. ether. On heating with NaOAc and Ac, 0 it yields a base C,H,N, [2049.—B'HCl. [1299]. Needles, insole ether.—B',H,PtCl., [2009].—B'HNO., [1169]. Crystals (from alcohol), v. sol. water (C. Lossen, A. 265, 167).

Reference. -- OXY-PROPIONAMIDINE. PROPIONE v. DI-ETHYL KETONE.

PROPIONIC ACID C,H_O,i.e. CH_, CH_, CO_, H.

Metacetonic acid. Mol. w. 74. [-23] (Petterson, J. pr. [2] 24, 295). [140·7° cor.) (Zander).

S.G. 3° 9946 (B.); 1½ 9983; 3½ 9896 (Perkin).

M.M. 3*462 at 20° µ_p = 1-391. R_∞ = 28·01 (Brthh). S.V. 85°3. C.E. (0°-10°) 00106. H.F.p. 100.450. H.F. 107.10 (Thomson Th.) S. H. 109,450. H.F.v. 107,710 (Thomsen, Th.). S.H. 440 at 0° (R. Schiff, A. 234, 800). Oritical temperature 340° (Pawlewski, B. 16, 2634). Occurs in the fruit of Gingko biloba (Bechamp, A. 180, 864), in suint (Buisine, Bl. [2] 48, 639), and in wood vinegar (Anderson, C. N. 14, 257; Barré, Z. [2] 5, 445).

Formation .- 1. By exidation of metacetone with chromic soid (Gottlieb, A. 52, 121) .- 2. By potash-fusion from sugar, starch, mannite, and angelic acid (G.).—3. By reduction of acrylic acid (Linnemann, A. 125, 317), of lactic acid (Lautemann, A. 113, 217), and of pyruvic acid (Wislicenus, A. 126, 229).—4. By heating potassium oxalate with dry NaOEt (Van't Hoff, B. 6, 1107).—5. By heating NaOEt with CO at 180° (Fröhlich, A. 202, 290; cf. Hagemann, B. 4, 877).—6. From ZnEt,, sodium, and CO, (Wanklyn, A. 107, 125).—7. Together with di-ethyl ketone, by heating ZnEt, with CO, at 160° (Schmitt, J. pr. [2] 42, 568).—8. By the action of sunlight on a solution of succinic acid containing a uranium salt (Seekamp, A. 133, 253). 9. By heating barium succinate with NaOMe for 3 hours at 300° (Mai, B. 22, 2133).—10. Among the products of destructive distillation of colophony (Renard, C. R. 103, 157).

Preparation.-1. By oxidation of n-propyl alcohol (Pierre a. Puchot, A. Ch. [4] 28, 75).— 2. By saponification of the nitrile (Linnemann, A. 148, 251; Beckurts a. Otto, B. 10, 262). 3. By heating lactic acid with HIAq (Freund, J. pr. [2] 5, 446).

Properties .- Liquid, miscible with water, alcohol, ether, benzene, and ligroin. Separated from its aqueous solution by CaCl₂, but not by NaCl and Na, SO₄. Heated in a scaled tube with ICl, it gives C₄Cl₈, CO₂, and HCl (Krafft, B. 9, 1085). On boiling the dry acid with Br and P for some time the product is α-bromo-propionic acid (Volhard, A. 242, 141).

Salts.—NH,A'.—(NH,)HA', (Sestini, Z. 1871, 34).—NaA'. S. 99 at 15°; 187 at 100° (R.). S. (alcohol) 2·4 at 20°, 3 at 100°.—NaA'aq.— KA'aq: deliquescent plates (Renard, C. R. 104, 913). S. (of KA') 178 at 16°; 309 at 100°.— KHA'₂.—LiA' aq.—CaA'₂ aq. S. 54 at 17° (L.); 41 at 0°; 39 at 80° (K.). Needles, insol. alcohol.— Ca₂HA', 5aq.—BaA'₂aq. S. 60 at 17° (Linnemann, A. 160, 220); 48 at 0°; 68 at 80° (von Krasnicki, M. 8, 605).—BaA', 6aq.—BaHA', 8aq (Mixter, Am. 8, 343).—SrHA', 3½aq: long thin crystals. [67°-75°].—SrA', 6aq. Crystals. crystals. [67°-75°].— SrA'₂Gaq. Crystals.— Ba, Mg, A'₁₈ 12aq (Fitz, B. 13, 1312; 14, 1085).— Mg, Pb, A'₁₈ 12aq.— Ca, Pb, A'₁₈ 12aq : monometric crystals.—BaCa, A'₁: monometric octahedra.— SrCa, A'₁:—MgA'₂ aq.—Ba, A'₁₈Ac₂ (Fitz, B. 11, 1897).— PbA'₂, [100°]. Crystalline mass.—Pb, A'₂O₄. S. c. 11 at 14°.—Pb, A'₂O₅ S. 88 at 20°; 6°3 at 85°.—CuA'₂ aq; green prisms.—Cu, A'₂O aq.—"CdA'₂. V. e. sol. water.—ZnA'₂ aq: needles. S. (of ZnA'₂) 32 at 15°.—HgA'₂: [110°]. S. 19°2 at 15°.—HgA'₂. [225°]. S. 14 in the cold.—NiA'₂ 2aq.—CoA'₂ 3aq.—FeA'₂: pale-green crystals.—Fe, A'₁.—Al, A'₂O; white pp.—Cr₂A'₄O.—AgA'. Crystals. S. 9 at 18.

**Mathyle ather MeA'. (80°). S.G. 9°9878

Methyl ether MeA'. (80°). S.G. $\frac{9}{2}$.9878 (Elsässer, A. 218, 313); $\frac{9}{6}$.9403 (Gartenmeister). C.E. (0°-10°) .001296. $\mu_{\rm p} = 1.3812$. H.F.p. 107,330. H.F.v. 105,010 (Thomsen, Th.). S.V. 104.6.

Ethylether EtA'. Mol. w. 102. (99° cor.).
S.G. 2 9124 (E.); \$ 8958; \$\$ 8868. M.M.
5 452 at 15 7° (Perkin). C.E. (0°-10°) 001215.
S.V. 127 7 (B. Schiff, A. 220, 110). Formed from AgA' and Etl and also by distilling the soid with alcohol and H.SO. Oil.

Propyl ether PrA'. (122° cor.). S.G. ? 9619 (Elsisser, A. 218, 821); ½; 8868; ½; 8781 (Perkin, C. J. 45, 497); § 99023 (Gartenmeister). M.M. 6429 at 21.3°. C.E. (0°-10°) 001052. S.V. 150.

Isopropyl ether PrA'. (110° cor.). S.G. 2 ·8931 (Pribram a. Handl, M. 2, 687); \$\frac{1}{2} \cdot 8717; 35 .862C. M.M. 6 595 at 14°.

n Butyl ether C.H.A'. (145°). S.G. 8 8953. S.V. 173·2. C.E. (0°-10') 00106 (Gartenmeister, A. 233, 265).

Isobutyl ether PrCH.A'. (137°). S.G. *8876. C.E. (0°-10°) *001015 (E.). S.V. 174 (R. Schiff, A. 220, 332)

Isoamyl ether C₅H₁₁A'. Mol. w. 144. (160°). S.G. 2 *8877 (Elsüsser, A. 218, 330). C.E. (0°-10°) *00099. S.V. 197 (Schiff); 195 (E.).

Heptyl ether C.H., A. (208°). S.G. § 8847. C.E. (0° 10°) 00096. S.V. 247·1 (Gartenmeister).

Octylether C₈H_{1.5}A'. (226°). S.G. % 8833. C.E. (0°-10°) 00093. S.V. 270.5 (Gartenmeister).

Ethylene ether C.H.A'.. (211° cor.). S.G. 15 10544 (Perkin, C. J. 45, 505). Phonyl ether PhA'. (200° i.V.) at 744

Chloride C.H. COCl. (80°). S.G. 20 1.0646 (Brühl, A. 203, 14; cf. Sestini, Bl. [2] 11, 470). $\mu_{\theta} = 1.4107$. $R_{\infty} = 34.12$. ZnMe₂, followed by water, forms methyl ethyl ketone and oily C₈H₁₄O (168°). S.G. ^o 877 (Pawloff, A. 188,

138).

Bromide C,H,OBr. (104° i.V.). S.G. 25
152 (Lobry de Bruyn, R. T. C. 3, 389).

Iodide C.H.OI. (128°). Anhydride (C.H.O).O. Mol. w. 130. (162°) at 708 mm. (L.); (165°) (Limpricht a. Uslar, A. 94, 322); (167°) (Kahlbaum, B. 16, 2481); (169°) (Perkin, C. J. 28, 10). Formed by the action of Pb(NO₃)₂ (also of nitrates of other heavy metals) upon propionyl chloride; PbCl2 is formed, and N.O. and oxygen evolved; the yield is 77 p.c. of theoretical (Lachowicz, B. 18, 2991). Reacts with hydroxylamine hydrochloride, forming CH, CH, C(OH): NOH [85°] (Miolati, B. 25, 700).

73. [79²]. (213²). H.C.p. 436,000. H.C.v. 435,600. H.F. 88,400 (Berthelot, C. R. 111, 145; A. Ch. [6] 22, 20; Bl. [3] 4, 229). Formed from propionic ether and NH, (Dumas, C. R. 25, 657; Sestini, Cimento, 4, 21; L. Meyer, B. 22, 24). Prepared by heating ammonium propionate at 230° under pressure; the yield being 55 p.c. of the theoretical amount (Hofmann, B. 15, 981). Got also by heating propionic acid (46 g.) with ammonium sulphocyanide (18 g.) for 4 days, and distilling the product (J. Schulze, J. pr. [2] 27, 517).—B'₂HCl. Needles, v. e. sol. water, v. sl. sol. ether. - Hg(NH.C,H,O), Large dimetric plates, sl. sol. cold water.

Bromo-amide C.H.O.NHBr. [80°]. Formed from propionamide, bromine, and KOHAq (Hofmann, B. 15, 753). Colourless needles, sol. alcohol. Converted by hot KOHAq into ethylamine. - C.H.O.NNaBr. [c. 100°]. Needles.

Acetyl-amide O.H.O.NHAc. [82°]. (230°-). Formed from propionamidine hydroshloride, NaUAc, and Ac,O, a compound C,H,,N,

[204°] being formed at the same time (Pinner, B. 22, 1604).

Imide (C₄H,O)₂NH. [154*] (Otto a. Tröger, B. 23, 759). (210°-220°). Formation.—1. By heating the amide in a current of HCl.—2. By heating the amide with the chloride and AlCl₄.— 3. By the action of AlCl, at 100° on a mixture of propionitrile with AcCl or propionyl chloride. 4. By heating propionic acid with propionitrile for some hours at 200°. Properties. - Rectangular tables or silky needles, sl. sol. cold water. May be sublimed.

Anilide C,H,ONHPh. [105°]. S. 42 at 24°. Formed by heating the amide with aniline (Kelbe, B. 16, 1200). Plates, sol. other. With oxalio ether, benzene, and NaOEt it forms CO.CO NPh [192°] (Wislicenus a. Sattler,

B. 24, 1256).

Methyl-arilide C.H.O.NPhMe. [58.5°]. Formed from the anilide and Mel (Norton a. Allen, B. 18, 1998).

Ethyl - p - toluide C.H.O.NHC,H.Me. (c. 270°). From the chloride and ethyl-toluidine

(Norton a. Livermore, B. 20, 2271).

(Norton a. Livermore, B. 20, 2271).

Nitrile O.H.N. i.e. Et.CN. Propionitrile.

Ethyl cyanide. (97°). S.G. ½ 7998; \$\frac{3}{2}\frac{3}{2}\frac{1}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1} boiling KCy with EtI and alcohol (Williamson, P. M. [4] 6, 205; Buckton a. Hofmann, C. J. 9, 250; Rossi, A. 159, 79). -3. From the amide and P₂O₅ (Dumas, A. 64, 334). 4. From ZnEt₂ and cyanogen or CyCl (Gal. Z. 1868, 252; Frankland a. Graham, C. J. 37, 740). - 5. By the action of Ac.O on the oxim of propionic aldehyde in the cold (Dollfus, B. 25, 1915). Preparation. -The nitrile cannot be freed from alcohol by distillation, since the compound C,H,N3HOEt boils constantly at 79°, and is not decomposed by water or CaCl2. It is best, therefore, to prepare it from the amide. Properties. - Colourless liquid, v. sol. water, but separates on addition of NaCl or CaCl2. Miscible with alcohol and other. Combines with metallic chlorides, yielding (C,H,N)SbCl,, C,H,NAuCl,, C,H,NPtCl,, (C,H,N),SnCl,, and (C,H,N),TiCl, (Henke, A, 106, 280). Forms also (C.H.N.).TiCl. (Henke, A.106, 280). Forms also (C.H.N.).FcCy, 6aq. (C.H.N.).FcCy, 2aq (C.H.N.). FcCy, 2aq (Than, A. 107, 315). Reactions.—1. Potash forms propionic acid. Dilute H.SO, acts in like manner, 2. Dry chlorine forms CH., CCl., CN (Otto, A. 116, 195).—3. Bromine forms C.H.NBr, [64], converted by water into (C.H.BrO). NH (Engler, A. 142, 65).—4. Dry Hol slowly forms C.H.NCl. [1212] (Gautier, A. 142, 289). while HBr gives [121] (Gautier, A. 142, 289), while HBr gives C,H,NBr, [50°-55°] (Engler, A. 149, 807). Hi below 0° forms EtCl,NH, crystallising in plates (Bitz, B. 25, 2542).—5. Sodium converts it on heating into the polymeric cyanethine (q. v.). Sodium added to its solution in dry ether gives off H and ethane, and forms a product which is left when the ether is evaporated as a white powder (Et.C(NH).CMeNa.CN?). This powder is con-

verted by water into C.H., N. [48°] (258° uncor.). and by HClAq into C.H., NO or C.H., CO.CHMeCN (198.5°). The white powder treated with MeI yields C.H., N. (48°) (262°), whence HClAq forms liquid C.H., NO (175°), S.G. 2°945, mol. w. 125 (obs.). Etl and HClAq acting on the white powder yield C₈H₁₃NO (195°), S.G. 2 ·943 (E. von Meyer, J. pr. [2] 38, 336; Hanriot a. Bouveault, C. R. 108, 1171; Bl. [3] 1, 551). The compounds C,H₁₁NO and C,H₁₂NO are converted by heating with HClAq in scaled tubes into ethyl isopropyl ketone and ethyl butyl ketone respectively .- 6. A mixture of propionitrile and benzonitrile in ethereal solution is converted by Na, followed by water, into CPh(NH).CHMe.CN [97°], whence warm dilute HClAq forms oily C.H. CO.CHMe.CN (E. von Meyer, J. pr. [2] 39, 189).—7. Zinc and HClAq yield propylamine together with smaller quantities of di- and tripropylamine (Pisanello, G. 16, 446).—Ac₂O at 200° forms C₇H₁₄N₂O₂ [68°] (220°) (Gautier, Z. 1869, 127).

References .- AMIDO-, BROMO-, BROMO-NITRO-, CHLORO-, CHLORO-BROMO-, IODO-, NITRO-, and OXY-AMIDO-PROPIONIC ACID and PROPIONITRILE.

PROPIONIC ALDEHYDE C.H.O The property of the property by oxidation of propyl alcohol (Michaelson, A. 134, 69; Chancel, A. 151, 301; Lieben a. Zeisel, M. 4, 14) and by distilling calcium formate with calcium propionate (Rossi, C. R. 70, 129). Pungent liquid, sol. water. Readily oxidised by air. Reduces ammoniacal AgNO₂, forming a mirror. Readily dissolves in aqueous NaHSO. Decomposed by hot KOHAq. Coloured brownish-red by alkaline sodium nitroprusside, the colour being destroyed by HOAc (Von Bitto, A. 267, 876).

Reactions.-1. Reduced in aqueous solution by sodium-amalgam to n-propyl alcohol .-2. H₂S passed into its aqueous solution, acidified by HCl, forms oily (C₂H₈S)C₂H₆O (Alexejeff, B. 10, 1739).-8. Dry ammonia passed into propionic aldehyde dissolved in ligroin cooled by a freezing mixture forms a white flocculent pp. of C.H. (OH)NH., which readily deliquesces, forming O₁₁H₁₀N, [74°], crystallising in triclinic tables, a.b.c = 1:1·185: 801, insol. water, sol. alcohol and cther (Waage, M.4, 708).—4. PH, and HCl form (CH, CH₂, CH₂), PH, Cl [128°], while PH₃ and HBr give (C,H₄O), PH, Br [106°]. These compounds are decomposed by water (Messinger a. Engels, B. 21, 331). PH, at 0° forms, in like Engels, B. 21, 351). PH,1 at 0° forms, in like manner, (O₂H₂O),PH₂I [96°] (Girard, A. Ch. [6] 2, 24). — 5. Mercaptan and ZnOl, give OH₂CH₂CH₃(SEt)₂ (198°) (Fromm, A. 253, 150). 6. Propyl alcohol and HOAc at 100° form OHEt(OPr)₂ (166° cor.) (Schudel, M. 5, 247).

Oxim C.H., CH.NOH. (181°). Formed from the aldehyde and aqueous hydroxylamine (Petraczek, B. 15, 2784). Liquid, sol. water. It is a syn-oxim, because it is converted by Ac O and ether in the cold into propionitrile (Dollfus, A. 25, 1915).

Phenyl-hydraside CHEt:N.HPh (152° in vacuo) (Bischoff, B. 23, 1916).

References .- Brown CHLORO . IODO . and OXY- PROPIONIC ALDEHYDE.

PROPIONIC IMIDO-ETHYL ETHER

C2H3.C(NH).OEt. The hydrochloride, B'HCl, formed by passing gaseous HCl into a mixture of propionitrile and alcohol diluted with ether (\frac{1}{3}\times vol.), crystallises in prisms, decomposing at about 92° into EtCl and propionamide (Pinner, B. 16, 1654).

PROPIONITRILE v. Nitrile of PROPIONIC

PROPIONYL-ACETOPHENONE v. PHENYL-METHYLENE-ETHYL-DIKETONE.

PROPIONYL-BENZOIC ACID v. PHENYL ETHYL KETONE CARBOXYLIC ACID.

PROPIONYL BROMIDE v. Bromide of Pro-PIONIC ACID.

PROPIONYL-BUTYRIC ACID

C,H,.CO.CMe,.CO,H.

Methylether MeA'. (188° uncor.). Formed by the action of MeOH and HCl on the nitrile C₂H₃.CO.CMe₂.CN (175°), which is got by the action of cold HCl upon C₂H₃.C(NH).CMe₂.CN [43°] which is made by the action of McI on the product of the action of Na on propionitrile (Bouveault, C. R. 111, 531). Liquid.

PROPIONYL CHLORIDE v. Chloride of Pro-

FIONIC ACID.

PROPIONYL CYANIDE C.H.NO i.e.

CH3.CH2.CO.CN. (109°). Prepared by heating organized (12 g.) with silver cyanide (8 g.) in closed tubes for 1 hour at 100°. The product is fractionally distilled (Claisen a. Moritz, C. J. 37, 692). HCl converts it into ethylglyoxylic acid (q. v.).

Di-propionyl di-oyanide (Et.CO) C.N. [59°]. (208°). V.D. 5-6 (calc. 5-7). Obtained in the preparation of the preceding (C. a. M.) and by the action of AgCy on propionyl bromide (Lobry de Bruyn, R. T. C. 3, 390). Prisms, sl. sol. water, sol. alcohol and ether.

PROPIONYL-CYANO-ACETIC ETHER v. ANO-ACETIC ACID.

PROPIONYL-MALONIC ETHER C₁₀H₁₀O₅ i.e. C_{.H.2}, CO.CH(CO₂Et)₂. (239°-242° uncor.). Formed by the action of propionyl chloride upon sodio-malonic ether (Lang, B. 20, 1326). Colourless liquid.

PROPIONYL-PHENOL v. OXY-PHENYL ETHIL

a-PROPIONYL-PROPIONIC ACID C.H.,O.

i.e. CH, CH, CO.CHMe.CO,H.

Methyl ether C,H, CO.CHMe.CO,Mo or
C,H, C(OH):CMe.CO,Me. (187° cor.). S.G. 22
107. Formed by the action of Na on methyl propionate (Pingel, A. 245, 84). Colourless liquid with aromatic odour. Converted by ammonia into C,H₁₃NO₂ and a hygroscopic substance C₁₂H₁₂N,O₄(?) [82°]. Aniline forms oxymethyl-ethyl-quinoline [295°] (Bouveault, C. R. 111, 41). NaOHAq yields a mixture of di-ethyl ketone and methyl cthyl ketone. NaOEt followed ketone and methyl cthyl ketone. NaUEt followed by alkyl iodides yields the alkyl derivatives: C.H., MeO. or CEt(OMe):CMc.CO.Me [194°], C.H., EtO. (208°), C.H., PrO. (220°), and C.H., (CH.Pr)O. (231°), all being liquid.

Ethyl ether Eth. (199°). S.G. 2 -995;

12 983. Formed by digesting propionic ether in EtO. with Na. (Origentain a. Hellon B. 10.

in Et.O with Na (Oppenheim a. Hellon, B. 10, 699; Israel, A. 231, 197). Gives no colour with FeCl. Ammonia forms C.H., NO. (195°), insol.

water, and a hygroscopic substance [75°]. NaOHAq forms di-ethyl ketone. NaOEt and NaOHAq forms di-ethyl ketone. NaOEt and EtI yield propionic ether and CH, CHEt.CO, H (Genther, A. 239, 386). Na followed by Etl added to the solution in benzene forms C.H., C(OEt): CMe.CO, Et (206°), S.G. 12 966. Reduced by HI and P to CHMePr.CO.H (1932). Nitrous acid yields CH, C(NOH).CO.Et [94] (Hantzsch a. Wohlbrück, B. 20, 1320).

C,H,O.CHMe.CO.NH., Amida Formed by adding water to the product of the action of AlCl, on a mixture of propionyl chloride and propionitrile (Otto a. Tröger, B. 22, 1455).

Needles, sl. sol. cold water.

Nitrile C.H.CO.CHMe.CN. Nitrile C.H. CO.CHMe.CN. (c. 188°).

Formed by the action of cold conc. HClAq on the product of the action of Na on propionitrile (Meyer, J. pr. [2] 38, 339). Oil. Converted by ammonia into the imide [45°]. Hydroxylamine forms the oxim C.H., C(NOH), CHMe, CN [44°] (180° at 200 mm.) (Hanriot, C. R. 112, 796). Aniline yields amido - methyl - cthyl - quinoline (Hanriot a. Bouveault, Bl. [3] 1, 552).

Propionyi-propionic acid CH, CH, CO.CH, CH, CO, H. [33°]. A product of the action of boiling water on di-bromo-hexoic acid (from hydrosorbic acid and Br) (Fittig, A. 268, 69). Crystalline, v. e. sol. water, alcohol, and ether. —CaA'₂1;aq: plates. —AgA'.

PROPIONYL - PROPIONIC ALDEHYDE

C, H, CO.CHMe.CHO. [c. 40°]. (165°). Formed by adding a well-cooled mixture of formic ether (11 g.) and di-ethyl ketone (13 g.) to NaOEt (10.5 g.) suspended in dry ether (10 g.). 12 hours the product is acidified and distilled under 50 mm. pressure (Claisen a. Meverowitz, B. 22, 3273). Crystals, v. sol. water. Deliquesces and turns brown in air. NH₃ forms deliquescent crystals of (C₈H₁₆O₂)NH₃. Cu(OAc)₂ added to its alcoholic solution forms Cu(C,H,O,j, [168]. Phenyl-hydrazine produces $C_{12}H_{11}N_2$ (283°).

PROPIOPHENONE v. PHENYL ETHYL KETONE.

PROPYL. The radicle CaH,. n-Propyl CH. CH. CII, changes in some reactions to iso-

propyl (CH,)2CH and vice versa.

Pr changes to Pr: 1. When cumyl alcohol is reduced to n-cymene by boiling with zinc-dust (Kraut, A. 192, 225; Jacobsen, B. 12, 434). -2. When cumyl chloride is reduced to n-cymene by zinc and HCl (J. 1879, 369). - 3. When nitro-cymylene chloride is reduced to n-cymidine by boiling with zine and HCl (Widman, B. 15, 166; 19, 245) .- 4. When isopropyl-cinnamic acid is reduced by sodium-amalgam to n-cumyl-propionic acid. -5. When o-amido-isopropyl-cinnamic acid is reduced by sodium-amalgam to (B. 5)-n-propyl-(Py. 3)-oxy-quinoline dihydride. Pr changes to Pr: 1. When n-cymene is

oxidised to cuminio acid—(a) by passing through the organism, (b) by air and gaseous NaOH (B.5,749; 12,512; 11,369; 14,1144).—2. When n-cymene sulphonic acid is oxidised to oxyisopropyl-sulpho-benzoic acid by alkaline KMnO. (Meyer a. Boner, B. 14, 1136, 2391; A. 220, 6). 8. When n-cymene is oxidised to oxyisopropylbenzoic acid by alkaline KMnO₄.—4. When thymol is oxidised by KOH fusion to the oxycuminic acid, which is obtained from m-nitrocuminic acid by reduction and diszotisation (Barth, B. 11, 1571).—5. When carvacrol (which contains n-propyl, since by distillation with P.S.

it gives n-cymene) is oxidised by KOH fusion to the oxy-cuminic acid [93°], which is obtained from o-amido-cuminic acid by diazotisation (B. 6, 936; 9, 1061) .- 6. Since cuminol is always accompanied in plants by n-cymene, it is probably produced by oxidation of the latter.—7. When n-propyl bromide is boiled with AlBr. (Gustavson. C. J. 44, 565).

From the above may be deduced the general law: When a propyl group in a benzene derivative occurs in the para-position to Me, CHO, or CO.H., it is predisposed to be NORMAL by Me, 180 by CHO or CO.H (Widman, B. 19, 251, 273,

DI-PROPYL ACETAL v. ALDEHYDE. PROPYL ACETATE v. Acetyl derivative of PROPYL ALCOHOL.

PROPYL-ACETIC ACID v. VALERIC ACID.

Di-propyl-arstic acid v. Octobe Acid. PROPYL-ACETOACETIC ETHER v. vol. i. p. 23.

DI-PROPYL-ACETONE V. METHYL HEPTYL RETONE PROPYL-ACETYLENE v. PENTINENE

DI-PROPYL-ACRYLIC ACID v. ENNENOIG

n-PROPYL ALCOHOL C.H.O i.e. СП₂СП₂СП₄ОН. Mol. w. 60. (97·4° i. V.). S.G. § *8177 (Zander, A. 224, 79); 15 *8088; 25 *8025 (Perkin); 20 *8044 (Bruhl, A. 203, 268). C.E. S.H. 670 (Diaconoff, Bl. [2] 38, 172). Qurs in fusel oil, especially in that of wine (Chancel, C. R. 37, 410; 68, 659, 726; Pierre a. Puchot, C. R. 66, 302; 70, 406; Linnemann, A. 160, 195; Fittig, Z. [2] 4, 44; Ekman, Chem. Zeit. Thus 40 g. of it were found in 100 12, 564). litres of old cognac (Ordonneau, C. R. 102, 217; Clandon a. Morin, C. R. 104, 1187; 105, 1019). A litre of potato-fusel oil was found to contain 30 c.c. of n-propyl alcohol, 150 c.c. of isopropyl alcohol, 115 c.c. of butyl alcohols, 335 c.c. of amyl alcohols, 125 c.c. of water, and 245 c.c. of other bodies (Rabuteau, C. R. 87, 501). Propyl alcohol also occurs, together with isopropyl alcohol, among the products of the lactic and butyric fermentation of sugar (Bouchardat, C. R. 78, 1145; Meyer a. Forster, B. 9, 535), and in the fermentation of glycerin (Fitz, B. 18, 36, 1311).

Formation .- 1. By reducing propionic anhydride with sodium amalgam (Linnemann, 4. 148, 251; 160, 231; 161, 18).—2. By adding sodium-amalgam and dilute H₂SO₄ to a solution of propionic aldehyde (1 pt.) in water (18 pts.) (Rossi, C. R. 70, 129).—3. By heating allyl alcohol with KOH (Tollens, Z. [2] 7, 242).

Properties.-Liquid with alcoholic odour, miscible with water, but separated from the solution by CaCl. Does not yield isopropyl alcohol when heated in sealed tubes (Aronstein, R. T. C. 1, 194). When propyl alcohol (71-46 c.o.) is mixed with water (28-54 c.o.), contraction (1-85 c.o.) is observed (Ramssy a. Young, C. J. Proc. 4, 101).

Reactions .- 1. Chromic acid oxidises it to propionic aldehyde and acid .- 2. HBr and H.SO, give propyl bromide, propylene bromide,

and C,H,Br, (Niemilovitch, M. 10, 820).—3. I and KOHAq form iodoform (Lieben, A. Suppl. 7, 280).—4. Fused ZnCl, forms propylene, isoutyl alcohol, CH,:CMe,, and CHMc:CHMe (Le Bel a. Greene, C. R. 89, 413).—5. Phosphoplatinous chloride followed by water forms crystalline P(OPr), PtCl, (Pomey, C. R. 104, 364).—6. Calcium chloride yields (C,H,O), CaCl, crystallising in needles (Göttig, B. 23, 181).

Metallie derivatives. KOPr (De Forcrand, C. R. 104, 68).—NaOPr2HDOR (Fröhlich, A. 202, 295). Ba₂(OPr)₂(OH)₂. Formed by heating propyl alcohol with BaO under pressure (Destrem, A. Ch. [5] 27, 32). Yields propylene, methane, and hydrogen when heated. The corresponding lime compound yields di-ethyl ketone when heated.—Al(OPr)₃. [c. 60°]. S.G. ± 1.026. Formed in small quantity from propyl alcohol, AlI₄, and Al (Gladstone a. Tribe, C. J. 39, 6). Isopropyl alcohol does not react in this way.

Acetyl derivative ProAc. Propyl acetate. (102°). S. 1.5 at 16° (Linnemann, A. 161, 30). B.G. 2° 9091 (E.); 2° 8856 (Brühl); 2° 9093 (Gartenmeister); 1½° 8933; 2½° 8840 (Perkin, C. J. 45, 421). C.E. (0°-10°) 001197 (Elsässer, A. 218, 320). S.V. 128·3. μ_S 1·3890. R_∞ 43·11. M.M. 5·487 at 15·2°. Liquid. Not changed into isopropyl acetate by heating in a sealed tube (Aronstein, R. T. C. 1, 134).

Bensoyl derivative BzOPr. (230° cor.). S.G. 14 1.032 (Linnemann).

Isopropyl alcohol (CH₃) CH.OH. (83° cor.). S.G. § '7996 (Zander); $\frac{15}{12}$ '7914; $\frac{25}{22}$ '7845 (Perkin); $\frac{2}{30}$ '7887 (Brühl, A. 203, 12.). $\mu_{\theta} = 1.8821$. R_{co} 27-99. M.M. 4-019 at 17-9°. S.V. 817 (R. Schiff, A. 220, 331); 82-8 (Zander). C.E. (0°-10°) 00108. H.F.p. 71,000. H.F.v. 69,970 (Thomson, Th.).

Formation.—1. By distilling PrO.SO₃H (made from propylene and H₂SO₃) with water (Berthelot, J. 1855, 611).—2. By reducing acetone or propylene oxide with sodium-amalgam (Friedel, A. 124, 327; Linnemann, A. 140, 178).—3. By heating a solution of n-propylamine nitrite (Linnemann, A. 161, 43; B. 10, 1111; Meyer, B. 9, 536).—4. By the action of sodium-amalgam on (CH₂Cl)₂CH₂OH dissolved in wet ether (Buff, Z. [2] 4, 124).—5. From CH₂I.CH₂OH by successive treatment with ZuMe₂ and water (Butlerow a. Ossokin, A. 145, 257).

Preparation.—1. Acetone (1 vol.) is diluted

Preparation.—1. Acetone (1 vol.) is diluted with water (5 vols.) and sodium-amalgam is slowly added. The liquid is distilled and the process repeated upon the distillate (Linnemann, A. 186, 87).—2. By boiling isopropyl iodide (1 pt.) with water (10 pts.) and Pb(OH)₂ (Flavitzky, A. 175, 880).—3. By heating isopropyl iodide (1 pt.) with water (20 pts.) at 100° for 40 hours (Niederist, A. 186, 891).

Properties.—Liquid with peculiar odour, not solid at -20°. Inactive to light. Miscible with water, yielding on distillation the hydrate (C₂H₂O)₂ 2aq (80°), S.G. 12 832. When K₂CO₃ is added to an aqueous solution of the alcohol a hydrate (C₂H₂O)₂ aq separates (Erlenmeyer, A. 126, 80°). After drying over CuSO₃ the hydrate (C₄H₂O)₃ aq (81°) S.G. 12 800 is left. Dilute CrO₃ forms acetone. Bromine forms acetone and FrBr.

Acetyl derivative ProAc. Isopropyl

acetate. (91°). S.G. 2 917 (Friedel, A. 124, 327; Pribram s. Handl, M. 2, 686).

Benzoyl derivative ProBz. (218°) (Silva, Bl. [2] 12, 225). Liquid. Split up by distillation into benzoic acid and propylene (Linnemann, 4. 161, 51).

References.—BROMO-, CHLORO-, CHLORO-IODO-, and IODO- PROPYL ALCOHOL.

PROPYL ALDEHYDE v. Propionic alde-

PROPYL-DI-ALLYL-CARBINOL v. DECINYL

PROPYLAMIDOACETIC ACID

NHPr.CH., CO₂H. Formed from CH₂Br.CO₂Et and NH₂Pr (Chancel, Bl. [3] 7, 409; C. R. 114, 756). Needles, v. sol. water and alcohol, insol. ether.—(HA'), H.PtCl_a aq.—CuA'₂2aq: crystals, v. sol. water and alcohol.

PROPYL-AMIDO-ISOPROPYL ALCOHOL C_aH_{1,5}NO *i.e.* CH₂CH(OH).CH₂NHC₃H₄. Formed by heating allyl-propyl-amine with H₂SO₄ (3\frac{1}{3}\text{pts.}) at 135° (Liebermann a. Paal, B. 16, 532).—B'₂H₃PtCl₄ 2aq: nodules (from water).

Di-propyl-amido-isopropyl alcohol CH₂.CII(OII).CH₂.N(C,H₂)₂. Formed in like manner from allyl-di-propylamine.—B'₂H₂PtCl₆.

n-PROPYLAMINE C3H3N i.e.

CH_,CH_,CH_,NH_, Mol. w. 59. (49°). S.G. $\frac{15}{2}$. 7222; $\frac{25}{2}$. 7144. H.F.p. 22,760. H.F.v. 20,420 (Thomsen, Th.). S.V. 85°6. M.M. 4°564 (Perkin, C. J. 55, 693). $\mu_D = 1°3873$ (Gladstone, C. J. 59, 290).

Formation .- 1. By reduction of propionitrile. Using 36 g. of propionitrile, 500 g. alcohol, 200 g. water, zinc, and 500 g. of 20 p.c. HClAq, the yield is 9g. (Mendius, A. 121, 129; Linnemann, A. 161, 44).—2. From n-propyl iodide by successions. sive treatment with silver cyanate and KOHAq (Silva, Z. [2] 5, 638).—3. By heating n-propyl iodide with alcoholic NH, and distilling the product with potash. The fraction boiling below 78° is mixed with alcohol and oxalic ether, and the di-propyl-oxamide [161.5°] thus formed distilled with alcoholic potash (Vincent, C. R. 103, 208). n-Propyl iodide heated with conc. NHAq for 13 hours at 100°-150° forms propylamine hydriodide and NPr.I (Malbot, A. Ch. [6] 13, 480, 546).-4. When n-propyl chloride is heated with aqueous ammonia in equimolecular proportions at 140°-165°, one-fifth of the product is n-propylamine and is nearly all contained in the lower layer. The upper layer consists of free di- and tri- propyl-amines, water, and alcohol (Malbot, C. R. 104, 998).—5. By heating n-propyl nitrate with alcoholic NH₂ at 100° (Wallach, A. 214, 311).

Walker, H. 24, 541, 11.

Preparation.—1. A mixture of equimolecular quantities of bromine and butyramide is run into an excess of a 10 p.c. solution of KOH at 60° and the propylamine distilled off; the yield is 80–90 p.c. (Hofmann, B. 15, 769). It may be dried over CaO and afterwards over Na.—2. PrOI (1 mol.) heated with aqueous NH, (1 mol.), and enough alcohol to effect solution, in sealed tubes at 110° forms 45 p.c. propylamine, 35 p.c. dipropylamine, and 20 p.c. tri-propyl-amine (Chancel, Bl. [3] 7, 405). The product is neutralised with HOI, the alcohol distilled off, cooled, filtered from separated NH, OI, the syrup mixed with NaOH, distilled, and fractionated.

The bases may be further purified by means of |Bl. [2] 46, 287) or of aqueous NH, on PrCl at their oxalates.

Properties .- Mobile liquid with ammoniacal smell; mixes with water, becoming hot. When wet it boils at 78°-82°. Its aqueous solution ppts. salts of Cu and Fe, the pp. not dissolving in excess, but with AgNO, it gives a pp. sol. AXCARS.

Reactions .- 1. Chromic acid yields propionic acid (Chapman a. Thorpe, A. 142, 176).-2. Nitrous acid forms n- and iso- propyl alcohols and propylene (Meyer a. Forster, B. 9, 535).-3.

Benzoic aldehyde forms C.H., CH.NPr (210°) (Zaunschirm, A. 245, 282).-4. Oxalic ether added to a mixture of equal volumes of propylamine and water forms CONHPr.CONHPr and CO2H.CONHPr [110], which yields CaA', 2aq. S. 1.38 at 17°.

Salts .- B'HCl. [158°] · (Topsoë, J. 1883, 621). -B'HHg,Cl, - B'HHg,Cl, -B'HAuCl, -921).—B HIR, Cli. — B HR, Cli. — B HAUCI.
F. H., PtCl., Monoclinic crystals. — Oxalate,
NH, Pr C., H., O., Laq. Plates. S. 14.8 at 18°; S.
(alcohol) 6 at 18°.—Pierate [135°].
Nitramine CH, CH, CH., NH, NO. (129°
at 40 mm.). S.G. 12 1 102. Formed by heating

PrN(NO2).CO2Et in a current of dry NH2, and decomposing the product with dilute II.SO₄ (Thomas, R. T. C. 9, 75). Liquid, crystallising at -23°. Decomposes at 142°. Sl. sol. water; decomposes carbonates. - PrNK.NO. Formed by dissolving the nitramine in alcoholic potash and ppg. with ether. Small pearly plates, forming an alkaline solution in water.-PrNAg.NO. Slender needles, blackening in light. AcCl yields N₂O.

Isopropylamine (CII,),CH.NH., (32°). S.G. 49 ·690.

Formation.-1. By the action of HClAq on isopropyl-carbamine (Siersch, A. 148, 263; Gautier, C. R. 67, 723). -2. By running a mixture of bromine (1 mol.) and isobutyramide (1 mol.) into an excess of a 10 p.c. solution of KOH at 60°; the yield being 65 p.c. (Hofmann, B. 15, 768).-3. By reducing acctoxim dissolved in alcohol with sodium-amalgam and HOAc at 40° (Goldschmidt, B. 20, 728).—4. By heating isopropyl iodide with conc. NH₃Aq (Malbot,

C. R. 111, 650; cf. Jahn, M. 3, 166).

Preparation.—By reduction of a solution of acetone-phenyl-hydrazide (1 pt.) in 96 p.c. alcohol (10 pts.) by means of acetic acid (24 pts.) and sufficient '67 p.c. sodium-amalgam, the temperature being kept below 25°; the yield is 70 p.c. of the theoretical (Tafel, B. 19, 1926).

Properties .- Mobile liquid, with ammoniacal smell, miscible with water. Converted by nitrous

acid into isopropyl alcohol. Salts. — B'HCl. [1 [140°]. Deliquescent

Satts. — B Dick. [140]. Defiquescents cubes.—B'₂H.PtCl₆: orange plates, m. sol. Aq.

Nitramins PrNH.NO₂. [-4°]. (91°).

S.G. 15 1098. Formed from PrN(NO₂).CO₂Et by successive treatment with dry NH, and dilute H,SO, (Thomas, R. T. C. 9, 78). Needles.—
PrNK.NO. Slender hygroscopic needles.—
PrNAg.NO. Thin plates. Converted by PrI

Fring.No. Thin plates. Converted by PrI into PrNPs.No. (67° at 10 mm.).

Di-n-propylamine Pr.NH. (110°) (P.; C.); (98°) (V.). S.G. 12. 7480; 23. 7857 (Perkin, C.J. 55, 698). M.M. 7, 549. µ. = 1.4088 (Gladstone, C. J. 59, 290). A product of the action of alcoholic Mil. on Pri at 100° (Vincent, C. R. 103, 208;

190° (Malbot, C. R. 105, 575). Purified by means of its nitrosamine. Liquid with ammoniacal smell, sl. sol. water. The pps. that it forms with salts of Ag and Al are sol. excess; those with salts of Cu and Zn are insol. excess.

Salts.—B'H.C.O. Flat needles. S. 5 at 17°. S. (alcohol) 33 at 18° (Chancel, Bl. [3] 7, 406). Picrate. [75°]. S. 2.2 at 19°. Melts under water at 45°.

Nitrosamine Pr.N.NO. (206°). S.G. & 931. Liquid smelling like hay. Decomposed by HClAq, with formation of dipropylamina

Nitramine PraN.NO. A liquid, got from PrNK.NO, and PrBr (Thomas, R. T. C. 9, 79).

Di-isopropylamine Pr.NH. (84°), S.G. 22 '722. A product of the action of alcoholic NH, on PrI at 100° (Van der Zande, R. T. C. 8, 202; on Fr at 100° (Van der Zande, R. T. C. 8, 202; cf. Siersch, Z. [2] 5, 145). Liquid with very ammoniacal offour, miscible with water. — B'MNO₂. [138°].—B'₂H.PtCl₂: orange tables. Nitrosamine Pr.N.NO. [46°]. (195°). Nitramine Pr.N.NO. [56° at 10 mm.).

Formed from PrNAg.NO, and PrI (Thomas, R. T. C. 9, 82). Liquid.

Tri-n-propylamine Pr. N. (157°). S.G. 9 .770; 15, 760; 25, 754 (Ferkin). S.V. 2221 (Zander, A. 214, 171). M.M. 11·664. $\mu_0 = 1\cdot4171$ (Gladstone, C. J. 59, 290). C.E. (0'-10°) ·00105. A product of the action of Prl on alcoholic NH, V.). It is the chief product got by heating PrCl with cone. NH, Aq (Malbot, A. Ch. [6] 13, 480, 546). Purified by means of its picrate (Chancel, Bl. [3] 7, 407). Liquid with faintly ammoniacal odour, almost insol. water. Pierate. S. 3 at 18; S. (94 p.c. alcohol) 4.4 at 19°.

Propylo-iodide Pr.NI. The chief product of the action of PrI on NH,Aq at 150°-190°. Prisms. Yields (Pr.NCl) PtCl, and deliquescent Pr. NOH, which is decomposed by heat into Pr.N, propylene, and water (Roemer, B. 6,

References .- BROMO-, CHLORO-, CHLORO-10DO-, and Oxy. PROPYLAMINE.

PROPYL-ISOAMYL-GLYOXALINE

C₆H₅(C₅H₁₁)N₂. Oxalisoamyl-butyline. (251°). S.G. ¹² 920. Formed from propyl-glyoxaline and CaH, I (Rieger, M. 9, 609).

PROPYL ISOAMYL OXIDE Pr.O.C.H ... (125°-130°) (Chancel, A. 151, 305).

PROPYL-ANILINE CoH13N 6.6. PhNHPr. (222° i.V.) (Pictet a. Crépieux, B. 21, 1111). S.G. 14° 949. Formed by heating aniline with PrBr (Claus a. Roques, B. 16, 909; Wacker, A. 243, 290). Liquid. Salts.—*B'HCl. [150].— *B'₂H₂C₂O₄. [152°]. Large tables, v. sol. water. Formyl derivative PhNPr(CHO). (269°

i.V.). S.G. 16 1.044. Got from formanilide and n-propyl bromide.

Acetyl derivative PhNPrAc. [48 (269° i.V.). Hexagonal plates (from ligroin).
Nitrosamine. Yellowoil.

Isopropyl-aniline Isopropyl-aniline PhNHPr (213° 1.V.). Liquid. Yields an oily nitrosamine.—B'.H.PtCl... Red prisms (P. a. C.).

Formyl derivative PhNPr.NO. (264°LV.). Formed from formanilide and PrBr.

Acetyl derivative PhNPrAc. [89°]. (265 i.V.). Transparent leaflets (from ligroin).

Di-n-propyl-aniline NPhPr₂. (245° i.V.): S.G. § 9240. S.V. 2431 (Zander, A. 214, 168). (245° i.V.): O.E. (0°-10°) 00081. Formed from aniline and Pri (Lippmann a. Fleissner, M. 3, 711).—
B'_H_PtCl₆. Decomposed by water.

Di-isopropyl-aniline NPhPr₂. (220° i.V.). S.G. 2 9338. S.V. 235.4 (Zander). C.E. (0°-10°) (220° i.V.).

.00087.

References .- NITRO- and NITROSO- PROPYL-AWILINE.

DI-PROPYL-ANTHRACENE DIHYDRIDE

C₂₀H₂₄ i.e. C₆H₄ < CPr₂ < C₆H₄. Formed from dipropyl-anthrone, HI, and P at 140°-170° (Hallgarten, B. 22, 1070). Plates, getting soft at 47°. Di-isopropyl-anthracene dihydride

 $C_eH_aPr < CH_2 > C_eH_3Pr$. [90°]. (above 360°). Formed by boiling C_cH₄Pr.CH₂Cl alone or with ZnCl₂ (Errera, G. 14, 280). Antorphous yellow powder, insol. alcohol, sol. ether. Its solutions are red with green fluorescence.

PROPYL-ANTHRANOL. Propyl derivative. $C_{20}H_{22}O$ i.e. $C_{u}H_{4} < \stackrel{CPr}{C(OPr)} > C_{u}H_{4}$. [72°]. Formed by boiling anthranol with KOHAq and Pri (Hallgarten, B. 22, 1070). Needles, sol. ether and alcohol, insol. alkalis. Chromic acid ether and alcohol, insol. alkalis. solution converts it in the cold into propyloxanthranol C, H16O, [164°], v. sol. benzene.

DI-PROPYL - ANTHRONE C20H22O C.H. CO CPr. C.H. [124°]. Formed, together with the preceding body, by boiling anthranol (5 g.) with KOH (5 g.), water (25 c.c.), and PrI (13 g.) (Hallgarten, B. 22, 1069). Trimetric crystals, sol. hot alcohol. CrO₃ in HOAc oxidises it to anthraquinone.

TRI-PROPYL-ARSINE v. vol. i. p. 319. PROPYL-BENZENE v. CUMENE.

Di-n-propyl-benzene C₆H₄Pr₂[1:4]. Formed from p-di-bromo-benzene, n-propyl bromide, and Na (Körner, B. 11, 1863; A. 216, 223). Formed also, together with the m-isomeride, by the action of AlCl, and HCl on n-cumene (Heise a. Töhl, A. 270, 165). Liquid, volatile with steam. Bromine forms C.H.Br.Pr. [48°].

C.H.PrPr[1:4]. n-iso-Di-propyl-benzene (212° cor.). S.G. º ·8713. Formed from C_sH₄Pr.CH₂Cl and ZnEt₂ (Paterno a. Spica, B. 10, 1746) and from PrBr, p-bromo-cumene, and Na. Formed also, together with the m- isomeride, by the action of AlCl, at -2° on a mixture of π -cumenc and PrBr (Heise, B. 24, 772).

m-Di-isopropyl-benzene CoH4Pr2[1:3]. (204°). Formed, together with the p- isomeride, by the sotion of propyl or isopropyl chloride on benzene in presence of AlCl, (Silva, Bl. [2] 43, 320; Uhlhorn, B. 23, 3142) and by the action of AlCl, and HCl at 100° on cumono (H. a. T.). Yields isophthalic acid on oxidation.

p-Di-isopropyl-benzene C_eH₄Pr₂[1:4]. (c. 202⁵). Formed as above. Yields terephthalic scid on oxidation.

PROPYL-BENZENE SULPHONIC ACID . CUMENE SULPHONIC ACID.

p-M-n-propyl-benzene sulphonic acid C.H.Pr., SO.H. [62°]. Formed from di-propyl-benzene and fuming H.SO. (Körner, B. 11, 1865; 4. 216, 224; Remsen, Am. 5, 162). Deliquescent

needles, with pearly lustre.-NaA'4aq.-KA'4aq. -BaA'₂ ½aq. — BaA'₂ 2aq. — CaA'₂ 9aq. — PbA'₂ aq. Amide C₈H₃Pr₂SO₂NH₂. [103°]. Hexagonal crystals (from alcohol), sl. sol. hot water.

n-iso-Di-propyl-benzene sulphonic acid

[1:4:x] C₈H,PrPr.SO,H. [60°]. Needles (Heise, B. 24, 771). –BaA'₂xaq. –PbA'₂aq: minute needles, m. sol. cold water. –PbA'₂8aq: needles.

Amide. [96°]. Needles.

m-Di-isopropyl benzene sulphonic acid C.H. Pr. SO.H [1:3:x]. Formed by shaking with H.SO, (11 pts.) the fraction (200°-210°) got by the action of AlCl, on a mixture of PrCl and benzene, and separated from the accompanying p-di-isopropyl-benzene sulphonic acid by means of its Ba salt (Uhlhorn, B. 23, 3142). - BaA'22aq: A mide C_uH₃Pr_xSO_xNH_x. [145°].

p-Di-isopropyl-benzene sulphonic acid

C,H,Pr,(SO,H) [1:4:2]. Formed as above.— BaA',: nodules, v. sol. water.—CuA', 0\frac{1}{2}aq. A mide C,H,Pr,SO,NH, [102']. m.Di.n-propyl-benzene disulphonic acid

C_aH_aPr₂(SO₃H)₂. Deliquescent tables (Heise).— K_aA''xaq.—BaA'' 1½aq: tables, v. sol. water.— PROPYL-BENZOIC ACID v. Cuminic Acid.

PROPYL-BENZOYL-ACETIC ACID v. Benz-OYL-ACETIC ACID and PHENYL BUTYL KETONE CARBOXYLIC ACID.

PROPYL-BENZYL- v. CUMINYL-.

n-PROPYL BORATE (PrO), B. (172°-175°). S.G. 12 ·867 (Cahours, C. R. 76, 1383).

Isopropyl borate (PrO), B. (140° cor.). Formed by heating B,O, with isopropyl alcohol at 120° (Councler, J. pr. [2] 18, 389). Mobile oil, slowly saponified by water.

n-PROPYL BROMIDE PrBr. (71°). S.G. 8 propyl alcohol and HBr (Linnemann, A. 161, 40; Pierre a. Puchot, J. Ph. [4] 13, 9). When heated in scaled tubes at 280° it partially changes to isopropyl bromide (Aronstein, R. T. C. 1, 134). When heated for a short time with AlBr, it is completely changed to isopropyl bromide (Kekulé a. Schrötter, B. 12, 2279; Gustavson, J. R. 15, 61). Bromine forms propylene bromide. — C₃H,Br(H₂S)₂23aq (Do Forerand, A. Ch. [5] 28,

Isopropyl bromide PrBr. (60°). S.G. § 1-3397 (Z.); № 1-3097 (B.); ‡ 1-3198; 25 1-3058 (Perkin). C.E. (0°-10°) -00127. μ_S = 1-4317. R_∞ 38·58 (Brühl). M.M. 7-003 at 17·1°. S.V. 99. Formation.—1. From isopropyl alcohol and

HBr at 150° (Linnemann, A. 136, 41).-2. From n-propyl bromide and AlBr. -3. From propylene bromide and HI (Linnemann, A. 161, 57).

Preparation.-By adding bromine (65 g.) gradually to PrI (100 g.) in the cold; the yield being 45 g. (R. Meyer, J. pr. [2] 34, 105).

Properties .- Liquid, not attacked by Cl. ISOPROPYL-BUTENYL-BENZENE v. Bu-

TENYL-CUMENE. n-PROPYL-ISOBUTYL-AMINE C.H., N

PrNH.C.H., (124°). Formed by reducing iso-butyl-propargyl-amine in alcoholic solution with

sodium (Paal a. Heupel, B. 24, 3048).—B'HCl. [185°].—B'H.C.O. [224°]. Needles. ISOPROPYL-BUTYL-AMINE DICARB-

OXYLIC ACID C.H., NO, i.e.

CO.H.CMe, NH.CMe, CH, CO.H. A product of the oxidation of triacetonamine with chromic acid mixture (Heintz, A. 198, 69). Crystalline grains, m. sol. hot water. Yields amido-iso-butyrio acid when heated. — H.A"HCl. — KHA" 2aq. — Zn(HA"), 6aq. — ZnA" aq. — CuA" aq. — Ag. HA". — Ag. A"HNO, aq: grains. PROPYL-ISOBUTYL-GLYOXALINE

(241° at 738 mm.). S.G. 18 .915. Formed from isobutyl-glyoxaline and PrBr (Radziszewski a. Szul, B. 17, 1295). Liquid.— B'aH.PtCla: minute orange prisms.

Propyl-butyl-glyoxaline CH.N:CPr CH.N:(C,II,y).

(243°) at 728 mm. S.G. 12 938. Formed from propyl-glyoxaline and butyl iodide. Oxidised by H.O., to butyl-oxamide [198°] (Rieger, M. 9, 609). -B'HZnCl, -B',H,CdCl, -B',H,PtCl,

Propyl-isobutyl-glyoxaline (H.N:CPr CH.N(C.H.)) (232°) at 736 mm. S.G. 13 .940. Formed from

propyl-glyoxaline and isobutyl iodide (Rieger). PROPYL ISOBUTYL KETONE Pr.CO.C.₁H_y. (155°) at 750 mm. S.G. ^o. 831. Formed from isovaleryl chloride and ZnPr2 (Wagner, J. R. 16,

668). Liquid.

Isopropyl isobutyl ketone Pr.CO.CH.Pr. (160°). S.G. 12 865. Formed by oxidising secoctyl alcohol with cold dilute K.Cr.2O, and H.SO. (Williams, C. J. 35, 130). Liquid, not solid at -17°. Does not form a crystalline compound with NaHSO3

PROPYL-ISOBUTYL-MALONIC ACID

C₄H₉.CPr(CO₂H)₂. [129°]. This appears to be the composition of the acid got by saponifying C,H,C(C,H,)(CO,Et), (219), which is got from malonic ether, isobutyl iodide, allyl iodide, and NaOEt (Ballo, B. 14, 335)

PROPYL BUTYL OXIDE Pr.O.C.H., (117°). S.G. 9 .7773. C.E. (0°-10°) .00124. S.V. 174.4

(Dobriner, A. 243, 7). ISOPROPYL-ISOBUTYL-PHOSPHINE

PHPr.CH, Pr. (140°). Formed from isopropylphosphine and isobutyl iodide at 130° (Hofmann, B. 6. 300).

ISOPROPYL-ISOBUTYL-QUINOLINE

C.H.CPr N=C.CH.Pr. (296°) at 710 mm. Formed by the action of isovaleric aldehyde and conc. HClAq upon aniline (Spady, B. 17, 1718; 18, 8378).—B',H.PtCl, Yellow needles, sl. sol. 8373).—B'.H.PtCl. Yellow needles, sl. sol. water.—B'C.H.(NO.),OH. Large yellow plates. - B'HCl aq. - B'HNO, aq. - B'H.SO,. B'H.Cr.O.: orange needles, sol. hot water.

B'Mel aq. Methylo-iodide Yellow needles, v. sol. alcohol.-B'2Me,PtCla: yellowish-

red triclinic prisms

PROPYL TRICARBALLYLIC ACID

CHPr(CO,H).CH(CO,H).CH2.CO2H. Formed by saponifying its ether, which is made by the action of fumaric ether on sodium propylmalonic ether (Auwers, B. 24, 311, 2898). Prisms (containing xaq), v. c. sol. ether.

Ethyl ether Et,A". (206° at 16 mm.). B.G. Y 1 092,

Isopropyl-tricarballylic acid

CHPr(CO,H).CH(CO,H).CH,CO,H. [162°]. Prepared in like manner from isopropyl-malonic ether. Plates or prisms, v. sl. sol. ligroin.

Ethylether Et.A'". (206° at 20 mm.).

S.G. 19 1.085.

PROPYL CARBAMATE NH...CO.OPr. [52°]. (195°). Formed by heating ures with propyl alcohol (Cahours, C. R. 76, 1387). Formed also from Cl.CO, Pr and NII, (Roemer, B. 6, 1102). Prisms, v. e. sol. water and alcohol.

Isopropyi carbamate NH, CO.OPr. Formed from Cl.CO, Pr and dry NH, (Spica a. Varda, G. 17, 165). Hygroscopic needles.

Varda, G. 17, 165). Hygroscopic needle ISOPROPYL-CARBAMINE PrnC. S.G. 2.760. Formed from isopropyl iodide and AgCy (Gautier, C. R. 67, 723; A. 149, 155). HClAq forms isopropyl-formamide.

PROPYL-CARBAMIC ACID NHPr.CO.H.

Methyl ether MeA'. (180° at 755 mm.).

S.G. 15: 992. Liquid (Thomas, R. T. C. 9, 71).

The nitramine NPr(NO.), CO.Mo. S.G. 15

1.187 is made from NAgPr(NO.) and Cl.CO.Me. Ethyl ether EtA'. (1869). Formed from propylamine and chloro-formic ether (Schreiner,

J. pr. [2] 21, 125).

Isopropyl-carbamic acid NHI'r.CO.II. Methyl ether MeA'. (165.5°). S.G. 14 981. Liquid. The nitramine

NPr(NO.).CO.Me S.G. 14 1:159 is also liquid. PROPYL-CARBINOL v. BUTYL ALCOHOL.

Di-propyl-carbinol v. HEPTYL ALCOHOL.

DI-PROPYL-CARBOBENZONIC ACIDS $C_{2a}H_{\infty}O_{2a}$. Two acids of this formula [139°] and [90°] are formed by heating phenyl bonzyl ketone with n-propyl alcohol and KOH (Zagu-

meany, A. 184, 166). The acid [189°] forms a di-nitro- derivative [176°]. PROPYL CARBONATE CO(OPr)... cor.). S.G. 12 949 (Roese, A. 205, 230).

Propyl orthocarbonate C(Olr), (224° cor.). S.G. 2 911. Formed from NaOPr and chloropicrin (Roese, A. 205, 253)

n PROPYL CHLORIDE PrCl. Mol. w. 783. (46° i.V.). S.G. § 9123 (Zander, A. 214, 156); $\frac{2}{3}$ ° 8898 (Brühl, A. 200, 179), $\frac{1}{3}$ ° 8930; $\frac{2}{3}$ 5813 (Perkin). M.M. 5-056 at 16°. $\mu_B = 1$ 3934. $R_{\infty} = 33$ 36. S.V. 91-6. H.F.p. 37,760. H.F.v. 36,020. C.E. (0°-10°) 00137. Formed by the action of chlorine on propane and on PrI. Prepared by saturating n-propyl alcohol with gaseous HCl, and heating at 125° with conc. HClAq (Malbot, Bl. [3] 2, 136; cf. Pierre a. Puchot, A. Ch. [4] 20, 234). Acts with extreme slowness on alcoholic NH, (Vincent, Bl. [2] 45, 504). Not changed to PrCl by heating in scaled tubes (Aronstein, R. T. C. 1, 134).—PrCl(H_xS)₂ 23aq (De Forerand, A. Ch. [5] 28, 34).

Isopropyl chloride PrCl. (36°). S.G. 3 8825 (Z.); 13 8688; 29 8575 (P.). M.M. 5159 at 17·2°. S.V. 94. C.E. (0°-10°) 00142. Formed from isopropyl alcohol and HCl. Chlorine converts it into CH_CCl_CH_and CH_CHC.CH_CL. Partially converted into NH.Pr by heating with conc. NH.Aq at 140° (Malbot, C. R. 111, 650), ISOPROPYL CINNAMIC ACID v. CUMYL-

ACRYLIC ACID.

References .- AMIDO-, CHLORO-, and NITRO-PROPYL-CINNAMIC ACIDS

PROPYL-m-CRESOL C.H.MePr.OH. (230°-235° at 734 mm.). Formed, together with its propyl ether and di-propyl-m-cresol, by heating m-cresol with propyl alcohol and MgCl. (Mazsara, G. 12, 187, 332). Liquid, sl. sol. water, sol. alcohol and ether. Not solid at -15° . Not coloured by FeCl. Yields a crystalline nitrosoderivative [140°].

Methyl ether MeA'. (226°) at 740 mm. Propyl ether PrA'. (235° 240°). Acetyl derivative AcA'. (240°) at 743

Isopropyl-m-cresol CoH3PrMe.OH. (238°). Formed in like manner by heating m-cresol with isopropyl alcohol and MgCl₂ (Mazzara, G. 12, 505). Oil. Yields C₂H₂(NO)PrMe.OH [167°].

Methyl ether MeA'. (215°-220°).

Isopropyl ether PrA'. (230°-235°).

Isomeride v. THYMOL.

Propyl-o-cresol v. Carvacrol and Cymenol. Isopropyl-cresol CaHaPrMe.OH. (229° cor.). S.G. 2 1 0012. Formed by potash-fusion from the m-isocymene derived from camphor (Spica, G. 12, 552). Not coloured by FeCl.

Ethyl ether EtA'. (228° cor.)

Di-propyl-m-cresol C.H.Pr.Me.OH. (250°). Formed as above. Liquid, yielding a liquid acetyl derivative (255°-260°).

Di-isopropyl-m-cresol C.H.Pr.Me(OH). (251°). Formed at the same time as isopropylm-cresol (M.). Liquid smelling like phenol, sl. sol. water, insol. dilute potash.

Methyl ether McA'. (243°)

Acetyl derivative AcA'. (255°-260°) ISOPROPYL-CUMIDINE

C.H.Pr.NHPr. (245°-250°). A product of the action of aniline and ZnCl₂ on isopropyl alcohol (Louis, B. 16,

111). Liquid. Forms a granular picrate.

180PRUPYL CYANATE v. vol. ii. p. 315.

PROPYL CYANIDE v. Nitrile of BUTYRIO

PROPYLENE C.H.. Mol. w. 42. S. 44 at 0°; 22 at 20° (von Than, A. 123, 187). S. (alcohol) 13. S. (H.SO.) 200 (Berthelot). H.F.p. 8,220. H.F.v. 2,060 (Thomsen, Th.).

Formation.-1. By passing fusel oil, valeric acid, or light petroleum through a red-hot tube (J. W. Reynolds, A. 77, 118; Prunier, J. 1873, 847).—2. By distilling calcium oxalate with KOAc (Dusart, A. 97, 127).—3. By the action of mercury (containing a trace of zine) and fuming HClAq on allyl iodide (Berthelot a. De Luca, A. 92, 306).—4. Mixed with H (\frac{1}{3} vol.), by reducing allyl iodide in alcoholic solution with granulated zinc and HClAq (Tollens a. Henninger, A. 156, 156).-5. From allyl iodide and HI (Butlerow, A. 145, 271).—6. A product of the action of ZnEt, on CCl, (Rieth a. Beilstein, A. 124, 242) on allyl iodide (Wurtz, Bl. 5, 51) and on CHBr, (Beilstein, Bl. [2] 2, 51).—7. By boiling n- or iso-propyl iodide with alcoholic potash (Freund, M. 8, 633; Erlenmeyer, A. 139, 228).—8. Together with other hydrocarbons, by treating propylene bromide with water and sodiumamalgam or with zine and HClAq (Prunier, C. R. 76, 98).-9. By heating CCl, Me, or CBr, Me, with Na at 140° (Friedel a. Ladenburg, Z. 1868, 48; Reboul, A. Ch. [5] 14, 488).—10. Together with cresol, by heating thymol with P₂O₃ (Engelhardt a. Latschinoff, Z. 1869, 616).—11. In the manufacture of oil-gas (Armstrong, C. J. 49, 74). 12. Together with ethylene, by heating allyl alcohol with P₂O₄ (Béhal, A. Ch. [6] 16, 860),— 18. By heating N(C,H,), with C,H,Cl at 190° (Malbot, A. Ch. [6] 13, 546).

Preparation.—1. By dropping propyl alcohol on strongly-heated ZnCl, (Le Bel a. Greene, Am. 2, 23).-2. By passing gaseous HI into allyl iodide, PrI being also formed (Malbot, C. R. 107. 114; Bl. [2] 50, 449) .- 3. By pouring an alcoholic solution of allyl iodide on zinc (Gladstone a. Tribe, B. 6, 1550; Niederist, A. 196, 358).—
4. By dropping propyl alcohol (4 pts.) on P₂O₈ (3 pts.) (Beilstein, B. 15, 1498).-5. By mixing isopropyl alcohol (200 g.) with ZnCl, (650 g.) and heating after twenty-four hours (Friedel a. Silva. J. 1873, 322).

Properties.—Colourless gas, liquefied by pressure of eight atmospheres (Moltschanoffsky, J. R. 21, 31). Unites with Cl and Br. Its solution in H.SO, yields isopropyl alcohol on distilling with water. Cuprous chloride in HClAq absorbs it somewhat. HClAq heated with propylene for seventy hours at 100° forms isopropyl chloride (Berthelot, A. 104, 184); HBr and HI act in like manner. Dilute CrO_2 forms acetone acetic acid and CO_2 (Berthelot, A. 150, 373). Alkaline KMnO, forms formic and acetic acids (Truchot, C. R. 63, 274). KCl added to a solution of propylene in PtCl, and HClAq ppts. CaHaPtClaKCl aq (Birnbaum, A. 145, 72).

Di-propylene v. HEXYLENE.

DI - BROMO - IODO-References. - Bromo. CHLORO-, CHLORO-IODO-, DI-CHLORO-NITBO-, and IODO- PROPYLENE.

PROPYLENE-ACETOACETIC ACID v. ACETO-ACETIC ACID and METHYL TRIMETHYLENYLMETHYL KETONE CARBOXYLIC ACID.

PROPYLENE-ALLYL-4-THIO-UREA

CH₂N(C₃H₅)>C:NH. Formed from propyleneψ-thio-urea and allyl iodide (Hirsch, B. 23, 973). Oil.-B'C_eH_aN₃O_r. [120°]. Triangular prisms.

Isomeride CHMe.S C:NC_aH_a. [56°]. Got

from \$B-bromo-propyl-amine and mustard oil. Prisms (from ligroin).—B'C₅H₄N₄O₇. [130°].—B'C₃H₄NCS. [52°]. White prisms.

PROPYLENE-DIAMINE C₃H₁₀N₃ i.e. S.G. 15 ·878. CH₃.CH(NH₂).CH₂.NH₂. (119°). S.G. 15 878. Formed by heating propylene bromide with alcoholic ammonia at 100°-150° (Hofmann, B. 6, 308; Strache, B. 21, 2358). Hygroscopic liquid, fuming in the air. Yields a hydrate $(C_3H_{10}N_2)_2$ aq, boiling at the same temperature as the base, and dehydrated by Na. Benzoic aldehyde forms oily C₃H₆(N:CHPh)₂, decomposed by HCl into the parent substances. Acetoacetic ether forms oily C_zH_e(NH.CMe:CH.CO₂Et)₂.

Salts.—B'H.Cl., [220]. Very hygroscopic needles.—B'H.PtCl., Small four-sided tables. Acetyl derivative C.H. (NHAc), [139°].

Needles, v. e. sol. water and alcohol.

Benzoyl derivative C.H.Bz.N. [1980]. PROPYLENE-AMYL-4-THIO-UREA

CHMe.S C.NHC, H₁₁, [32°], (267°), Formed by heating allyl-amyl-thio-ures with conc. HClAq at 100° (Avenarius, B. 24, 264).

PROPYLENE BROMIDE v. Dr.BROMO-PRO-

PROPYLENE TRICARBOXYLIC Ethyl other CO.Et.CH;CH.CH(CO.Et),. (1710.

FROPYLENE BULPHUUTANIDE.

at 15 mm.). Formed by the action of water or of NaOHAq upon $CH \leqslant C(CO,Et).C(OEt) > O[94°]$, which is got by distilling di-carboxy-glutaconic ether in vacuo (Guthzeit a. Dressel, B. 22, 1425). It is identical with iso-aconitic ether.

Isomeride v. Aconitic acid.

Propylene tetra-carboxylic acid (CO2H)2CH.C(CO2H):CH.CO2H. [192°]. Got by saponifying its ether. Colourless crystals (containing 2aq). Gives off CO, at 180°.

Salts. - Na HAiv Sag. - Ba Aiv 11 ag. -Ca,Aiv 3 aq.

Ethyl ether Et, Air. (220°-230° at 40 mm.). Formed from sodium-malonic ether and bromo-maleïc ether (Schacherl, A. 229, 91).

Isomerides .- DICARBOXY-GLUTACONIC ACID and TRIMETHYLENE TETRACARBOXYLIC ACID.

PROPYLENE CHLORHYDRIN v. Chloro-PROPYL ALCOHOL. PROPYLENE CHLORIDE v. DICHLORO-

PROPANE.

PROPYLENE CHLOROBROMIDE v. CHLORO-BROMO-PROPANE.

PROPYLENE GLYCOL CaHaOai.e. CaHa(OH)2.

Formation.—1. By saponifying its acetylderivative (Wurtz, A. Ch. [3] 55, 438).—2. By reduction of CH,Cl.CH(OH).CH OH by sodiumamalgam (Lourenco, C. R. 52, 1043) .- 3. By heating propylene bromide with PbO and much water at 150° (Eltekoff, J. R. 10, 210).-4. By boiling propylene bromide with aqueous K.CO, for some days (Hartmann, J. pr. [2] 16, 383). 5. By boiling propylene bromide (1 pt.) with water (36 pts.), the yield being 43 p.c. (Niederist, A. 196, 359).-6. By the action of the copperzine couple and some HClAq on the product of the action of AcBr on glycerin (Hanriot, C. R. 86, 1139) .- 7. By treating allyl alcohol with dilute H.SO. (20 p.c.) or HCl (10 p.c.) (Solonina, Bl. [2] 46, 816).

Preparation. - Glycerin (1,300 g.) is distilled with NaOH (550 g.) and the aqueous layer concentrated and distilled; the yield is 140 g. (Belohoubek, B. 12, 1872; Morley a. Green, C. J. 47, 182).

Properties. - Liquid, with sweet taste; miscible with water and alcohol.

Reactions .- 1. Water containing a trace of HCl forms propionic aldehyde at 215° (Linnemann, A. 192, 61). It also yields propionic aldehyde on heating with ZnCl. (Flavitzky, B. 11, 1256). -2. Conc. HIAq forms isopropyl iodide (Wurtz, A. Suppl. 1, 381) .- 8. PCl, forms dichloro-propane.—4. KOH at 250° forms oxalic acid and H.—5. Chromic acid mixture forms acetic acid (Flavitzky, B. 11, 1256).-6. Oxidised by platinum black and air to lactic acid.-7. Glyceryl trimetric forms, at 100°, oily CH, CH(O.NO).CH, O.NO (109°), S.G. 2 1.44, which explodes in sunlight (Bertoni, C. C. 1887, 85).

Acetyl derivative C,H,,O, i.e. C.H. (OAc). Propylene acetale. (186°). S.G. 21:109. S. 11. Formed by heating C.H. Br. with AgOAc and HOAc (Wurtz, A. 105, 202). Neutral liquid.

Mono-bensoyl derivative CH, CH(OBz).CH, OH. Formed from the amine CH, CH(OBz).CH, NH, and HNO, (Gabriel a. Heymann, B. 23, 2501). Oil.

Di bensoyl derivative

Liquid (Friedel a. Silva, C. R. 78, 1879).

Di-nitrate C.H. (O.NO.). S.G. 1835.

Formed by dropping propylene oxide into strongly-cooled fuming HNO. (Henry, A. Ch. [4] 27, 261). Oil.

Chlorhydrin v. CHLORO-PROPYL ALCOHOL.

Bromhydrin v. BROMQ PROPYL ALCOHOL.

Iodhydrin C,H,I(OH). (105° at 60 mm.). Formed from propylene oxide and HI (Markownikoff, Z. 1870, 423). Liquid.

Active propylene glycol $C_3H_6(OH)_2$, $\alpha_0 = -4^\circ 35'$ to $-1^\circ 15'$ in a 22 mm, tube. Formed, together with propionic and lactic acids, by allowing Bacterium termo to breed in ordinary inactive propylche glycol (Le Bel, C. R. 92, 532). Yields active propylene oxide (35°) $a_D = +1° 10°$ in a 22 mm. tube.

n-Propylene glycol v. TRI - METHYLENE GLYCOL

PROPYLENE IODIDE v. DI-10DO-PROPANE. Di-oxy-propane. Mol. w. 76. (189°). S.G. 3 PROPYLENE MERCAPTAN C₃H₀(SH)₂. 10527 (Z.). C.E. (0°-10°) 00069. S. (ether). (152° in vacuo). Formed by reducing propylene sulphocyanide with Zn and HClAq (Hagelberg, R = 23 - 1087

PROPYLENE OXIDE C.H.O i.e.

CHMe O. Mol. w. 58. (35°). S.G. 2 859. V.D. 2.0. Formed by warming propylene chlorohydrin with KOHAq (Oser, Bl. 1860, 237; Morley, B. 15, 179). Dried over KOH. Neutral liquid, smelling like acctone. Miscible with water, alcohol, and ether. Reduced by sodium-amalgam to isopropyl alcohol. Yields acetic acid when oxidised by moist Ag.O (Linnemann, M. 6, 869)

PROPYLENE-OXIDE CARBOXYLIC ACID v.

METHYL-GLYCIDIC ACID.

PROPYLENE PHENYL ETHYL KETATE CHMe.O CPhEt. (235° cor.). S.G. 22 .988. Formed by dropping CaHaCl.OBz into a mixture of ZnEt, and toluene, and then adding water (Morley a. Green, C. J. 47, 134; B. 17, 8015). Oil, with pleasant odour; sol. ether. Not on, with pleasant odour; soil etner. Not attacked by alcoholic potash, by AcCl, by Na, by hydroxylamine, by phenyl-hydrazine, or by HClAq at 155°. HI at 200° yields PrI and phenyl ethyl ketone. By dissolving in H.8O₄ and pouring into water, it is split up into w propylene glycol and C_aH₅.CO.C_aH₅. Nitric acid oxidises it to acetic and benzoic acids. Bromine forms a mono-bromo- derivative (230°).

PROPYLENE - PROPYL - 4 - THIO - UREA CHMe.S C.NHPr. [237°]. Formed by heating allyl-propyl-thio-urea with conc. HClAq at 100° (Avenarius, B. 24, 264). Oil.—Picrate [1280].

PROPYLENE SULPHIDE C.H.S. Formed from C3HBr, and alcoholic Na2S (Husemann, 4. 126, 296). Amorphous powder.

PROPYLENE SULPHOCYANIDE C.H.N.S. i.e. CH, CH(SCy).CH, (SCy). Formed by heating C,H,Br, with potassium sulphocyanide and alcohol at 100° (Hagelberg, B. 28, 1086). Insol. water, sol. alcohol and ether.

PROPYLEME DISULPHONIC ACID v. Pro- | [192°].-B',H,C,O, 2aq: [161°]; plates or needles. PANE DISULPHONIC ACID.

PROPYLENE SULPHONIC ACID CH₂:CH.CH₂:SO₂H. Formed by boiling allyl iodide with conc. K₂SO₂Aq (Von Rad, A. 161, 218).—KA'. Crystalline solid.—(KA'),K (KA'),K,I. White solid. PROPYLENE TRI-THIO-CARBONATE Crystalline solid .- (KA'), K.I. .-

C₂H₆;CS₂. S.G. ²⁰ 1.31. Formed from C₃H₆Br₂ and Na₂CS₃ (Husemann, A. 126, 269). Thick

liquid, of disagreeable smell.

PROPYLENE-\(\psi\)-THIO-UREA C₁H_{*}N₂S i.e. CHMe.S C:NH. Imido-methyl-thiazole tetrahydride. Formed by heating allyl-thio-urea with HClAq (8.G. 1-17) under pressure at 100° (Gabriel, B. 22, 2985). Formed also from B-bromo-propyl-amine hydrobromide and po-B'C₄H₃N₃O₇. [200°]. — Mot hylo - iodide [172°], Colourless prisms.

CHMe.O >C:NH. PROPYLENE U-UREA Formed by heating allyl-ures with HClAq at 100° (Gabriel, B. 22, 2990), and by heating \$\beta\$-bromo-propyl-amine hydrobromide with potassium cyanate at 100° (Hirsch, B. 23, 966).-

B'C,H,N,O, [186°]. Needles.—B',H,PtCl,. PROPYL ETHER v. DI-PROPYL OXIDE. PROPYL-ETHYLENE v. AMYLENE.

PROPYL-EUGENOL v. EUGENOL. PROPYL FLUORIDE PrF. (2°). V.D. 2·161 at 20° (calc. 2·175). S. 1 at 15°. Formed by gently warming AgF with PrI (Meslans, C. R. 108, 352). Gas, with ethereal odour and hot, sweet taste. Has no action on glass when dry.

V. sol. alcohol, ether, and benzene. Isopropyl fluoride PrF. (-5°). S. 1.5 at 15°; S. (alcohol) 29 at 16°. V.D. 2.171. Formed from AgF and PrI. Gas, not affected by KOHAq at 100°. Br at 30° forms a liquid (143°), while chlorine forms a liquid (105°).

ISOPROPYL-FORMAMIDE v. Formamide in article on FORMIC ACID.

DI-PROPYL-FURFURANE C,H,Pr,O. (120°). One of the products of the distillation of sodium citrate with lime (Bischoff, B. 23, 1918).

DI-PROPYL-GLUTARIC ACID C,1H20O, i.e. (CO.H.CH.Pr),CH₂. [89°]. Formed by heating ((CO.H),CPr),CH₂ above 170° (Dressel, A. 256, 190). Needles, v. sl. sol. water, v. sol. ether.

PROPYL-GLYCOL v. PROPYLENE GLYCOL. PROPYL-GLYOXAL. Mono orin

C.H., CO.CH:NOH. [51°]. Formed from methyl propyl ketone, amyl nitrite, and HCl or NaOEt (Claisen a. Manasse, B. 22, 528). Pearly plates.

Chaisen a. Manasse, B. 22, 525). Fearly flates,
Di-oxim Pr.C(NOH).CH(NOH). [168°],
Di-phenyl-di-hydraxids
PrC(N,HPh).CH(N,HPh). [163°]. Needles.
PROPYL-GLYOXALINE C.H.,N., (210°–228°). S.G. 19 267. Formed by heating glyoxaline with PrBr (Wallach, B. 15, 650; 16, 534; A. 214, 321). Liquid, miscible with water. HgCl, added to its aqueous solution gives a pp. sol. HOlAq.—B',H,PtCl. Crystals, sol. hot water.

Propyl-glyoxaline CH.NH CPr. Formed from glyoxal, n-butyric aldehyde and NH, (Rieger, M. 9, 603). Oil. — B'₂H₂C₁O₄.

-B'_H.PtCl.: yellow prisms.
Isopropyl-glyoxaline. Glyoxal-isobutyline. [129°]. (c. 250°). Formed from glyoxal and isobutyric aldehyde-ammonia (Radziszewski, B. 16, 747). Needles, sol. alcohol, benzene, and hot water .- B'HCl. [105°] (Rieger) .- B'HBr.

hot water.—B'H.C.O. [195°].

Di-propyl-glyoxaline C₄H,PrN, (227°).

S.G. 12 '939. Formed by heating propyl-gly-

oxaline with PrI (Rieger, M. 9, 607).

n-PROPYL-GLYOXYLIC ACID Pr.CO.CO.H. (180°-185°) at 760 mm.; (115°) at 84 mm. Got by the action of HCl on the nitrile (1330-137°) which is made from AgCy and butyryl chloride (E. Moritz, C. J. 39, 16). Liquid.

Amide C,H,O.CONH,. [10 from the nitrile and conc. HClAq. [106°].

Oxim PrC(NOH) CO.H. [1449]. Formed by the action of alcoholic soda and NaNO, on propyl-acetoacetic ether (Fürth, B. 16, 2180). Small needles, v. sol. alcohol, sl. sol. water.

Isopropyl-glyoxylic acid *Pr.CO.CO.H. mixture (93° at 45 mm.) of this acid with isobutyric acid is got by the action of HCl on diisobutyryl dicyanide (Moritz, C. J. 39, 14).

Amide * Pr.CO.CONH, [126°]. PROPYL HEPTYL KETONE C,H,.CO.C,H,, [12°]. (222°). S.G. 20 828. Formed by distilling calcium butyrate (Limpricht, A. 108, 185).

PROPYL HEPTYLOXIDE ProC, H₁₅. (188°). S.G. § .7987. S.V. 245·6. C.E. (0°-10°) ·00099 (Dobriner, A. 243, 7).

DI - ISO - PROPYL - HEXINYL DIKETONE Pr.CO.C₃H₅:C₃H₅.CO.Pr. Di-isobutyrone. 266°). Formed by the action of sodium on iso-

butyric ether (Bruggemann, A. 246, 151). PROPYL - HEXYL - CARBINOL v. DECYL

PROPYL-HEXYL-GLYOXALINE C.H., PrN., Oxalpropylænanthyline. (286°). S.G. 4. 919. Formed from hexyl-glyoxaline and PrBr (Karez,

M. 8, 222). Oil.
PROPYL HEXYL KETONE Pr.CO.C,H,, [-9.5°]. (207°]. S.G. 21 -824. Formed by oxidation of the corresponding alcohol (Wagner, J. pr. [2] 44, 271). Needles. Oxidised by K.Cr.O. and H.SO. to heptoic and propionic

Isopropyl hexyl ketone Pr.CO.C. H15. (200°-210°). S.G. 17 .841. Formed by distilling calcium isobutyrate with calcium heptoate (Fuchs, J. R. 7, 334). Yields acetone, HOAc, and heptoic acid on oxidation.

PROPYL HYPOPHOSPHATE Pr.P.O. 15 1-134. Formed from Ag.P.,O., and Pri (twice the calculated quantity) at 120° (Sänger, A. 232, 12). Oil. Decomposed by hot water.

Propyl-hypophosphate of barium

PREMIP O See Nordles

PrBaHP, O, 6aq. Needles.
PROPYLIDENE-ACETIC ACID v. PENTENOIC

ISOPROPYLIDENE-AMIDO-PHENOL

CMe,:N.C,H,.OH. [168°]. Formed from p-amido-phenol, acetone, and HOAc (Haegele, B. 25, 2755). Colourless plates.

ISO-PROPYLIDENE-ANILINE C.H.N:CMe. (228°). V.D. 66.4 (calc. 66.5). From acetone and aniline in presence of dehydrating agents (Engler a. Heine, B. 6, 638; Riehm, A. 238, 10). Liquid; rapidly turning brown in air. Its salts are v. sol. water and alcohol. -B', H, SO, : decomposes at 235°.

PROPYLIDENE CHLORIDE v. DI-CHLORO-

PROPANE.

PROPYLIDENE - HYDRAZIDO - BENZENE p-SULPHONIC ACID CMe_:N.NH.C.H.SO.H. Got from p-hydrazido-benzene sulphonic acid (phenyl-hydrazine p-sulphonic acid) and acetone (Pfülf, A. 239, 216). Plates, m. sol. hot water. 180-PROPYLIDENE HYDRAZINE

CMe,:N.NH, (125°). Formed from acctone and hydrazine hydrate (Curtius, J. pr. [2] 44, 543). Mobile liquid decomposing when kept, with evolution of N and NH

ISO.PROPYLIDENE-PHTHALIDE C,1H,0O, i.e. $C_4H_4 < \frac{C(CMe_2)}{CO} > 0$. [96°]. Formed by heating phthalic anhydride with NaOAc and isobutyric acid or pyrotartaric acid (Gabriel a. Michael, B. 11, 1683; Roser, B. 17, 2776). Needles, sl. sol. hot water. Converted by boiling alkalis into Pr.CO.C.H.,CO.H.
DI-ISO-PROPYLIDENE DISULPHONE v.

Tetra-methyl-di-methylene disulphone.

ISOPROPYLIDENE - DI - THIO - DIGLY-COLLIC ACID CMe.(S.CH2.CO.H). [127°]. Formed from thioglycollic acid, acetone, and ZnCl₂ (Bongartz, B. 21, 482). Crystals (from chloroform)

ISOPROPYL INDOLE C, H, N i.e.

 $C_{s}H_{s} < CPr_{NH} > CH$. (288°). Formed by heating the phenyl-hydrazide of isovaleric aldehyde with ZnCl, at 180° (Trenkler, A. 248, 106). Oil, solidifies by cold. Yields a dihydride (c. 260°) and a picrate [99°] crystallising in red needles. Di-isopropyl-indole C, H, N i.e.

CPr:CII.C.CPr CII. [65°]. (295° 300°). Formed CII:CH.C.NH by the action of dilute H SO, on isopropyl-pyrrole in the cold (Dennstedt, B. 21, 3430). Needles (from dilute alcohol). Colours acidified pinewood red. Yields a picrate [115] and an acetyl derivative [186]. Benzoie aldehyde and ZnCl, form C., H., N. [c. 164].

**n-PROPYL 10DIDE C., H., I. (102-5)* (Brown,

Pr. 26, 238). S.G. 21.7829 (Dobriner, A. 243, 24); 10 1 7673; 15 17585 (Perkin); 29 1 7427 (Brühl, A. 203, 15). C.E. (0°-10°) 00105. $\mu_{\rm p}$ 1 5157. R. 4705. M.M. 11 08 at 18°. S.V. 106°9. Formed from propyl alcohol (60 g.), iodine (127 g.), and red P (10 g.), the yield being 90 p.c. of the theoretical amount (Chancel, Bt. [2] 39, 648;

Cf. Linnemann, A. 160, 240). Oil.

Isopropyl iodide PrI. (89°). S.G. 32 1-7033
(Brühl); 15 1-7163; 25 1-7005 (Perkin). M.M.
11-182 at 26°. μ_B1-5108. R_ω 47·48. S.V. 108·3.
Formed by the action of HI on isopropyl alcohol, propylene glycol, glycerin, allyl iodide, or propylene (Linnemann, A. 161, 26; Wurtz, A. Suppl. 1, 381; Erlenmeyer, A. 126, 305; 139, 228; Maxwell Simpson, A. 129, 127; Berthelot, A. 104, 184; Butlerow, A. 145, 275). Prepared A. 104, 164; Butterow, A. 145, 276). Frepared by distilling glycerin (200 g.) with I (300 g.), water (160 g.), and clear phosphorus (55 g. added slowly) in a current of CO₂ (Mar-kownikoff, A. 138, 364; R. Meyer, J. pr. [2] 34, 98). Obtained also by saturating allyl iodide with HI and heating in sealed tubes at 100° (Malbot, C. R. 107, 114; Bl. [2] 50, 449; A. Ch. [6] 19, 352). Oil, converted by Br into PrBr.

The copper-zinc couple decomposes it at 50° giving off gases (Gladstone a. Tribe, C. J. 26.

PROPYL-ITACONIC ACID C.H., O. 4.6. CO,H.CH, C(CO,H):CHPr. [159°]. Formed by heating propyl-paraconic ether with alcoholic NaOEt, and saponifying the product (Fittig, A. 256, 106; cf. Schmidt, A. 255, 83). Tufts of 256, 106; cf. Schmidt, A. 255, 83). Tufts of prisms, insol. chloroform, v. sol. other. Reduced by sodium amalgam to butyl-succinic acid [81°]. Bromine, followed by hot water, gives rise to CHPr< $\stackrel{C(CO_2H)}{O.CO}$ >CH [124°].—BaA".

DI.PROPYL-KETINE ₹. DI-METHYL-DI PROPYL-PYRAZINE.

DI-PROPYL KETONE C,H,O i.e. COPr2. Bulyrone. Mol. w. 114. (145°). S.G. 35 8217; 389). Prepared by distilling calcium butyrate alone or mixed with CaCO, (Chancel, A.52, 295; Kurtz, A. 161, 205; Schmidt, B. 5, 597). Formed also from ZnPr, and butyryl chloride, by the oxidation of di-propyl-carbinol (Schtscherbakoff, J. R. 13, 346), and by heating butyry chloride (1 mol.) with FeCl, (1 mol.) at 50° (Hamonet, Bl. [2] 50, 355). Got also by heating butyric anhydride with sodium butyrate at 180° (Perkin, C. J. 49, 325). It is also one of the products formed by the action of sodium on butyric ether (Brüggemann, A. 246, 140). Oil, sol. alcohol. Does not combine with NaHSO. or NH₃. Chromic acid yields propionic and butyric acids. Treatment with Zn and EtI followed by water gives ethyl-di-propyl-carbinol; while Zn, McI, and water give methyl-di-ethyl-carbinol (A. Saytzeff, J. pr. [2] 31, 320). Sodiumamaigam forms sec-heptyl alcohol and a pinacone C₁₄H₂₀O₂ [68°] (c. 260'). PCl, yields C.H₁₄Cl₂ (181°) and C.H₁₄Cl (141°) (Tavildaroff, B. 9, 1442). Gives on chlorination, when cooled by ice and salt, the compound Pr.CO.CHCl.Et by ice and sait, the compound Pr.CO.CHCi.Ed.

(c. 175°) converted by NH₂ into tetra-propylpyrazine (Vladesco, Bl. [3] 6, 835). P.O. forms

(C,H_{1,2})₂ (200³-250') (Tavildaroff, B. 9, 1442).

Oxim Pr₂C:NOH. (190°-195°) (Meyer a.

Warrington, B. 20, 501). Yields an acetyl

derivative.

 $(124^{\circ}$ Di-isopropyl-ketone Pr.CO. S.G. 2 8230; 20 8063 (Poletical, J. R. 20, 672). H.C. 1,044,559 (L.). R_∞ 33·46. Formed by distilling calcium isobutyrate (Popoff, B. 6, 1255; Münde, B. 7, 1370; A. 180, 327). Formed also by heating tetra-methyl-phloroglucin with HClAq at 200° (Spitzer, M. 11, 288). Oil, with ethereal odour, miscible with alcohol and ether. Does not unite with NaHSO,. Reduces ammoniacal AgNO, Yields isobutyrio and acetic acids and CO, on oxidation, and secheptyl alcohol (c. 140° cor.) on reduction.

Oxim Pr₂C:NOH. [8°]. (c. 183°). Liquid, converted by AcCl into Pr₂C:NOAc, which on heating produces PrCO.NHPr (M. a. W.).

Dipropyl-diketone v. DIBUTYRYL.

Reference. — CHLORO-DI-ISOPBOPYL-KETONE.

PROPYL-LUPETIDINE v. DI-METHYL-PROPYL-PYRIDINE HEXAHYDRIDE.

PROPYL-LUTIDINE v. DI-METHYL-PROPYL-PYRIDINE.

PROPYL-MALONIC ACID C.H.,O. i.s. CHPr(CO.H) Mol. w. 146. [84°] (S.); [96°]

(F.). H.C.p. 675,000. H.C.v. 674,700. H.F.

234,000 (Stohmann, J. pr. [2] 40, 211).

Ethyl ether Et.A". (222°) (Fürth, M. 9, 809). S.G. 15 9931; 25 9854. M.M. 10:367 at 18° (Perkin, C. J. 45, 514). Formed from malonic ether, PrI, and zinc or NaOEt.

Isopropyl-malonic acid CPrH(CO2H)2. H.C.v. 674,900. H.C.p. 675,200. H.F. 233,800 (Stohmann). Formed by saponifying its ether, which is made from sodium-malonic other and PrI (Conrad a. Bischoff, B. 13, 595; A. 204, 144). Prisms, sol. water, alcohol, and ether. Yields iso-valeric acid at 180°.—Ag.A".

Ethyl ether Et.A". (214°). S.G. 10 '997 (C. a. B.); 15 '9927; 25 '9852 (Perkin). M.M. 10 '482 at 17°.

References .- DI-BROMO- and Oxy- PROPYL-

MALONIC ACID.

ISOPROPYL-MALONIC ALDEHYDE NI-TRILE PrCH(CN).CHO. (137°). V.D. 3.83 (calc. 3.87). S.G. 15 911. Formed by heating iodoisovaleric aldehyde with KCy or AgCy (C'autard, A. Ch. [6] 16, 188). Oil which reduces Fehling's solution. Miscible with alcohol and ether.

n-PROPYL MERCAPTAN PrSH. Mol. w. 76. (68°) (Roemer, B. 6, 784 sh Schatzmann, A. 261, 7). Formed from PrBr and alcoholic KSH. Oil, smelling like mercaptan. Hg(SPr).

Isopropyl mercaptan PrSH. (57°-60') (Henry, B. 2, 495; Claus, B. 5, 659; 8, 532). Formed from PrI and alcoholic KSH. Hg(SPr)2: white plates (from alcohol).

PROPYL-METHANE is BUTANE.

Di-propyl-methane v. HEPTANE. DI PROPYL TRIMETHYLENE TRISUL.

PHONE CPr₂ SO₂ CH₄ SO₂. [297°]. Formed

from sodium trimethylene trisulphone and PrI in alcohol (Camps, B. 25, 244). Slender needles, m. sol. boiling alcohol.

Hexa - propyl . trimethylene trisulphone CPr₂ SO₂ CPr₂ SO₂. [133°]. Formed from the trisulphone, PrI, and alcoholic NaOH Prisms. (Camps).

ISO-PROPYL-NAPHTHALENE C13H1, i.c. C₁₀H,Pr. (265°). V.D. 5·85. Formed by heating naphthalene with PrBr and AlCl₃ (Roux, Bl. [2] 41, 379; A. Ch. [6] 12, 289). Oil, sol. alcohol and benzene. Yields (β) -naphthoic acid on oxidation.-B'C,H,N,O,. [90°]. Lemon-yellow

PROPYL NITRATE PrNO, (110.5°) (Perkin, C. J. 55, 683). S.G. 15 1.0031; 22 1.0531. M.M. 4.085. Formed by distilling n-propyl alcohol with HNO, and a little urea (Wallach a. Schulze, B. 14, 420). Forms with anthracene C₁,H₁₀PrNO₃ [92°] crystallising in four-sided prisms (Perkin, jun. a. Mackenzie, C. J. 61, 866).

Isopropyl nitrate PrNO, (102°). S.G. 2 1.054 (Silva, A. 154, 256).

Reference.—Chloro-isopropyl nitrate. PROPYL NITRITE Pro.NO. (43° $(43^{\circ}-46^{\circ})$ (Cahours, C. R. 77, 749); (53°-60°) (Pribram a. Handl, M. 2, 655). S.G. 21 935 (C.); § 998 (P. a. H.). Formed by passing nitrous acid gas into n-propyl alcohol.

(44°). Isopropyl nitrite PrNO, (44°). S.G. 2 *856; 25 844 (Silva, Bl. [2] 12, 227; Kissel,

J. R. 1882, 226).

PROPYL ψ -NITROLE C,H,N,O, i.e. CH, C(NO₂)(NO) CH, Mol. w. 118. [70°] (Bewad, B. 24, 976). Formed by adding KNO₂ and dilute H.SO, to an alkaline solution of isonitro-propane CHMo, NO, (V. Meyer a. Locher, B. 7, 670; A. 175, 120). Monoclinic crystals, insol. water and alkalis. Forms a blue liquid when fused. Its solutions in alcohol and chloro-

form are blue. PROPYL-NITROLIC ACID C.H.N.O. CH3.CH.CH(NO2)NO or CH3.CH.C(NO2):NOH. [60°]. Formed by adding potassium nitrite and dilute H₂SO₄ to an alkaline solution of nitropropane CH₂CH₂CH₂NO₂. Formed also from Et.CBr₂NO₂ and hydroxylamine (V. Meyer, B. 7, 670; 9, 395). Prisms, with sweet taste, v. sol. water, alcohol, and ether. Alkalis form a deep-red solution. Conc. H.SO, forms propionio acid and N.O.

PROPYL OCTYL OXIDE Pr.O.C.H ... (207°

S.G. © 8039. C.E. (0°-10°). ·00101. S.V. 272·4 (Dobriner, A. 243, 7). DI-PROPYL OXIDE Pr₂O. Propyl ether. (90.7° i.V.). S.G. 9.7633 (Zander, A. 214, 163). C.E. (0°-10°) .00125 (Dobriner, A. 243, 20). S.V. 150.9. Formed from PrI and KOPr (Chancel, A. 151, 304). Got also from PrI and Ag₂O (Linnemann, A. 161, 37) and by heating n-propyl alcohol with H.SO, at 135° (Norton a. Prescott, Am. 6, 243).

Di-isopropyl oxide Pr.O. (68.8° i.V.). S.G. (7435. C.E. (0°-10°) (00130. S.V. 151.6 $^{\circ}$ 7435. C.E. $(0^{\circ}-10^{\circ})$ $^{\circ}$ 00130. S.V. 1516 ander). Got from PrI and Ag₂O (Erlenmeyer, (Zander).

A. 126, 306). PROPYL OXYBUTYL KETONE

C3H7.CO.CH(OH).C3H7. Butyroin. (180°-190°). Formed from di-n-propyl diketone and alcoholic KOH (Klinger a. Schmitz, B. 24, 1273). Yields a phenyl-hydrazide | 135°].

PROPYL-PHENOL v. CUMENOT

PROPYL-PHENOL CARBOXYLIC ACID v. OXY-CUMINIC ACID.

Isopropyl-phenol dicarboxylic acid

C.H.Pr(OH)(CO2H)2. [295°]. Formed, together with oxy-cuminic acid, by the action of Na and CO. on isopropyl-phenol (Fileti, G. 16, 126). Tables or needles, sol. water and alcohol.

p-PROPYL-PHENYL-ACETIC ACID C₂H₁.C₆H₁.CH₂CO₂H. [52°]. Formed by saponifying the nitrile, which is got from e-chloro-cymene, alcohol, and KCy at 100° (Rossi, A. Suppl. 1, 139). Small needles (from hot water). - AgA': slender needles.

References .- AMIDO- and OXY-PROPYL-PHENYL-ACETIC ACID.

PROPYL-PHENYL-AMINE v. AMIDO-PHENYL-PROPANE and PROPYL-ANILINE.

ISOPROPYL-PHENYL- v. CUMYL-

ISOPROPYL-PHENYL-CINNAMIC ACID Pr.C.H..C(CHPh).CO.H. [184°]. Formed from Pr.C.H., CH., CO., Na, benzoic aldehyde, and Ac. O (Magnanini, G. 15, 509). Needles (from dilute alcohol).—CaA',.—AgA'.

ISOPROPYL: PHENYL.—COUMARIC ACID.

Methyl derivative

Pr.C.H.,C(CO,H):CH.C.H.,OMe. [199°]. Formed from Pr.C.H.,CH.,CH.,CO,Na, anisic aldehyde, and Ac.O (Magnanini, G. 15, 511). Prisms (from

alcohol).—AgA'. DI-p-PhOPYL - DI - PHENYL - CYANAMIDE C(N.C.H.Pr), [168°]. Formed by heating

CS(NH.C.H.Pr), with benzene and PbO (Francksen, B. 17, 1228). Needles.
PROPYL-BENZONITRILE v. Nitrile of Cv-

MINIC ACID.

ISOPROPYL - DI - PHENYL - ETHYLENE C.H., CH:CH.C.H.Pr. [84°]. Formed by heating phenyl-acetic acid with cuminic aldehyde and NaOAc at 250° (Michael, Am. 1, 314).

Scales (from alcohol), v. sl. sol. hot water.

DI -p - PROPYL - DIPH ENYL - GUANIDINE

NH:C(NH.C₄H₄Pr), [113°]. Formed by heating
di-propyl-di-phenyl-thio-urea with alcoholic NH₄ and PbO (Francksen, B. 17, 1225). Needles, v. sol, warm alcohol and ether .- Platinochloride (C₁₀H₂,N₃) II.PtCl₃: yellowish brown pp. Tri-propyl-tri-phenyl-guanidine

C.H.PrN:C(NH.C.H.Pr). Formed by heating CS(NH.C.H.Pr). with C.H.Pr.NH., alcohol, and Amorphous resin, v. sol. alcohol. -

B'2H2PtCl6: brown powder.

pm.PROPYL-PHENYL METHYL KETONE CH₃.CO.C₆H₄Pr. (259° i.V.). S.G. ¹⁵/₂ 979. Formed from n-cumone, AcCl, and AlCl, (Widmann, B. 21, 2224). Colourless liquid. Yields mann, B. 21, 2224). Colourless liquid. an oxim [540], which melts at 440 after fusion. The phenyl-hydrazide [92°] forms six-sided hatchet-shaped tables.

Isomeride CH3.CO.C6H4Pr. (253°). Yields an oxim [71°] and a phenyl-hydrazide [82°]. ISOPROPYL PHENYL PHOSPHATE

PO(O.C, H, Pr), (375° 380° at 280 mm.). from isopropyl-phenol and PBr, (Fileti, G. 16, 130). Viscid liquid, insol. water, sol. alcohol.

p-ISOPROPYL-(Py. 3)-PHENYL-QUINOLp. 180 FROT IL-(1 y. ... CH; CH; CH; CH; CH; Pr. ... C Formed by heating its carboxylic acid with sodalime (Döbner, A. 249, 102). Needles, sl. sol. water. — B'₂H₂PtCl₃ 2aq. — B'₂H₄Cr₂O₅, — Picrates: [195]; plates (from alcohol).

Carboxylic acid $C_bH_i < \frac{C(CO_2H):CH}{N} = \frac{C.C_0H_iPr.}{C.C_0H_iPr.}$ [201°]. Formed from cuminic aldehyde, pyruvic acid, and aniline (Döbner). Yellow plates (from HOAc). -AgA': white powder.

p-PROPYL-PHENYL-THIOCARBIMIDE C.H.Pr.N:CS. (263°). Formed by heating dipropyl-di-phenyl-thio-ures with syrupy 11,100, (Francksen, B. 17, 1223). Oil, volatile with steam, v. sol. alcohol and ether.

p-PROPYL-PHENYL-THIO-UREA $C_{i0}H_{11}N_2S$ i.e. NH, CS.NH.C.H.Pr. [159°]. Formed from amido-phenyl-propane hydrochloride and ammonium sulphocyanide (Francksen, B. 17, 1222). Needles, sol. alcohol and ether.

Di-propyl-di-phenyl-thio-urea

CS(NH.C,H,Pr), [138°]. Formed from amidophenyl-propane, CS, and alcohol (F.). Plates.

PROPYL-PHENYL-UREA C₁₀H₁₁N₂O i.e. NH., CO.NHC₀H₁Pr. [143°]. Formed by the action of potassium cyanate on amido-phenyl-propane hydrochloride (Francksen, B. 17, 1225). Plates, sol. hot alcohol. insol. water.

Di-p-propyl-di-phenyl-urea CO(NHC,H,Pr), [205°]. Formed by heating amido-phenyl-propane with urea. Formed also by the action of COCL on amido-phenyl-propane in benzene, and by heating amido-phenyl-propane sulphate with a saturated solution of potassium cyanate. Needles, v. sol. ether and hot alcohol.

PROPYL PHOSPHATE PO(OPr), Formed, together with PrCl and PO(OH) (OPr) (which is sol. water) by the action of PCl, on n-propyl alcohol (Winssinger, Bl. [2] 48, 111). Oil. sl. sol. water, its insolubility being greatest at 75°. Cannot be distilled, even in vacuo.

ISOPROPYL PHOSPHINE PrPH, Formed, together with Pr.PH (118°) and Pr.P. by heating PrI with PH,I and ZnO for 6 hours at 100° (Hofmann, B. 6, 292). Liquid, with penetrating odour. Readily absorbs oxygen, taking fire on a hot day. - B'III : decomposed by water.

Tri-isopropyl-phosphine Pr.P. Oil. Forms red crystals with CS₂. -Pr₃PHI. Large crystals, v. sol. water. -Pr₄PI. Cubes or octahedra.

Di-chloro-isopropyl-phosphine PrPCl. 135°). Formed by heating HgPr, with PCl, (Michaelis, B. 13, 2175). Liquid.

Reference. - OAY-TRI-PROPYL-PHOSPHINE.

(240°). PROPYL PHOSPHITE P(OPr). S.G. 15 1.004. Formed from PCl, and NaOPr (Jachne, A. 256, 282). Liquid. •

ISOPROPYL ISOPHTHALIC ACID C, H, Pr(CO, H), [1:3:5]. [285°]. Formed by heating pyruvic acid with isobutyric aldehyde and Ba(OII)₂ (Doebner, B. 23, 2380; 24, 1748). Plates (from dilute alcohol, v. sl. sol. cold water).

—ВаА" 2 јаq. —СаА" 2 јаq. —Ад₂А" аq. PROPYL PHYCITE. According to Fauconnier (C. R. 107, 629), the substance described under this name by Carius (A. 134, 71) is glycerin.

PROPYL-PIPERIDINE v. PROPYL-PYRIDINE HEXARYDRIDE.

PROPYL-PROPANE v. HEXANE.

(a)-PROPYL-PYRIDINE C,II,1N i.s.

N CH. CH CH. Conyrine. (168°). Formed by distilling coniine hydrochloride with zincdust (Hofmann, B. 17, 825; Ladenburg, A. 247, Light oil, with blue fluorescence. picolinic acid [134°] on oxidation. Reduced by conc. HIAq at 290°. to conline. -B'2H2PtCl. [160°] and [172°]. Orange monoclinic tables. a:b:c = 1.0622:1:1.5356; $\beta = 87^{\circ}$ 13′.—B'MeI. Oil. -B'2Me2PtCle. Crystals, sl. sol. water.

Tetrahydride NII CII, CH, CH, CH₂-CH₂-CH₂-CH₂-CH₂-This is (γ)-coniceine (vol. ii. p. 248). Yields conline on reduction with tin and HCl (Lellmann a. Müller, B. 23, 680).

Hexahydride NH CH, CH, CH, CH, Inactive coniine. (167°). S.G. 9 .8626. Formed by reducing (a)-allyl-pyridine (derived from (a)methyl-pyridine and paraldehyde) in alcoholic solution with sodium (Ladenburg, B. 19, 2579; A. 217, 80). Oil, optically inactive. Can be separated by means of the acid tartrate into a dextro- modification (contine) and a lavo- modidextro- moduleativi (color) (L.); [213°] (L.) a. M.). V. sol. water.—B'₂H.PtCl₂.—B'₂H.Cdl₄. [118°]. (β) Propyl-pyridine N CH.CH. CH. Col-

lidine. (170°). Got by passing nicotine through a red hot tube (Cahours a. Etard, J. 1881, 928). Yields nicotinic acid on oxidation.

(a) - Isopropyl - pyridine NCH .CH >CH. (159°). S.G. 2 .9342. Formed, together with the (7)-isomeride, by heating pyridine with PrI and PrI at 290° (Ladenburg, B. 17, 772, 1121; 18, 1587; A. 247, 22). Liquid, with unpleasant 15, 1051; A. 221, 221. Inquia, with unpressant odour, sl. sol. water. Gives picolinic acid on oxidation with KMnO₄.—B'₂H₂PtCl₆. [170°]. Hexagonal rhombohedra, a:c=1:9489.—B'HAuCl₄. [91°].—B'C₆H₂N₄O₇. [116°]. Needles. Mercuric chloride double sglt: [90°].—

B'MeAuCl₄. [128°]. Tetra-hydride C₈H₁₅N. (164°). S.G. 2 896. Formed from the hexahydride, Br. and NaOHAq (Ladenburg, B. 20, 1646).—B'₂H₂PtCl₆. [189°]. Tables.

Hexahydride C.H., N i.e. NH CH₂ .CH₂ CH₂ CH₂ (159°). S.G. 2 ·8668. Formed by reduction in alcoholic solution by Na (Ladenburg, A. 247, 73). Liquid, more sol. cold than hot water. Converted by MeI into NMe CH₂ .Ch₂ CH₃ (167°). $(C_8H_{17}N)_2CS_2$ [105°]. — B'HCl. [210°]. metrie prisms; a:b:c = 814:1: 419. — B'HBr. [233°].—B'HI. [243°].—B'₂H₂PtCl₃. [193°]. Monoclinic prisms; a:b:c=·977:1:1·385; β = 89° 88'.—*Β',Η,CdI,. [133°].

v-Propyl-pyridine hexahydride

NPr CH, CH, CH, (149°-150°). Formed from piperidine and PrI (Ladenburg, B. 14, 1348). Liquid .- B'2H2SnCI : monoclinic crystals.

v-Isopropyl-pyridine hexahydride

NPr CH, CH, CH, -B', H, SnCle: monoclinic orystals (Hjortdahl, J. 1882, 1085).—B'2H2PtCla.

(γ) · Isopropyl · pyridine N CH:CH CPr. (178°). S.G. 2 .9439. Formed as above, being separated by means of the platinochloride, which is more soluble than that of the (a)-isomeride. Oil. Yields isonicotinic acid [305°] on oxidation.—B'2H2PtCl6. [205°]. Plates.

NH CH, CH, CH, CHPr. Hexahydride (171°). Formed by reducing (γ)-isopropyl-pyridine in alcoholic solution by Na. Funning liquid, v. sol. cold water.—B'₂H₂PtCl₂. [172°]. Golden prisms, sl. sol. water.

References. - OXY-PROPYL-PYRIDINE and OXY-

PROPYL-PIPERIDINE. PROPYL PYRIDYL KETONE v. PYRIDYL

PROPYL KETONE. PROPYL PYROGALLOL C,H,O, i.e. C,H,Pr(OH), [80°]. Got by heating its dimethyl ether with conc. HClAq at 130° (Hotmann, B. 8, 67; 11, 329). Prisms (from benz-ene), v. e. sol. water and alcohol. FeSO, colours

its aqueous solution blue (Pastrovitch, M. 4, 182).

its aqueous solution blue (Pastrovitch, M. 4, 182).

Methyl ether C₂H_Pr(OH)₂(OMe). (290°
cor.). S.G. 18 1-023. Occurs, together with the di-methyl ether, in beech-wood tar (Pastrovitch). Oil, with smoky smell. Gives an intense bluish-green colour with FeCl₂ in alcohol.—C₂H_Pr(OK)₂(OMe). Pearly crystals (from dilute alcohol).—C₂H_Pr(OAc)₂(OMe). [83°]. Needles (from alcohol).—C₃Br₂Pr(OAc)₂(OMe). [79°]. Golden needles.

Di-methyl ether C.H.Pr(OH)(OMs). Picamar. (c. 286° cor.). Occurs in beech-wood tar (Reichenbach, A. 8, 224; Niederist, M. 4, 487). Oil, with bitter, burning taste. Reduces salts of Au and Ag. Yields the di-methyl ether of di-oxy-quinone on oxidation .- C11H18O3K. Pearly leaflets (from spirit).—C₁₁H₁₈AcO₄. [87°]. Monoclinic prisms; a:b:c=39:1: 547; B Petry leaders (100 prisms; a:b:c='39:1:'547; B Monoclinic prisms; a:b:c='99:...'G₁H₁₃Br₂AcO, [101°]. Trimetric prisms; a:b:c='99:1:1:'93.-C₁H₁BzO₂. [91°]. Trimetrio

Tri-methyl ether C.H.Pr(OMe). (164°). Formed from propyl-pyrogaliol and MeI (Will, B. 21, 2020).

n-PROPYL-PYRROLE C,H, N i.s.

NPr CH:CH. (147°). Formed from potassium

pyrrole and PrI (Zanetti, B. 22, 2518). Liquid. Isopropyl-pyrrole C,H,PrN. (174°). Formed by boiling pyrrole with acetone and ZnCl₂ (Dennstedt a. Zimmermann, B. 20, 851; 21, 1480). Liquid. Dry HCl passed into its ethereal solution forms (C,H₁₁N)₂HCl, a crystalline salt yielding a liquid base (c. 287°) and a picrate (C,H₁,N₂C,H₁N₂O, [146°]. Ac₂O forms C,H₁!r:NAc (222°-232°) and C,H₂AcPr:NH [64°] (251°).

ISOPROPYL-PYRRYL STYRYL KETONE NHC, H.Pr.CO.CH:CHPh. [143°]. Formed by boiling NHC, H.Pr.CO.CH, with benzoic aldehyde and dilute KOHAq (Dennstedt a. Zimmermann, B. 20, 853). Yellow crystals.

(B. 3)-ISOPROPYL-QUINOLINE C, H, N i.e. CH:CH.C.CH:CH Cumoquinoline. CPr:CH.C.N = CH by heating (Py. 3)-chloro-isopropyl-quinoline with a solution of HI in HOAc (Widman, B. 19, with a solution of ri ii in lock (Widman, B. 13, 267). Oil, easily volatile in steam.—Salts: B'2H_PtCl_2aq. [220°].—Piorate: [206°].—Chromate: [c. 92°]. Large red prisms.

Methylo-locked B'Mel. [c. 200°].

(Py. 2).Isopropyl-quinoline C_cH₄CH₇CPr. [c. 10°]. (275°-280°) at 715 mm. Formed by distilling its (Py. 3)-carboxylic acid (Spady, B. 18, 3383). Liquid, v. sol. alcohol and ether.—B'₂H₂PtCl₈.—B'₂H₂Cr₂O₄.— B'C,H,N,O,: long slender needles.

(Py. 3)-Isopropyl-quinoline C_8H_4 N = CPr(255°). Formed by heating its (Py. 1)-carboxylic acid with soda-lime (Doebner, B. 20, 279; A. 242, 279). Oil, smelling like quinoline. B' H.PtCl, 2aq: yellow needles.—B'C.H.N.O.,. [150°]. Yellow plates (from alcohol).

Reference.-CHLORO- and OXY- ISOPROPYL-

QUINOLINE.

(Py. 2)-ISOPROPYL-QUINOLINE (Py. 8)-CARBOXYLIC ACID C.H. CH:CPr [189°]. Formed by oxidation of (Py. 2,3)-isopropyl-isobutyl-quinoline with CrO₂ and dilute H₂SO₄ (Spady, B. 18, 3379). Plates (from dilute alcohol).—AgHA',HNO₂.—(HA'),H,PtCl₂: prisms.

(Py. 3)-Isopropyl-quinoline (Py. 1)-earboxylic acid C₂H₂C(CO₂H):CH₂C(P₂C). [146°]. Formed, together with C,H,N,O [222°], by adding aniline to an alcoholic solution of isobutyric aldehyde and pyruvic acid (Doebner, A. 242, 276; B. 20, 279). Prisms (containing 1;aq).

lemon-yellow needles .-- AgA'.

PROPYL SILICATE Si(OPr). (226°). S.G. 12 .915 (Cahours, C. R. 76, 1383). On heating On heating with SiCl, at 160° it yields (PrO), SiCl (209°) and (PrO), SiCl, (187°).
DI-PROPYL-DI-STYRYL KETONE

(C,H,C,H,CH:CH),CO. [106°]. Formed from cuminic aldehyde, acetone, alcohol, and NaOHAq (Claisen a. Ponder, A. 223, 148). Prisms.

ISOPROPYL-STYRYL-PHENOL. ether. C.H.Pr.CHICH.C.H.OMe. [152°]. Gob by heating C.H.Pr.C(CO₂H); CH.C._eH₄OMe (Magnanini, G. 15, 513). Pearly scales (from alcohol). PROPYL-SUCCINIC ACID C.H.₁₂O₄ i.e. CO₂H.CH₂.CHPr.CO₂H. Oxy.hexic acid. [92°].

Formed by heating pentane tri-carboxylic acid (Waltz, B. 15, 608; A. 214, 59). Got also by reducing oxy-hexic acid with zinc and H.SO, (Gorboff, J. R. 1887, 605; Walden, B. 24, 2036).
Iso-propyl-succinic acid v. Pimelic acid.

Di-isopropyl-succinic acid C_{1e}H_{1e}O₄ i.e. CO₂H.CHPr.CHPr.CO₂H. [168°]. The ether is formed from a-bromo-isovaleric ether and finelydivided silver (Hell a. Mayer, B. 22, 48). Dendritic crystals (from water).—BaA" 5aq. S. 7-7 at 17°.—CuA" aq. S. °099 at 24°.—SrA" 3aq.—CaA" 4aq.—MgA"7aq.—CoA" 7aq.—NiA" 5aq.—CdA" 4aq.—MnA" 7aq. S. 4.71 at 21°.—ZnA".

—PbA".—Ag,A". S. °062 at 20°.

Tamparid. C. H. O. (2000).

Isomeride $C_{10}H_{18}O_4$. [200°]. Accompanies preceding acid. Granular crystals. the preceding acid. Granular crystals. — BaA"2aq.—SrA"4aq.—CaA"2aq.—MgA"5aq.— MnA" 3aq - NiA" 4aq. -- CuA" 3aq. -- CdA" 3aq.

-ZnA".-PbA".-Ag₂A".

Reference. - OXY-PROPYL-SUCCINIC ACID. TETRA-PROPYL-SUCCINIMIDINE C, H, N,

i.e. CH:C(NPr₂) N. Got from succin-imido-CH, C(NPr₂) N. Horizond alcohol at ethyl ether hydrochloride, NHPr., and alcohol at 50° (Pinner, B. 23, 2930).—B'2HNO, [53°].— B'₄H.PtCl. [174°]. Needles, sl. sol. hot water. PROPYL SULPHATES.

Propyl sulphuric acid Pro.So..OH. Formed arom propys atconol and H₂SO₄ (Chancel, C. R. 87, 410). — KA': needles, v. sol. water. — BaA'₂ 8aq (Schmidt, Z. 1870, 576).
Di-propyl sulphate Pr₂SO₄. Formed from propyl alcohol and CISO₂OH (Mazurowska, J. pr. [2] 18, 162). Oil. from propyl alcohol and H₂SO₄ (Chancel, C. R.

DI-n-PROPYL SULPHIDE Pr.S. (Winssinger, Bl. [2] 48, 109). S.G. 17 ·814 (C.). Occurs in raw petroleum (Mabery a. Smith, \hat{B} . 22, 3303). Formed by heating K2S with PrCl or Pri in alcohol (Cahours, C. B. 76, 133). Fetid oil. Brome-acetic acid forms the acid Pr.SBr.CH.CO.H. which yields Pb.A'Br, and Pb2A'Br3 (Letts, Tr. E. 28, 586).

Compounds with platinum salts (Blomstrand, J. pr. [2] 38, 354, 408).— (Pr.S).PtCl. Occurs in three varieties: (a) [46°] S. (alcohol) 15°6 at 15°, (a) [66°], and (γ) [63°]. Alcoholic KOH (1 mol.) acting on the (a)-com-Alcoholic ROH (1 mol.) acting on the (a)-compound forms crystalline (Pr.S),Ptcl(OH).—

(Pr.S)(Et,S)PtCl.; syrup.—(Pr.S),Pt.Cl., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [185°].—(Pr.S),PtBr., [181°].—(Pr.S),PtJ., [181°].—(Pr.S),PtJ.

HAHG. — (HA), H.PtOl, aq. — (HA'), HAuCl.; | [210°] and [195°].—(Pr,S), Pt(NO,), Occurs in [210°] and [195°].—(Pr.B),Pt(NO₁).—Occurs in two varieties, an oil and a crystalline body [70°] which yields (Pr.S),Pt(NO₂)(OH) [145°].— (Pr.S),PtCrO₂. Bod prisms (from chloroform). (Pr.S),PtC₂O₄: crystalline pp.—(Pr.S),Pt(SON₂: yellow pp.—(Pr.S),PtOl,HgCl₂. [82°]. Trimetrie crystals, a:b:c=:554:1::591.

Propylo-iodide SPr.I. Yields the compound (SPr.Cl).PtCl, (Cahours).

Isopropyl sulphide Pr.S. (121° i.V.). Formed by distilling PrI with alcoholic K.S (Henry, B. 2, 495; Beckmann, J. pr. [2] 17, 459). Oxidised by KMnO, to Pr.SO, [36°]. Yields Pr.SHgOL.

by Kand, to Fr₂SO₂ [30°]. Items Fr₂SI₃GU₂ Compounds with salts of platinum (Blomstrand):—(Pr₂S)₂PtCl₂. [163°].— (Pr₂S)₂PtBr₂. [174°].—(Pr₂S)₂Ptl₃. [176°].—(Pr₂S)₂Pt(SON)₂. [102°].—(Pr₂S)₂Pt(NO₃)₂. Prisms, decomposing at 210°.—(Pr₂S)₂PtI₄, [189°]. Di-propyl disulphide Pr.S. (193°). (Spring a. Legros, B. 15, 1940)

Di-isopropyl disulphide Pr.S. (175°). A product of the action of Na and MeI on isopropyl mercaptan in ether (Obermeyer, B. 20, 2928).

PROPYL SULPHOCYANIDE PISCN. (163°). Liquid (Schmidt, Z. 1870, 576).

Isopropyl sulphocyanide PrSCN. (Henry, B. 2, 496); (153°) (Grlich, A. 178, 90). S.G. 2º 963. Formed from PrI and potassium sulphocyanide. Liquid, decomposed by boiling water. H₂S yields NH₂.CS₂Pr [97°].

DI-n-PROPYL SULPHONE Pr₂SO₂.

Formed by oxidising Pr.SO (Winssinger, Bl. [2] 48, 111). Scales, sol. water, alcohol, and ether Volatile with steam.

Di-isopropyl sulphone Pr., SO., [36°]. Got by oxidising Pr., S with KMnO. (Beckmann, J. pr., [2] 17, 459). V. sol. water and HClAq. Not

affected by reducing agents.
DI-PROPYL SULPHONE DICARBOXYLIC ACID SO. (CHEt.CO.H). Sulpho-dibutyric acid. [152°]. Formed from SO. (CH. CO.Et), Et1. Dimetric and NaOEt (Lovén, B. 17, 2817). octahedra.

Di-isopropyl sulphone dicarboxylic acid SO₂(CM₂,CO₂H)₂, [188°]. Formed from SO₂(CH₂,CO₂Ht)₄ (1 mol.), MeI (4 mols.) and NaOEt (4 mols.) (Lovén, B. 17, 2824).

DI.PROPYL SULPHOXIDE Pr.SO. [15°].

Got by oxidising Pr.S with dilute HNO. (S.G. 1.2) (Winssinger, B. 16, 329; Bl. [2] 48, 110). Needles, sol. water, alcohol, and ether. Decomposed by heat. Readily reduced to Pr.S. Calcium nitrate forms (Pr2SO),5Ca(NO2)2, a fibrous mass [80°].

B-ISOPROPYLTHIENYL ETHYL KETONE C,H,PrS.CO.C,H,. (251°). Formed from (\$). isopropyl-thiophene, propionyl chloride, and AlCl, (Thiele, A. 267, 136). Oil, volatile with steam. Appears to yield isopropyl-thienyl-glyoxylic acid on oxidation with alkaline KMnO

PROPYL THIENYL PLYOXYLIC ACID C,H2PrS.CO.CO,H. Formed by oxidising propyl thienyl methyl ketone with alkaline KMnO. (Ruffi, B. 20, 1745). Solid.—AgA'.
PROPYL-THIENYL METHYL KETOME

C.H.Prs.CO.CH., (255°). Formed by the action of AcCl and AlCl, on a solution of (a)-propylthiophene in ligroin (Ruffi, B. 20, 1744). Liquid. Yields an oxim [55°] and a phenyi-

Isopropylthienyl methyl ketone

C.H.Prs.CO.CH. (237°). Formed from iso-propyl-thiophene, AcCl, and AlCl, (Thiele, A. 267, 187). Oil. Yields a crystalline oxim and phenyl-hydrazide.

PROPYL-DI-THIO-BIURET C,H,1N,S, i.e. NH2.CS.NH.CS.NHPr. [121°]. Formed from sodium cyanamide and propyl-thiocarbimide (Hecht, B. 25, 754). Crystalline mass, v. sl. sol.

cold water.

PROPYL-THIOCARBIMIDE PrN:CS. (153°). S.G. % 9909; 89 8924. Formed from propylamine and CS₂ followed by HgCl₂ (Hecht, B. 23, 281. 1662). Pungent liquid, al. sol. water, miscible with alcohol and ether. Sodium cyanamide and alcoholic MeI form NHPr.CS.NCyMe [115°]. In the same manner may be prepared MHPr.CS.NCyEt [56°], MHPr.CS.NCyC₂H₅ [50°], NHPr.CS.NCyC₂F₆ [50°] erystallising in needles, and NHPr.CS.NCy.CH₂Ph [113°].

Isopropyl-thiocarbimide PrN:CS.

Pungent liquid (Jahn, M. 3, 168).

PROPYL DI-THIO-CARBONATE Pro.CS.SH. Unstable oil.—Pro.CS.SK. Formed from CS. and KOH dissolved in propyl alcohol (Scala, G. 17, 78). Silky needles. Its aqueous solution gives an orange pp. with CuSO₄. Iodine forms oily (Pro.CS)₄S₂ decomposing at 180°. – Pro.CS.SMe. (202°). Oil.—Pro.CS.SEt. (216°).

(a)-PROPYL-THIOPHENE C.H.PrS. (158° cor.). S.G. 16 974. Formed from iodo-thio-phene, PrBr, and Na (Meyer a. Kreis, B. 17, 1561). Oil. Yields (a)-thiophenic acid on oxidation.

Isopropyl-thiophene C_4H_3PrS . (154° cor.). S.G. 19 9695. Formed from PrBr, thiophene, and AlCl, (Schleicher, B. 19, 672). Oil with powerful odour. With HOAc, phenanthaquinone, and H2SO4 it gives a deep violet colour.

\$-Isopropyl-thiophene CH:CH S.

Formed by distilling sodium isopropyl-succinate with P.S. (Thiele, A. 267, 133). Oil, smelling like benzene, insol. water, miscible with alcohol. ether, and benzene. Forms C3H, C4H2S.HgCl [137°] crystallising from alcohol in white needles, and C,H,.C,HS(HgCl)2 as white grains, insol. alcohol (Volhard, A. 267, 183).

References. — Bromo-, Iodo-, and Nitro-

PROPYL-THIOPHENE.

PROPYL-THIOPHENE CARBOXYLIC ACID C.H.PrS.CO.H. [57°]. Formed from iodopropyl-thiophene, ClCO,Et, and sodium-amalgam; the product being saponified by alcoholic potash (Ruffi, B. 20, 1743). Needles (from warm water), or plates (from dilute alcohol).
PROPYL THIOSULPHATE.

Prs.SO, Na 5aq is made from Na, S,O, and PrI

(Spring a. Legros, B. 15, 1938). PROPYL-THIO-UREA NHPr.CS.NH₂. [110°]. Formed from propyl-thiocarbimide and NH Aq in the cold (Hecht, B. 23, 283). Four-sided plates, sol. alcohol.

Isopropyl-thio-urea NHPr.CS.NH2. [157°].

Plates (Jahn, M. 3, 168).

Di - propyl - thio - urea CS(NHPr)2. Formed in the preparation of propyl thiocarb-

imide. Pearly plates (from water).

Di-isopropyl-thio-urea CS(NHPr)2. [1619]. Reedles (from hot water) (Juhn).

PROPYL-TOLUENE v. CYMENE.

PROPYL-TOLUIC ACID v. CYMENE CARBOXYLLC

n-PROPYL-p-TOLUIDINE C10H15N C₀H₁Me.NHPr. (232°). S.G. $\frac{32}{2}$ 9296. $\mu_{\rm D}$ = 1.5367. S.V. 197.53. R_{∞} = 82.5. Formed by heating *p*-toluidine (1 mol.) with PrI (1 mol.) for two days at 160°; the yield being 90 p.c. of the theoretical amount (Hori a. Morley, C. J. 59, 36). Purified by means of the nitrosamine. Oil. Salts.-B'HCl. [151°]. Needles (from boiling benzene), v. sol. water and alcohol .-- B'H2C2O4. [173°]. S. (alcohol) 1.4 at 21°. Ppd. on mixing alcoholic solutions of the base (1 mol.) and oxalic acid (1 mol.). Sl. sol. cold water and alcohol.—B'_HI_C_O_. [117°]. Occurs in the filtrate from the preceding salt, and formed also when a large excess of base is added to a cold alcoholic solution of the acid oxalate. Crystals, m. sol. cold water and alcohol. Decomposed by boiling water, B'H,C,O, being ppd.—B',H,FeCy.

Nitrosamine C,H,Me.NPr.NO. Oil, not

solid at -20°. Decomposes below 100° Isopropyl - p - toluidine C₀H₁Me.NPr.NO. (220° uncor.). S.G. ²³ 9129. $\mu_{\rm b}=1.5322$. S.V. 199.57. $\rm R_{\odot}$ 81.4. Formed by heating PrI with p-toluidine for two days at 130° (Hori a. Morley, C. J. 59, 34). Got also by heating diazotoluene toluide C.H., N., NHC, H., with alcoholic NaOEt and PrI for 5 hours on the water-bath,

distilling off the alcohol, pouring into water, and

decomposing the pp. with HCl. Oil.
Salts. - B'HCl. [171°]. Wax-like crystals. (from alcohol) or needles (from benzene), v. sol. water.—B₂H.G.O₄, [130°]. S. (alcohol) 5.76 at 22°. Crystals (from dilute alcohol). The acid

oxalate is not easily crystallisable.—B.H.FeCy,
Nitrosamine C.H.Mo.NPr.NO. [59°]. S.
(alcohol) 65 at 22° Yellowish crystals (from

alcohol), not volatile with steam.

Reference .- OXY-PROPYL-TOLUIDINE. PROPYL UREA. NH. CO.NHPr. Formed from propyl cyanate and NH3, and from potassium cyanate and propylamine sulphate (Chancel, Bl. [3] 9, 101). Long needles, sol. water and alcohol. Its oxalate and nitrate are v. sol. water. Decomposed by HClAq in a sealed tube at 160° into NH, NH, Pr, and CO, Butyryl derivative NHPr.CO.NH(CO.C, H.). [99°]. Formed by the action of cold KOHAq on a mixture of butyramide (2 mols.) and bromine (1 mol.) (Hofmann, B. 15, 757). Colourless plates, sl. sol. water.

Isopropyl-urea. Isobutyryl derivative NHPr.CO.NH.COPr. [86°]. Formed in like manner from the amide of isobutyric acid.

Tables, sol. alcohol and ether.

NH, CO.NPr, u-Di-propyl-urea Formed from dipropylamine and KCyO. Needles (from alcohol). Its oxalate crystallises in needles, sl. sol. water.

s-Di-propyl-urea CO(NHPr)2. [105°]. (255°). Got by boiling the corresponding thio-urea with HgO and water (Hecht, B. 23, 285), or from PrCyO and aqueous NH_Pr. White plates (from water). Sl. sol. cold water, v. sol. alcohol and ether. Its salts are decomposed by water.

Di-propyl-urea C,H₁₈N₁O i.e. NH₂-CO.NPr₂

[76°]. Formed from propylamine sulphate and potassium cyanate (Von der Zande, R. T. C. 8, 228). Needles. An ethereal solution of aldehyde forms CH, CH(NH.CO.NPr.); [118°]. Chloral

hydrate gives CCl₂.CH(OH).NH.CO.NPr₂ [128°] called peptones, which after absorption undergo and in aqueous solution (C₂H₁₂N₂O)C.HCl₂O aq reconversion into proteids, [51°]. CEnanthol in ethereal solution gives Although much work has been done in at C,H₁₄(NH.CO.NPr₂), [113°].—B', H₂C₂O₄. [103°]. -B'C.H.N.O,. [135°].-B'2HNO.

s-Di-isopropyl-urea CO(NHI'r)2. Formed as a by-product in the production of isopropyl Na_aCO₄ (Hofmann, B. 15, 756). Needles, sol.

u-Di-isopropyl-urea NH_CO.NPr.. Formed by evaporating a solution of isopropylamine sulphate with potassium cyanate (Von der Zande, R. T. C. 8, 231). Crystals (from ether). An ethereal solution of aldebyde forms CH_xCH(NH.CO.NPr_x)_x[147°]. Chloral in ethereal solution gives CCl_x.CH(OH).NH.CO.NPr_x [121°]. $-B'_{2}H_{2}C_{0}$, [111°]. Nécdles. $-B'C_{e}H_{3}N_{3}O_{7}$. [134°]. Necdles. $-B'HNO_{1}$. [79°].

Reference.—DI-BROMO-PROPYL-UREA.

PROTAGON v. LECTTHIN.

PROTAMINE C₉H₂₁N₃O₃ or C₁₈H₃₁N₉O₄.

Occurs in the seminal substance of the salmon in November (Micscher, B. 7, 376; Piccard, B. 7, 1714). Gummy mass, insol. alcohol and ether, sol. water with alkaline reaction. Its salts give with K_sFeCy_s a milky pp. composed of minute drops. Salts.—(C₀H₁N₁O₀) H₂PtCl_s (M.); C_{1s}H₃₁N₁O₁H₂PtCl_s (P.). Yellow powder.

PROTEIDS. (Πρωτείου, 'pre-eminence.') This

name is given to a large group of organic compounds which are also known as 'albuminous.' The word 'proteid' itself has been retained simply as a convenient general term, and not as implying any adherence to the theory, first advanced by Mulder, that they all contain a complex molecule to which he gave the name of 'protein.' The word albumin is now limited to a certain class of proteids, and the word albuminoid. though it is still largely used synonymously with proteid, is restricted by physiological chemists to a class of nitrogenous substances (which includes such substances as gelatin and mucin) which are not proteids, but still in certain reactions resemble those substances closely.

Proteids are never absent from the protoplasm of active living cells, whether animal or vegetable, and they are indissolubly connected with every manifestation of organic activity. A definition of proteids is not possible in the logical sense. Gamgee (Physiol. Chem. p. 4) gives in the following sentences a terse description of these substances, which must take the place of a definition: 'Proteids are highly complex, and for the most part non-crystallisable compounds of carbon, hydrogen, nitrogen, oxygen, and sulphur, occurring in a solid viscous condition or in solution in nearly all the solids and liquids of the organism. The different members of the group present differences in physical, and to a certain extent in chemical, properties; they all possess, however, certain common chemical reactions, and are united by a close genetic relationship.

In vegetables the proteids are constructed out of the simpler chemical compounds which serve as their food. In animals such a synthesis never occurs, but the proteids are derived directly or indirectly from vegetables. By the action of certain digestive juices all proteids are capable of being converted into closely allied substances

tempting to unravel the constitution of the proteids, there is at present but little positive to be said on this point. All we can do is to give the result of the experiments that have been performed which show the classes of products yielded by the proteids, and to enumerate the various theories held by different observers concerning their constitution.

The various proteids differ somewhat in elementary composition within the limits of the following numbers (Hoppe-Seyler, Handbuch d. Phys. und Path.-Chem. Analyse, 4to Aufl. p. 223):

The various decompositions that proteids undergo may be conveniently stated under the following heads:-

a. Decomposition in the body. In the alimentary canal the proteids are converted into proteoses (albumoses) and peptones: this change is probably due to hydration. Under the influence of the pancreatic ferment, a certain class of peptones called hemi-peptones are further acted upon, resulting in the formation of leucine, tyrosine, aspartic acid, ammonia, and proteinchromogen (a substance coloured purple by bromine). Putrefactive processes due to bacteria in the small intestine also occur; these result in the formation of indole, skatole, phenol, and oxyacids. Ethereal hydrogen sulphates can be detected in the urine as a result of these putrefactive changes (Baumann, H. 10, 123); when putrefaction is hindered by the administration of large doses of iodoform in dogs, these products do not appear in the urine (V. Morax, H. 10, 318). One of the sources of hippuric acid in the urine of flesh-feeders is the phenyl-propionic acid that results from the putrefaction of proteids in the alimentary tract (Salkowski, B. 12, 648; Tappenier, Z. B. 22, 236).

After the proteids have been absorbed from the alimentary canal, they become assimilated by the tissues, and there undergo combustion or metabolism, the chief ultimate products being water, carbonic acid, and urea. It is probable that glycocine, leucine, creatine, and ammonium carbonate are intermediate products in this change. Urea had not been obtained from proteids by experiments performed outside the body until quite recently, when Drechsel (B. 23, 3096) has succeeded in obtaining a crystalline base lysatin by acting on casein with zine and hydrochloric acid. Lysatin yields urea when boiled with baryta water. It has also been demonstrated, by experiments on animals, that proteid food gives rise to glycogen in the liver, and to fat in the subcutaneous and other tissues. That proteids can be converted into fats is also shown by the occurrence of adipocere in the muscular tissues after death.

b. Action of heat. By dry distillation the proteids yield an oily liquid called Dippel's oil, which contains ammoniacal salts of the fatty acids, amines, and aromatic compounds.

c. Action of putrefaction. The chief products

are ammonia, ammonium sulphide, carbonic acid, volatile fatty acids, lactic acid, amines, Nucine, tyrosine, and other complex aromatic

compounds.

d. Action of acids and alkalis. Prolonged boiling with strong sulphuric or hydrochloric acid, or fusion with caustic alkalis, gives rise to a large number of products, of which the following are the most important; leucine, tyrosine, aspartic acid, and glutamic acid. Prolonged heating with dilute acids gives rise to hydrolytic decomposition (Hermann) and the dormation of albumoses and peptones (Neumeister, Z. B. 23,

The effect of heating proteids with caustic baryta was investigated by Nasse, and subsequently by Schützenberger (Bl. Feb. 15, March 5 and 15, 1875). Ammonia was evolved, and carbonic acid remained in combination with barium; these two products occurred in the same ratio as would result from urea similarly treated. In addition oxalic acid, acetic acid, tyrosine, amidoacids of the fatty acid series (especially leucine, butylamine, and amido-butyric acid), acids allied to glutamic and aspartic acids, and lastly a dextrin-like substance, were found in the residue. Schützenberger (A. Ch. [5] 16, 289) explains the mechanism of the reaction as follows: the proteid molecule, losing ammonia and carbon as carbonic oxalic, and acetic acids, and assimilating water, is converted into a mixture of glucoproteins $C_nH_mN_2O_4$, containing as its principal term $C_0H_{1n}N_2O_4$; by the prolonged action of baryta at a high temperature these split up partly into leucines or amido- acids of the acetic series $C_nH_{m+1}NO_2$ and leuceines or amido-acids of the acrylic series $C_nH_{m-1}NO_2$, and partly into double compounds formed by the union of glucoproteins and leuceines with the leucines. For Schützenberger's recent attempts to synthesise proteids see C. R. 112, 198.

e. Action of hydrochloric acid and stannous chloride. Ammonia, aspartic acid, glutamic acid, leucine, and tyrosine are the chief products (Hlasiwetz a. Habermann, Anz. Wien. Acad. 1872, 1873; A. 159, 304; 169, 150; J. pr. 7, 897).

f. Action of oxidising agents. By means of manganese dioxide and sulphuric acid, or potassium chromate and sulphuric acid, many fatty and aromatic compounds are formed. Nitric acid produces first a yellow insoluble substance, xantho-proteic acid, which dissolves on further action, and yields ultimately para-oxybenzoic and oxybenzoic acids.

Mulder (J. pr. 16, 129; 17, 312; A. 31, 129) obtained by the action of potash on proteids a substance which is now called alkali-albuminate. but which was regarded by Mulder to be the base of all proteids; he gave it the name 'protein.'
Various definite compounds of protein were described, such as oxyprotein, trioxyprotein, sulphoproteic acid, &c. Liebig (A. 57, 132) was the first to disprove these assertions, and the only remnant of this theory now is the term 'proteid. For recent work on this subject and the related one of sulphur in proteids see Danilewski (H. 7, 440), and Krüger (Pf. 43, 244).

Gerhardt was of opinion that all the proteids are identical in constitution and molecular arrangement, but differ from one another in the

nature of the mineral substance with which they are associated. He designated the common organic element by the name 'albumin,' and it may be mentioned that in the elaboration of his theory he regarded egg albumin as the neutral albumate of sodium, and fibrin as a compound of albumin with earthy phosphates. Proteids, however, have been separated from all but traces of mineral matter, and still exhibit their peculiar characteristics; careful elementary analysis also has shown that there is a difference of the percentage amounts of carbon, nitrogen, sulphur, &c., in various proteids. Nevertheless, it is still a fact that some of the distinguishing features of certain proteids are due to the adhering salt; for instance, the coagulation of caseinogen by rennet occurs only in the presence of calcium

salts (Hammarsten).

Gautier (Chimie appliquée à la Physiologie, i. 251) states that the proteids behave as amides of the higher homologues of lactic and tartaric acids, and residues of aromatic acids; hence when proteids are oxidised there is a simultaneous production of fatty acids, of aromatic compounds, and doubtless of bodies analogous to urea; the products furnished by different proteids are not in the same proportions. It must, therefore, follow that the different radicles they contain differ not only in arrangement but in relative proportion, and sometimes even in their nature. It was Nasse who first observed (Pf. 6, 589) that the nitrogen in proteids appears to exist in two conditions, a certain fraction of it being more unstable and apparently more feebly combined than the rest. This view was fully confirmed by Schützenberger in the experiments already alluded to. The latter observer regards the proteids as complex ureides, i.e. combinations in various proportions of urea with amido-acids, some of which belong to the leucine series, others to the aspartic series. Representing albumin by the empirical formula $C_{r2}H_{112}N_{18}O_{22}S$ (Lieberkühn), it yields, when decomposed by caustic baryta, urea, acetic acid, a sulphur-containing body, and a substance with the formula $C_{88}H_{132}N_{14}O_{24}$, which may on further hydration be split up into the substances already mentioned (glucoproteins, leucines, leuceines, &c.).

Pflüger's view relative to the constitution of the proteids (Pf. 10, 251) may be thus summarised. One of the most striking features of the proteids is the difference that exists between nonliving proteid matter, such as white of egg, and that which forms part of living protoplasm. former may remain for years without undergoing decomposition, and is indifferent to neutral oxygen; while the latter is continually decomposing, undergoing intramolecular changes, and lives by breathing oxygen. The assimilation of proteid food is looked upon by Pflüger as an ether-like combination of a molecule of living proteid with one of the non-living proteid, water being climinated. This union of isomeric molecules, which forms a heavy mass but still remains a simple molecule, may be conceived to go on indefinitely. In this process it seems probable that the nitrogen of the food proteid, which exists there in combination as amides, passes into combination with carbon, so that in living proteid it is combined in the form of cyanogen. This view is strengthened by the fact that substances like uric acid, creatine, and guanine, are products of proteid metabolism, while such compounds are never obtained from non-living proteid material. O. Loew (Die chemische Kraftquelle im Lebenden Protoplasme, Munich, 1882, B. A. 1885, p. 1075) has also found that a striking difference between living and non-living proteids is the fact that the former reduce silver nitrate, probably owing to some radicle of the nature of addehyde, whereas the latter do not behave in this way. He suggests that albumin is a condensation product of aspartic aldehyde. The simplest formula for Schützenberger's leucene O,H,NO, is also that of aspartic aldehyde.

Latham (Brit. Med. Journ. [1] 1886, 629) regards albumin as a compound of cyan-alcohols united to a benzene nucleus. The cyan-alcohols resemble proteids in readily undergoing condensation and intramolecular changes; and, morcover, the various products of the disintegration of proteids can also be obtained as the decomposition products of these cyan-alcohols. See also Drechsel's art. in Ladenburg's Handw. d. Chem. 3, 541; Beilstein's Handw. 3, 1258.

GENERAL PROPERTIES OF PROTEIDS.

- 1. Indiffusibility. Solutions of proteids are non-diffusible. They belong to Graham's class of colloid substances. Peptones, and to a less extent cibumoses, are, however, diffusible. This property of indiffusibility enables us to separate proteids from saline admixtures, and also to separate various proteids from one another: e.g. if a mixture of albumin and globulin in a saline solution be dialysed, the salts pass out, the albumin remains within the dialyser in solution, while the globulin, which is insoluble in water, is precipitated.
- 2. Action on polarised light. Proteids all rotate the plane of polarised light to the left. The following table gives the specific rotatory power for the yellow line D of some of the chief proteids:

of various proteids is usually characteristic, but it can be varied somewhat by additions of small quantities of acid or alkali; the former lowers, the latter heightens, the coagulation temperature. Alkali albumin in the latter case is not coagulable by heat, and forms so readily that it is advisable to have the solution either perfectly neutral or faintly acid before performing the experiment. Rendering the liquid faintly soid with weak (2 p.c.) acetic acid also renders the flocculi of precipitate larger and easier to filter off. The alkalinity of a liquid is always increased, or its acidity diminished, after the separation of a heat congulum. Various neutral salts in excess also cause the coagulation temperature to vary; sodium chloride lowers the temperature. while magnesium sulphate has little or no effect. A solution of proteid enters into an opalescent condition a few degrees below that at which the separation of flocculi begins. In the dry state proteids are rendered insoluble, like coagulated proteid, at a temperature of 110°C. On the influence of salts on coagulation temperatures, see Limbourg (II. 13, 450). Haycraft criticises the method of fractional heat coagulation (Pr. Roy. Soc. Edin. 1888-9, 361). It is defended by numerous observers (for references see Halli-burton, J. Physiol. 13, 806; Hewlett, ibid. 798). The following table gives the heat coagulation temperatures of some of the most important pro

oteids:				
Proteid			Te	mperaturs of heat congulation
Egg albumin				72 8°C.
Serum albumin	α			72 -8°
Vitellin .	•	•	•	75°
Serum globulin		•	•	75°
Fibrinogen	٠	•	•	56°
Myosin .	•	•	•	560
Crystallin .	•	•	•	93° 65°
Hæmocyanin	•	•	•	09-

4. General tests for proteids. Solutions of the proteids are precipitated by strong mineral

•	1	
Proteid	Observer	Value of [a]
Serum albumin	Hoppe-Scyler (Zcit. f. Chem. und	
	Pharm. 1864, 737) .	-56°
	Starke (Maly's Jahrs. 11, 17)	60°
Egg albumin	Hoppe-Seyler	- 83·5°
	Haas (P. 12, 378).	- 38·08°
Fibrinogen		- 59·75°
	Hermann (H. 11, 508)	43°
Sodium albumate	Haas	-55°
Syntonin (from egg albumin) .	Наав	- 63·12°
Syntonin (from myosin)	Hoppe-Seyler	-72°
Casein (in weak MgSO, solution)	Hoppe-Seyler	80°
Serum-globulin	Haas	- 59·7 5°
Various albumoses	Kühne a. Chittenden (Z. B. 20, 51)	-70° to 80°

According to Haas, these numbers are unaltered by the salts adherent to the proteids.

3. Heat coagulation. Most of the native proteids are coagulated by heating their solutions, but more especially the globulins and albumins. By this means the character of the original proteid is lost, and all are converted into an exceedingly insoluble substance, called 'coagulated proteid.' When several proteids are mixed in a solution, if their temperature of coagulation differs, it is possible to separate them by a process of 'fractional heat accordation.' The heat coagulation temperature

acids, acetic acid and potassium ferrocyanids, by acetic or oxalic acid together with a large addition of concentrated solutions of neutral salts, by basic lead acetate, by mercuric chlorids, by copper sulphate, by tannic acid, by saturation with powdered potassium carbonate, ammonium sulphate or sodio-magnesium sulphate, and by alcohol.

'coagulated proteid.' When several proteids are mixed in a solution, if their temperature of coagulation differs, it is possible to separate them by a process of 'fractional heat engulation.' The heat coagulation temperature phuretted hydrogen, and the proteid again ob-

tained unaltered. Neutral salts like ammonium sulphate, or sodio-magnesium sulphate, completely precipitate all proteids but peptones, and in an uncoagulated condition—i.e. they can be re-dissolved in water or weak saline solutions, and exhibit their characteristic properties. Alcohol precipitates proteids, and after long contact with the precipitate converts them into 'coagulated proteid.' The following reactions are those most frequently employed in the de-

tection of proteids in solution:

(a) The xanthoproteic reaction. Nitrie acid is added; this usually produces a precipitate, but in the case of peptones, or if the quantity of proteid is very small, it does not. The mixture is then boiled, when the liquid and the precipitate turn yellow (xanthoproteic acid); if it is boiled sufficiently long with excess of acid the precipitate dissolves. Addition of ammonia causes the yellow colour to become orange. A similar reaction is given by gelatin and keratin. Analyses of xanthoproteic acid and its compounds made by Mulder and others are not of any value, as it has since been shown that this yellow substance is not constant in composition. The reaction is due to the aromatic radicle undoubtedly present in all proteids. On colour reactions of proteids see Salkowski (H. 12, 215), On colour Gnezda (Pr. 47, 202), Pickering (J. Physiol. 14).

(b) The liquid is rendered strongly acid with acetic acid, and solution of potassium ferro-cyanide added, which throws down the proteid

as a white flocculent precipitate.

(c) Millon's reaction. Millon's reagent' causes a white precipitate of the proteid. On boiling this precipitate and the surrounding liquid, both turn a brick-red colour. If only a trace of proteid is present there may be no initial precipitation. This test is given also by tyrosine, and it is in all probability owing to the aromatic radicle in proteids that those substances give it.

(d) Addition of a trace of copper sulphate and excess of potassium hydroxide causes a violet solution. In the case of albumoses and peptones the colour produced is a pink one (biuret reaction). See also Gnezda a. Pickering (loc. cit.) for similar reactions with nickel and cobalt.

(e) Proteids when dissolved in glacial acetic acid and treated with strong sulphuric acid exhibit a violet colour and faint fluorescence. and if sufficiently concentrated show an absorption spectrum very like that of urobilin (Adamkiewicz, B, 8, 161).

The reactions which are applicable to proteids which will not dissolve in water or neutral saline liquids, are the xanthoproteic, Millon's, and the Adamkiewicz colour reactions.

QUANTITATIVE ESTIMATION OF PROTEIDS.

A large number of different methods of estimating quantitatively the amount of proteid in a solution have been proposed and used; the polarimetric method has been much employed (Hoppe-Seyler, Virchow's Archiv, 11, 547). Among gravimetric methods various precipitants

¹ Millon's reagent. Equal quantities of mercury and strong pitric acid are mixed and gently warmed till the barecury is dissolved. The solution is diluted with twice the bulk of water, and the copious precipitate which forms allowed to settle. The supernatant liquid is the reagent.

of proteids have been suggested, e.g. tannin and sodium chloride (Girgensohn, N. R. P. 22, 557); hydrochloric acid and potassio-mercuric iodide (Brücke, Sitz. W. 1871), &c.; but the following methods are those most frequently employed:

(a) Clinical method. The rough method generally used for the comparison of albuminous urines consists in acidulating the urine, if it is alkaline, with acetic acid and then boiling it in a graduated tube. The flocculi which form are allowed to settle, and the proportion of the precipitate to the total volume of the liquid read off and expressed in fractions, such as a half, a tenth, and so on. Esbach's tubes are graduated to correspond to percentages of proteid; the precipitant being picric acid.

(b) Precipitation by heat. 50 to 100 c.c. of water are boiled and an accurately-weighed amount of albuminous fluid, about 15 or 20 g., poured in. The fluid is boiled for some minutes, a few drops of two per cent. acetic acid added, until the precipitate separates in flakes from a clear liquid. The precipitate is collected on a weighed filter, washed with water, alcohol, and ether, and finally dried, weighed, incinerated, and the ash deducted. This method is obviously applicable only to such proteids as are coagu-

lable by heat.

(c) Precipitation by alcohol. An accurately measured or weighed quantity of the liquid is mixed with three or four times its volume of spirits of wine, and set aside for some hours; the precipitate is then collected, washed with spirit, hot absolute alcohol, ether, warm water, and finally dried and weighed as before (Hoppe-Seyler, Handbuch, 3te Auft. 312). Or the liquid may be neutralised with acetic acid and mixed with ten times its volume of strong alcohol, and then boiled, the precipitate being treated as before (A. Schmidt, Pf. 11, 10; A. Hoffmann, Virchow's Archiv, 1879, 255).

(d) Precipitation with ammonium sulphate. Since Kühne (Z. B. 22, 423) has fully shown that saturation with this salt causes complete precipitation of all proteids but peptones, this method may be employed as follows for the quantitative estimation of these proteids:-The liquid is shaken or stirred with excess of the powdered salt, filtered, and the precipitate washed with saturated solution of ammonium sulphate. The filter with adherent proteid and salt is dried at 110°, by which means the proteid is rendered insoluble, and the salt can then be washed away with distilled water. The precipitate is then washed with alcohol and ether, dried, and weighed as before.

CLASSIFICATION OF PROTEIDS.

I. Albumins. These are proteids which are soluble in water, and not precipitable from their solutions by saturation with sodium chloride or magnesium sulphate. They are coagulated by heat. The important members of the group are egg albumin, serum albumin, and lactalbumin.

II. Globulins. These are proteids which are insoluble in water; they are soluble in dilute solutions of neutral salts; and are precipitated in an uncoagulated condition by saturation with sodium chloride and magnesium sulphate. They are coagulated by heat. The most important members of the group are: serum globulin, fibrinogen, myosin, crystallin, and globin.
III. Albuminates. This name is applied to

the metallic compounds of proteids, and also to acid albumin or syntonin, and alkali-albumin. Restricting the term to the two latter substances. they may be defined as proteids insoluble in water or in solutions of neutral salts, but readily soluble in dilute acids or alkalis. Their solutions are not coagulated by heat.

IV. Proteoses. These are proteids which are not coagulable by heat, and most of them are precipitable by saturation with certain neutral salts. They are precipitated by nitric acid, the precipitate dissolving on the application of heat and reappearing when the solution is cooled. They resemble peptones in being slightly diffusible, and in giving the biuret reaction. They are formed from other proteids as the result of the action of proteolytic terments on them, being an intermediate stage in the formation of peptones. They are also found in certain animal and vegetable tissues. The best-known members of the group are the albumoses.

V. Pentones. These are proteids which are very soluble in water; they are not precipitated by heat, by saturation with any neutral salt, nor by nitric acid. They are completely precipitated by tannin, by excess of absolute alcohol, and by potassio-mercuric iodide; incompletely by phosphotungstic acid, phosphomolybdic acid, and pieric acid. They give the biuret reaction. Peptones are subdivided into hemipeptones, those which yield leucine and tyrosine as the further result of pancreatic digestion, and antipeptones,

those which do not.

VI. Insoluble proteids. This class includes a number of proteids varying in their reactions which cannot be included in any of the foregoing classes, but which all resemble one another in their extreme insolubility in various reagents. This class includes fibrin, coagulated proteid, lardacein, antialbumid, and gluten.

DESCRIPTION OF THE PROPERTIES OF INDIVIDUAL PROTEIDS.

It will now be convenient to take the most important members of the various foregoing groups, and describe the characteristic properties of each. The animal proteids will be taken first.

CLASS I., ALBUMINS .- Egg albumin. This is the albumin occurring in white of egg; it may be separated from the globulin, which also occurs in that situation, by precipitating the latter with dilute acetic acid, or by saturation with magnesium sulphate. It is coagulated at a temperature of 70°-73°C. By fractional heat coagulation further pps. are obtained at 76° and 82° (Corlin a. Berard, Arch. de Biol. 9, 1). Its specific rotation is -35.5°. It is precipitated by agitation with ether. Crystalline egg albumin may be obtained by addition of an equal vol. of sat. sol. of ammonium sulphate and filtration to remove oviglobulin. On slow evaporation of the filtrate, crystals of egg albumin form (Hofmeister, H. 14, 165; Gabriel, 15, 456). Lieberkühn ascribed to albumin the formula

 $C_{22}H_{112}N_{18}SO_{22}$, Schützenberger $C_{248}H_{222}N_{18}O_{48}S_{2}$, Since Harnack (H.~5,~207) $C_{244}H_{222}N_{182}O_{48}S_{2}$. Since Lieberkühn attempted to establish the molecular weight of albumin by preparing and analysing

the copper compound, various investigations have been published bearing on the nature and composition of the compounds of albumin with the heavy metals, and especially with copper (F. Rose, Mitscherlich, Harnack, Bielitzki, Ritthausen, Lassaigne, &c. Further particulars will be found, with references to literature, in a paper by R. H. Chittenden and H. H. Whitehouse in Studies from the Laboratory of Physiol. Chem., Yale University, 2, 95). The results obtained are most contradictory, and illustrate that numerous compounds may be obtained by slightly modifying the conditions of precipitation; they are also very liable to dissociation. The only other proteid the metallic compounds of which have been studied is myosin; the percentage amount of the various metals in the compounds obtained differ from those formed from egg albumin (Chittenden a. Whitehouse, l.c.).

Uses of albumin. It is much used for clarifying vinous and syrupy liquids, as when boiled with it the heat coagulum carries down colouring matter and other impurities. In cookery white of egg is employed for this purpose, but in large operations, such as sugar refining, blood serum is used. Albumin is also largely used in photography, and in calico-printing for fixing colours. Its property of forming a hard compound with lime renders it useful as a coment in repairing earthenware. Spoilt albumin in print works may be recovered for practical purposes by the action of pepsin (Wagner a. Witz, Ď. P. J. 119, 166).

Scrum albumin. This is the albumin occurring in serum. Its specific rotation is -56°. Fractional heat congulation, and elementary analysis show that it is probably not a single proteid but consists in warm-blooded animals of three, a, β, and γ, coagulating respectively at 73°, 77°, 84° (v. Blood). Aronstein a. A. Schmidt (Pf. 2, 1) stated that serum albumin completely freed from salts by prolonged dialysis does not congulate by heat. This statement has not been confirmed by subsequent observers, who have found it impossible to free serum albumin from ash by this method, and have attributed the non-coagulation to a slight alkaline residue (Heynsius, Pf. 9, 514; Winogradoff, 2, 605; Hinzinga, 2, 392; Haas, 2, 378). On ash-free albumin sec also Harnack, B. 22, 3046; 23, 3745. Serum albumin is not congulated by ether. It is the proteid which most frequently occurs in morbid urine.

Serum albumin is not precipitated by saturating the scrum with magnesium sulphate; if, however, the globulin precipitated by this method be filtered off, and the filtrate saturated with sodium sulphate, the albumin is precipi-tated; this is due to the formation of sodio-magnesium sulphate (MgSO₄.Na₂SO₄.6H₂O) in the liquid (Halliburton, Journ. of Physiol. [5] 152). Albumin having nearly the same characters as serum albumin is found also in milk, muscle. lymphatic glands, and other tissues in small quantities.

CLASS II., GLOBULINS. - Serum globulin. (Synonyms, paraglobulin, fibrinoplastin, serumcasein.) This is the globulin occurring in serum. It is soluble in weak solutions of sodium chloride; it is partially precipitated when the 882 PROTEIDS.

percentage of sodium chloride reaches 0.03 to 1 0.07, re-dissolved on the addition of more salt, and again precipitated, though never completely, when the amount of salt present is 20 p.c. It is completely precipitated by saturation with magnesium sulphate. It does not coagulate on the addition of fibrin ferment, and probably takes no part in the formation of fibrin (v. art. BLOOD; v. also Hammarsten, Pf. 17, 447; 18, Its heat coagulation temperature is 75°C.
 The following methods have been suggested

for the separation of the globulin from the

albumin of serum:

(a) Dialysis. When the salts are dialysed the globulin is precipitated, the albumin remains in solution.

(b) Dilute the serum to 10 or 15 times its volume with water, and pass a stream of car-bonic acid through it, the globulin is precipitated (A. Schmidt, Arch. f. Angt. u. Physiol. 1862, 429); it is also partially precipitated by the addition of very weak acetic acid when the serum is similarly diluted (Panum, Arch. f. Pathol. Anat. 4); it was on account of this that a special alkali albumin or serum casein was formerly believed to exist in the blood.

(c) Saturation with sodium chloride precipitates the globulin, leaving the albumin in solution (A. Schmidt).

(d) Saturation with magnesium sulphate (Hammarsten). This is the only method commonly employed which effects a complete separation. Kauder has stated that half-saturation with ammonium sulphate will act similarly, and Halliburton (loc. cit.) that sodium acetate and sodium nitrate may also be used.

Serum globulin may be estimated quantitatively in serous liquids in the following way: a weighed or measured quantity of the liquid is saturated with magnesium sulphate, the precipitate collected on a weighed filter and washed with a saturated solution of magnesium sulphate, and then dried at 110 °C. for some hours; the proteid is thus rendered insoluble, and is freed from the salt by washing with water and alcohol. The precipitate is again dried on the filter to constant weight, weighed, and subsequently ignited and the ash deducted. In such a liquid as serum, viz. one containing a mixture of globulin and albumin, the latter may be estimated by deducting the amount of globulin from the amount of total proteids present.

Cell globulin found in lymph cells and other cellular structures coagulates at 47°-50°. A globulin (myoglobulin) which coagulates at 68°C. but otherwise resembles serum globulin

exists in muscle plasma.

Fibrinogen. This proteid, which occurs in blood plasma, very closely resembles the preceding; it differs from serum globulin in being completely precipitable by half-saturation with sodium chloride, and may thus be separated from that proteid (Hammarsten, Pf. 19, 563). It is precipitable by a stream of carbonic acid, but it is necessary to dilute the plasma with at least 20 times its volume of water before precipitation occurs, whereas serum globulin is precipitated when the dilution is less. It is coagulated by heat at 56°C. The heat coagulum is a very sticky one; the low temperature at which fibrinogen soagulates forms the basis of a method for esti-

mating it quantitatively: the coagulated proteid formed from the fibrinogen at 56°C. is collected on a weighed filter, washed with distilled water and alcohol, dried at 110°C., and finally weighed, ignited, and the amount of ash deducted (Fredericq). Under the influence of the fibrin ferment. fibringen is converted into fibrin; it is due to this change that blood coagulates when drawn, the fibrin entangling the blood corpuscles to form the clot. The term fibrinogen has been recently extended by Wooldridge to other ill-defined proteid substances which he considers to be precursors of fibrin. These are probably nucleo-albumins mixed with lecithin. For latest views on blood coagulation with references see Halliburton (J. Physiol. 13, 829; Goulstonian Lecture No. 3, Brit. Med. Jl. March 1893).

Plasmine. The term 'plasmine' was given by Denis (Mémoire sur le Sang, Paris, 1859) to the precipitate produced by saturating blood plasma with common salt; this has since been shown to consist of the two proteids, fibrinogen and serum globulin; serine was the name given to the proteid left in solution, or, as it is now

called, serum albumin.

Myosin. This is the proteid which is formed after the death of muscle; the muscle plasma separates into a clot composed of myosin, and muscle serum, as blood plasma separates into fibrin and blood serum. This produces a stiffening of the muscles called rigor mortis. The name given to the proteid precursor of myosin in the living muscle is myosinogen. The clot of myosin formed by diluting with water a saline extract of flesh is not so coherent as that of fibrin; it is readily soluble in 10 p.c. sodium chloride solution, from which it is precipitable by saturation with that salt or with magnesium sulphate; it forms a heat coagulum in such a solution at 56°C. Myosin is converted with great readiness into acid albumin or syntonin by weak hydrochloric acid; A. Danilewsky regards the compound so formed as being not ordinary syntonin but a combination of HCl with myosin, from which by suitable treatment myosin is recoverable. After long-continued dialysis, myosin can be freed from salts, and is thus rendered exceedingly insoluble, both in saline solutions and in dilute hydrochloric acid (A. Danilewsky, H. 5, 158; Halliburton, Journ. of Physiology, 8,

136). (See also Muscle.)
Vitellin. A proteid present in yolk of egg, which, although it resembles globulins in certain particulars, differs from them in not being precipitable by saturation with sodium chloride. Solutions coagulate at 70°-75°C. It is prepared by treating the yolk of hen's egg with ether, by which reagent most of the fatty and colouring matters are dissolved; vitellin remains undissolved as a white granular substance, which is insoluble in water, but readily soluble in dilute saline solutions. Nuclein appears to be united closely to, and may be obtained from, vitellin.

Crystallin. This was once called globulin, but that term has been extended to the whole group. It is obtained from the crystalline lens of the eye, composing, according to Berzelius, 85-9 p.c. of that structure. Its saline solutions become opalescent at 73°, but a coagulum is not deposited till 98°C. is reached. According to PROTEIDS.

Lehmann (Physiol. Chem. 1, 866) the formation of a heat coagulum is accompanied by the development of an acid instead of an alkaline reaction, as is the case with other proteids; he accounts for this by supposing that crystallin is united to ammonio sodic phosphate, which, on the application of heat, is resolved into ammonia and acid phosphate of soda. Valenciennes and Fremy (C. R. 44, 1122) state that other proteids are found in the lens, and have given the name phaconin to one in that of fishes (v.

also Béchamp, C. R. 90, 1255).

Hæmoglobin. When a solution of hæmoglobin, the red pigraent of the blood, is heated, the liquid becomes turbid, and a congulum of a reddish-brown colour separates out between 70° and 80°C. Heat decomposes the hamoglobin into two substances insoluble in water, one coagulated proteid, the other a colouring matter, hematin, which contains all the iron of the hæmoglobin. A similar decomposition occurs when hamoglobin is acted on by strong acids or alkalis, or by excess of alcohol. Prever described the proteid substance under the term globin, which is insoluble in water, and which swells in solutions of sodium chloride and sodium hydrate without dissolving. Kühne concludes from the action of reagents that a mixture of proteids rather than a single proteid results from the decomposition of hamoglobin; these would, however, seem to belong to the globulin class from the fact that hæmoglobin is precipitable from its solutions by saturation with such neutral salts as precipitate other globulins, and also by a stream of carbonic acid (v. art. HEMO-GLOBIN).

Hæmocyanin. This is a proteid associated with a colouring matter which takes the place of hæmoglobin as an oxygen-carrier in the blood of certain crustacea, arachnida, gastropoda, and cephalopoda. It was first described by Fredrica in the blood of the octopus; the blood which comes to the gills being colourless, and that leaving them being blue: the blue pigment is due to a loose combination of the proteid with oxygen, which, like oxy-hæmoglobin, parts with its oxygen to the tissues. Copper takes the place of the iron of hæmoglobin in this compound. It has not been separated into a pigment and a proteid, as hæmoglobin has. It coagulates by heat at 65°, and is precipitated by saturation with neutral salts, and by dialysis like other globulins (for references see Halliburton, Journ. of Physiol. 6, 800; Griesbach, Pf. 50.

CLASS III., ALBUMINATES.

Acid albumin. If a small quantity of dilute acid (hydrochloric or acetic) be added to serum or egg-albumin, no precipitation occurs, but after a short time it will be found that the albumin no longer coagulates on heating, and that its dextrorotatory power is increased. The albumin has been converted into acid albumin. On carefully neutralising such a solution with weak alkali, the whole of the proteid matter is thrown down as a white precipitate, which is soluble in excess of the alkali, and may be re-precipitated by neutralisation with weak acid, and again dissolved by excess of the acid, and so on. Acidalbumin is soluble in solutions of alkaline carbonates; it is precipitated, like globulin, by

saturation with sodium chloride or magnesium sulphate.

Acid-albumin may also be formed in a similar way from any globulin; myosin, for instance, is converted into acid albumin or syntonin, as it was first termed by Liebig, when prepared from muscle. The parapeptone of Meissner, which is formed in the first stages of peptic digestion, is also identical with acid albumin.

Alkali albumin. If, instead of dilute acid. dilute alkali be added to an albumin or globulin, coagulation by heat is similarly prevented, and the whole of the proteid is thrown down by neutralisation, and is soluble in excess of either acid or alkali. The name alkali-albumin is given to the proteid thus altered by alkali. Like acid albumin it is soluble in solutions of alkaline carbonates, and precipitated by saturation with sodium chloride or magnesium sulphate. In the presence of alkaline phosphates it is necessary to add more acid to obtain a precipitate than if the alkaline phosphate were absent; the acid is just used to convert the alkaline into neutral phosphate. When heated with strong solution of potassium hydrate, potassium sulphide is not formed.

Lieberkühn's jelly. When either tribasic phosphoric acid, acetic or tartaric acids, which do not precipitate moderately concentrated solutions of albumin, is added in excess to concentrated serum or white of egg, a jelly is produced which liquefies like gelatin on heating, and again solidifies on cooling. A similar jelly is formed by adding a strong solution of potesh to serum or white of egg. This substance, called Lieberkühn's jelly, is regarded as a variety of ac'd or alkali albumin respectively; it is soluble with difficulty in water; the aqueous solution remains, however, clear when boiled, and is precipitated by neutralisation.

Compounds of albumin with acids. On account of the present uncertain state of our knowledge concerning the constitution of the proteids, the statements concerning compounds which have been described of albumin with various acids must be received with caution, as is also the case with metallic albuminates (see

Egg albumin).

Trinitro-albumin C12H103(NO2)3N18SO22 in prepared by triturating or shaking dried and powdered albumin with 14 or 15 times its weight of nitric acid (HNO,); a gelatinous mass is the result, and on pouring this into water the in-soluble light-yellow tinted compound separates out. If the gelatinous mass be left to itself at a temperature below 10°, a small quantity of nitrogen tetroxide is given off, and a solution formed which, when diluted with water, deposits a dark-yellow tasteless hydroxytrinitro-albumin, $C_{72}H_{100}(NO_2)_2N_{10}(OH)_2(SO_2OH)O_{27}$. Both these compounds dissolve without alteration in dilute alkalis, from which solution they are precipitated in yellow flocculi on addition of acid (O. Loew, J. pr. [2] 5, 433). If, instead of using nitric acid, a mixture of concentrated nitric and sulphuric acids be employed, a bitter yellow pow-der, insoluble in water, alcohol, or dilute acids, but soluble in dilute alkalis, is obtained which is called hexnitro-albumin sulphonic acid, C₇₂H₁₀₁(NO₂),(SO₂OH)N₁₈SO₂₂; on treating this with ammonium sulphide, hexamido-albumin sulphonic acid $C_{rgH_{1ei}}(NH_2)_u(8O_xOH)N_{1e}SO_{22}$ is formed; this is decomposed by strong alkalis (J. pr. 29, 70, 110) distinguishes between casein with evolution of ammonia, and by nitric acid which forms the envelopes of the fat globules, with evolution of red fumes. It is insoluble in dilute acids, but readily dissolves in concentrated ones (O. Loew, J. pr. (2] 3, 180).

Gelatinous compounds of albumin with acids are prepared by leaving it twenty-four hours in a parchment paper dialyser and a dilute acid in the outer vessel. For a quantity of albumin represented by Lieberkühn's formula, C₇₂H₁₁₂N₁₈SO₂₂, the compounds contain 2 mols. nitric, 2 mols. hydrochloric, 1 mol. sulphuric, and 1\frac{1}{2} mols. phosphoric acid (G. S. Johnson, G. J. 27, 734).

Casein and Caseinogen. Caseinogen is the chief proteid in milk. By the action of rennet it is converted into a curd called casein. Caseinogen is thrown down by the addition of acetic or mineral acids, especially if the milk be first diluted; this precipitate when freed from fats is insoluble in water, soluble in dilute acids or alkalis (and alkaline carbonates), and re-precipitable by acidulation. It may also be prepared from milk by saturating it with magnesium sulphate, followed by washing the precipitate with saturated solution of that salt till the washings contain no albumin, and then re-dissolving the precipitated caseinogen by adding water. salt still adherent to the precipitate enables it to dissolve; the fat remains undissolved on the filter. Such a neutral solution of caseinogen becomes cloudy on heating, and the cloudiness disappears on cooling if the heating has not lasted too long. Lubavin states that caseinogen differs from alkali albumin in the following particulars: (1) when caseinogen is treated with caustic potash potassium sulphide is produced; (2) on digestion with artificial gastric juice, caseinogen yields a substance containing phosphorus, whereas an albuminate can be prepared from white of egg which contains no phosphorus (Lubavin, Hoppe-Scyler's Med. Chem. Untersuch. 1871, 468). C. Wurster (B. 20, 263) states that when hydrogen peroxide is passed through a solution of egg albumin in the presence of sodium chloride and an acid (lactic, acetic, phosphoric, or sulphuric) a proteid insoluble in water is thrown down, which he states to be a mixture of gelatinous acid albumin with a large quantity of proteid similar to caseinogen; he further supposes that hydrogen peroxide plays an important role in the living tissues of the body, and that the caseinogen of milk may be produced from the proteids of the blood by a similar means. The precipitate produced by adding ether to yolk of egg is also stated to have properties similar to

caseinogen (Bopp, A. 79, 16).

Most of the older writers use the word casein to include both it and caseinogen. Different varieties of casein have been described by different observers; Berzelius, Braconnot, and others described soluble casein, soluble in water, and unsoluble casein, insoluble in water (v. also Bopp, l.c.). The soluble casein probably consisted of the other proteids present in milk in addition to casein. More recently the view has, however, been again advanced that the only proteid in milk is casein; and that the apparent presence of albumin and other proteids is due to the action of reagents or ferments (Duclaux, C. R. 98, 378, 438, 526;

(J. pr. 29, 70, 110) distinguishes between casein which forms the envelopes of the fat globules, and that which exists in solution in the milk; both, however, have the same properties. A. Danilewsky (H. 7, 433) states that casein can be separated into caseo-protalbin, soluble in hot 50 p.c. alcohol, and caseo-albumin, insoluble in that reagent. Hammarsten (H. 7, 227) has, however, shown that this behaviour of casein depends in part upon its content of calcium phosphate, the presence of which impurity depends upon the use of hydrochloric acid in the precipitation of the casein, which acid does not favour the removal of the salt as well as acetic acid. Hammarsten, moreover, showed by elementary analysis that casein is a single body; this has been confirmed by Chittenden and Painter (Studies from the Lab. of Physiol, Chem., Yale Univ. 2, 156). The two last-named observers obtain the following as the percentage composition of casein: C, 53:30; H, 7:07; N, 15:91; S, 0:82; P, 0:87; O, 22:03. Hammarsten (H. 7, 269) and Ritthausen (Maly's Jahrsber, 1873, 28) have also published elementary analyses of casein.

It is owing to the presence of caseinogen that when rennet is added to milk a curd is produced, which is composed of the clotted casein and entangled fat globules; the whey or liquid residue contains the sugar, albumin, and salts of the milk. The spontaneous coagulation that sometimes occurs in milk is due either to the precipitation of caseinogen by lactic acid formed from lactose by fermentation, or to aërobic organisms which act like rennet. The coagulation that occurs when milk is boiled is due, not to the casein, but to the albumin in the milk. The ferment coagulation is a process which is entirely different from the precipitation by acid. A solution of pure caseinogen in dilute alkali will not coagulate on the addition of rennet; if, however, a small quantity of calcium phosphate or chloride be added, coagulation readily occurs. If caseinogen, precipitated by acctic acid, be well washed with water till the reaction is nearly neutral, and then neutralised with solid calcium carbonate, a pasty mass is formed which, on the addition of rennet thereto, sets into a solid clot; but here again if the caseinogen has been washed free from calcium phosphate rennet has no such action. This dependence of the rennet coagulation on the presence of earthy phosphate has been worked out by Hammarsten. The ferment causes the change from caseinogen to casein The lime salt combines with the latter and precipitates it. Hammarsten showed that on the coagulation of caseinogen by rennet a whey albumin easily soluble in water is formed in addition to the clot of casein. Soxhlet (J. pr. [2] 6, 1) states that alkaline solution of artificially prepared alkali albumin also coagulates on the addition of rennet, but this statement has not been confirmed. Metacasein is a name given to an early stage of the action of rennet and pancreatic juice on cascinogen. It coagulates by heat (Roberts, Proc. Roy. Soc. 1881; Edkins, Journ. Physiol. 12, 193).

Casein in the milk of different animals is stated by Simon to vary slightly; thus human casein is yellowish white, and very friable; it is incompletely precipitated from its aqueous solu-

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tion by alum or by acetic soid. Casein from cow's milk is less soluble in water, and becomes viscid and horny on drying. Canine milk gives a casein which does not become viscid and horny when dried, and is less soluble in water. Human casein is much more easily digested than that of cow's milk, which is more viscid, and sets into a more solid clot under the influence of the rennet ferment of the gastric juice. For recent papers on casein see Ringer, Journ. Physiol. 11, 464; 12, 164; Halliburton, 11, 459; Sebelien, 12, 95; Hewlett, 13, 798.

CLASS IV., PROTEOSES .- Under the name proteose it is convenient to include the large number of products which are intermediate in the formation of peptones from other proteids. Similar substances are formed by the action of both the peptic and tryptic ferment; those formed from fibrin or egg albumin have received the name ofalbumose; from globulin, globulose; from casein, cascose; from vitellin, vitellose, &c. various substances resemble each other in their general reactions, and differ from one another in origin, slightly in percentage composition, and in a few minor reactions. The albumoses are those which have been most studied. It will be sufficient here to describe the properties of the varieties of albumose. The globuloses, vitelloses, &c., are divided into similar varieties, with corresponding prefixes.

The properties of these substances have been chiefly worked out by Kühne and Chittenden. The names first given to them were propeptone (Kühne) and a peptone (Meissner). Kühne then adopted the name albumose, and subdivided the albumoses into hemi-albumoses, those which are converted into anti-peptones. Ampho-albumose is a term which includes both hemi- and anti- varieties.

The following are the chief albumoses:

- (i.) Proto-albumose, soluble in distilled water and weak saline solutions, partly precipitated by saturating its acidified solutions with sodium chloride. It is also precipitated by mercuric chloride and by copper sulphate.
- (ii.) Hetero-albumose, insoluble in distilled water, soluble in weak saline solutions, and completely precipitated therefron either by dialysing out the salt or by saturation with sodium chloride. It is precipitable by mercurio chloride only in acid solutions; it is precipitated by copper sulphate. By heating its saline solutions a cloudiness is produced, which is not caused by the formation of coagulated proteid, since it readily disappears on the addition of weak acid or alkali. By the action of alcohol hetero-albumose is partially converted into an insoluble product (dys-albumose).
- (iii.) Deutero-albumose. This is the albumose most nearly allied to peptone. It is soluble in distilled water, and in saline solutions; it is not precipitated by saturation with sodium chloride. It is precipitable by nitric acid only in the presence of excess of salt, and then does not dissolve so readily on heating as in the case of the other albumoses. It is precipitable by mercuric chloride, but not by copper sulphate. It can be separated from peptones by saturation with ammonium sulphate, which precipitates

deutero-albumose but not peptones. For latest work on this see Kühne, Z. B. 29, 1.

The above reactions are those in which the albumoses differ from one another; they resemble one another in their characteristic behaviour with nitric acid (already described), and in giving the birret reaction. Noumeister says that in the formation of peptones from albumin, in the first stage of digestion, proto-albumose (chiefly a hemi-product), hetero-albumose, and anti-albumid (an insoluble product only partially further changed, and that into antipeptone) are formed. Deutero-albumose is in all cases an intermediate product between these and the final poptones.

The following are the chief papers published in reference to this subject. On albumoses: Kühne and Chittenden, Z. B. 20, 11; R. Noumeister, ibid. 23, 381; Chittenden and Bolton, Studies from the Physiol. Lab., Yale Univ. 2, 126. On globuloses: Kühne and Chittenden, Z. B. 22, 409. On vitelloses: Neumeister, ibid. 23, 402. On caseoses: Chittenden and Painter, Studies from the Physiol. Lab., Yale Univ. 2, 156. On the digestion of casein: H. Thierfelder, H. 10, 577. On benzoylated ethers of the albumoses: Schrötter, B. 22, 1950.

CLASS V., PEPTONES. -The general reactions of these substances and of their chief varieties. hemi- and anti- peptone, have been already described. It is only since the introduction of the method of separating them from other proteids by saturating a solution containing such a mixture with ammonium sulphate that they have been obtained free from proteoses. Most of the peptones of commerce consist almost entirely of protecses. Peptones have also been described as occurring in milk, and in certain animal and vegetable tissues, whereas these proteids are in reality proteoses artificially formed during manipulation. Certain properties previously ascribed to peptones, e.g. a power of preventing blood from coagulating after intravenous injection, are now known to be due to proteoses.

When peptones are formed artificially a bitter taste is developed; what this is due to is unknown. Pure peptone has a meaty or cheesy taste; the albumoses are also free from bitterness. It is exceedingly difficult to dry pure peptone, and when dry it hisses and froths, with evolution of heat on the addition of water.

Anti-peptone—and the same appears to be true of other anti-products of digestion (e.g. anti-albumid)—do not only not yield leucine and tyrosine on further pancreatic digestion, but appear not to contain the tyrosine radicle; they do not give Millon's reaction, and do not yield tyrosine on boiling with sulpluric acid.

(For the most recent paper on peptones, methods of purification, and ultimate analysis, see Kühne and Chittenden, Z. B. 22, 423.)

CLASS VI., INSOLUBLE PROTEIDS.

Fibrin. This is the proteid formed from fibrinogen, probably under the influence of a ferment derived from the white corpuscles of the blood. It is owing to its formation that blood clots after withdrawal from the body (see Blood). It may be prepared pure by washing the clot free from corpuscles by a stream of water, or better, by allowing the plasma freed from corpuscles to coagulate, and then it is

washed free from other proteids by water. It is a white elastic solid, usually exhibiting fibrillation under a high magnifying-power. It is insoluble in water, partially soluble in dilute saline solutions, the proteid which goes into solution having the properties of serum globulin. Fibrin possesses the power of liberating oxygen from solutions of hydrogen peroxide. Fibrin swells up in cold weak hydrochloric acid (0·1 p.c.); it dissolves, forming acid albumin, on heating it with weak hydrochloric acid. It is readily digested by pepsin or trypsin, yielding albumoses and peptones. Hasebrook (H. 11, 348) and A. Herrmann (ibid. 11, 508) state that a first product in the digestion of fibrin is a substance with many of the properties of fibrinogen. (For elementary analyses and varieties of fibrin see Hammarsten, Pf. 22, 484; 30, 437. See also Fibrinogen.)

Cagulated proteid. This is proteid converted by heat or alcohol into a coagulum. It is insoluble in water or dilute acids or alkalis; it is, however, like fibrin, readily digestible by

proteolytic ferments.

Lardacein (so-called amyloid or albuminoid substance). This is formed in the disease known as waxy degeneration, the cells of the liver, spleen, and other organs being replaced by this substance. It is coloured brownish-red by iodine, hence the name amyloid (Virchow). Kekulé and Schmidt showed that it was a proteid. It is insoluble, like coagulated proteid, and it has been usually stated that it is not dissolved by gastric juice. Kostiurina (C. C. 1887, 120) finds, however, that it is soluble in pepsin solution acidified with hydrochloric acid.

The vegetable proteids have the same general reactions, and may be divided into the same classes as the animal proteids. Their percentage composition is also approximately the same, but varies with individual members of the group, as is the case with the animal proteids. Leucine, tyrosine, asparagine, and other amides are found in plants, which may perhaps be stages in the formation of proteids from the union of inorganic nitrogen with certain non-nitrogenous compounds in the plant tissues (C. O. Müller, L. V. 1886, 326). Various observers have found in vegetable tissues a crystallisable proteid, often spoken of as an albumin, but which has since been shown to consist of a globulin (vitellin). These crystals were first observed by Hartig (Botun. Zeitung, 1885, 881). Maschke obtained crystals from Para nuts by extracting them with water at 50°; the crystals formed on evaporating this extract at the same temperature (J. pr. 74, 436). Similar crystals have been obtained by Schmiedeberg (H. 1, 205), by Drechsel (J. pr. [2] 19, 331), Ritthausen (J. pr. 131, 481). G. Grübler obtained octahedral crystals from pumpkin seeds and castor-oil seeds by cooling to 7° a sodium chloride extract of the seeds made at 70° (J. pr. 131, 105). The aleurone grains of plants have been investigated by S. H. Vines (Pr. 30, 387; 31, 62); in the peony, castor-oil plant, blue lupin, and many other plants. Vines found that the grains are either wholly or partially composed of proteids, and classifies them according to whether (1) they are soluble in water, in which case they consist of vegetable peptone or hemi-albumose, (2) soluble in 10 p.c. sodium chloride solution, and (8) partially soluble in 10 p.c. sodium chloride

solution. In the two latter cases globulins and albumins are also present. For recent work on crystallised vegetable proteids see Osborne, Am. 14, No. 8.

CLASS I., VEGETABLE ALBUMINS.—In addition to the crystalline body just described, the position of which in our classification is properly in the next group, there are in vegetable juices true albumins. These have been prepared and analysed from rye by Jones (A. 40, 66), from wheat flour by Dumas and Cahours (A. Ch. [3] vi), by Boussingault (ibid. [2] 63, 225), from potatoes by Rüling (A. 58, 306), in the latex of several caoutchouc-yielding plants by J. R. Green (Pr. 40, 28), and in papaw juice by Martin (J. Physiol. 6, 336). Such albumins are coagulated by heat at about 70°, and are not precipitated by saturation with sodium chloride, magnesium sulphate, nor by acetic acid. The myrosin of mustard seeds also resembles vegetable albumin, and myco-protein from yeast and bacteria is also stated to be an albumin (Schaffler, J. pr. 131, 302).

CLASS II., VEGETABLE GLOBULING .-- These were first described by Vines (l.c.), and have since been classified by Martin (Proc. Physiol. Soc. 1887, 8), who has found them in the flour of wheat, rye, and barley, in papaw juice, and in the seeds of Abrus precatorius (jequirity). He divides them into two classes: vegetable myosine and vegetable paraglobulins. The myosins coagulate at 55°-60°, are precipitated by dialysing the salt away from their solutions; but this precipitate is no longer a globulin, being insoluble in saline solutions. It has the properties of an albuminate, i.e. soluble in weak acid or alkali and precipitated by neutralisation. similar transformation occurs when a solution of the myosin, especially a dilute solution, is placed in an incubator at 35°-40° for twelve to eighteen hours. The vegetable paraglobulins coagulate at 70°-75°C., and are not transformed into albuminates, either by dialysis or by a long exposure to a temperature of 35°-40°. This classification does not include plant vitellin (phytovitellin), the crystalline form of which has been already alluded to. The crystals are membraneless, doubly refracting, and the proteid of which they consist has all the reactions of vitellin prepared from yolk of egg. This vitellin was found to be free from nuclein and lecithin, and may be regarded as the purest globulin yet known. Elementary analysis gave C 52.43, H 7·12, N 18·1, S 0·55 p.c. (For further analyses of vegetable proteids see Barbière, J. pr. 126, 114.)

CLASS III., VEGETABLE ALBUMINATES.—Legumin and conglutin. Legumin, or vegetable casein, was discovered by Einhof in 1805, and called by him végéto-animale (N. allgem. J. D. Ch. v.; A. Gehlen, vi. 126, 548), in peas, beans, and lentils. Proust, H. Vogel, Boullay, Braconnot, and Liebig considered it to be identical with the casein of milk. Dumas and Cahours found that it contained less carbon and more nitrogen than casein (Gerhardt, Traite, 4, 491). The composition and properties of this proteid have been more recently studied by Ritthausen. He prepared it by extracting pulverised peas, beans, lettile, and vetches with dilute alkali, precipitating the strained liquid

with acetic acid, washing the precipitate with alcohol on a filter, and finally drying over sulphuric acid. It dissolves both in cold and boiling water; on analysis the following percentages were obtained: From peas, lentils, vetches, and field beans—C 51:48; H 7:02; N 16:77; O 24:32; S 0:40. From garden beans—O 51:48; H 6:92; N 41:71; O 26:35; S 0:45. Treated with sulphuric acid it yields leucine, tyrosine, glutamic, and aspartic acids. The legumin of almonds and lupines, called by Ritthausen conglutin, is richer in nitrogen, more glutinous, and more soluble in acetic acid (Ritthausen, J. pr. 103; 65, 78, 193, 273; [2] 26, several papers; Z. [2] iv. 528, 541; vi. 126; Gm. xviii. 427, 437). Legumin differing slightly in properties and composition has been prepared from many other sources.

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In spite, however, of the vast amount of work which has been done on this subject, and which is only briefly alluded to in the foregoing paragraph, the existence of this substance is now pretty generally denied. Fresh seeds or vegetable tissues and juices contain no proteids of the casein or albuminate group, and all the substances hitherto designated plant casein are artificial products produced by the alkali used to extract them from the various globulins and albumins which exist there normally (Hoppe-Seyler, Physiol. Chemie, Theil i. 75). Although Ritthausen defends his views (C. C. 1877, 567, 586) on the ground chiefly of the concordance of numerous elementary analyses, the recent work of Vines, Green, and Martin confirms Hoppe-Seyler's statement. For proteids of oats see Osborne, Am. 13, 327, 385; 14, 212; of maize, Osborne a. Chittenden, ibid. 13, 453, 529; 14, 20; of flax, Osborne, ibid. 14, No. 8.

CLASS IV .- VEGETABLE PROTEOSES. - These were first described by Vines (l.c.) in alcurone grains, and spoken of as hemi albumose by him. They were previously regarded as peptones. Martin (J. Physiol. 6, 336) has given the name phytalbumose to these substances. In papaw juice he found two phytalbumoses: a - phytalbumose, with which the ferment papain is associated; this resembles the proto-albumose of Kühne a. Chittenden, but differs from it in the fact that copper sulphate and saturation with sodium chloride do not precipitate it; \$-phytalbumose, which resembles hetero albumose, except that it is not precipitated by dialysing out the salts from its solutions, nor by copper sulphate, nor by mercuric chloride. Green (Pr. 40, 28) has described an albumose in latex; and Martin has found another albumose-insoluble phytalbumose-in wheaten flour (Brit. Med. Jour. 1886, 2, 104; see also under GLUTEN).

CLASS V. — VEGETABLE PEPTONES. — True peptone does not apparently exist as such in vegetable tissue; as the result of peptic or panoreatic digestion, however, peptones are formed with intermediate products (proteoses), as in the case of animal proteids. Some, moreover, are further acted on yielding leucine and tyrosine. It is interesting to notice that in the digestion of the proteids of papaw juice by papaïn, a proteolytic ferment present in that juice, no true peptones, but only phytalbumoses, are formed. Papain, however, which acts like trypsin best in

an alkaline medium, forms true poptones with animal proteids (Martin, J. Physiol. 5, 213; 6, 336). For ferments in pineapple juice see Chittenden, Trans. Connecticut Acad. 8, 1. It appears probable that such ferments are widespread in the vegetable kingdom to convert the proteid of the cotyledons into peptone-like substances, and so render it available for food in the growing plant.

CLASS VI.—INSOLUBLE VEGETABLE PROTRIDS. Gluten. This is the most important of the vegetable proteids which falls under this head. When wheat flour is made into a paste its stickiness is due to the presence of gluten, which can be obtained free from starch by washing the paste with water; this is most conveniently done by kneading the paste in a muslin bag under running water. Gluten is tenacious, almost tasteless, of a light brownish-grey colour; on being burnt it emits the smell of burnt horn. and on destructive distillation yields the same products as animal proteids. It dissolves in strong acids and alkalis; it also dissolves, but very slowly, in 0.2 p.c. hydrochloric acid (Bouchardat, C. R. 14, 962). Gluten has been stated to possess amylolytic powers, converting starch first into dextrin and then into dextrose. Taddei (Giornale fisica di Brugnatelli, 12, 360) first showed that gluten consists of two substances—one soluble, the other insoluble in alcohol. Ritthausen called the part insoluble in alcohol vegetable fibrin, and the part soluble in alcohol, and to which the stickiness of the gluten is due, he subdivided into two substances, mucedin or vegetable mucin, and glutin, gliadin or vegetable gelatin. These are extracted with boiling alcohol of 70-80 p.c. This extract becomes turbid on cooling, and after half the alcohol has been distilled off mucedin is deposited in flocculi. It may be purified by redissolving it in hot alcohol, and re-precipitating by cooling. The gliadin remains in solution in cold alcohol. Mucedin is soluble in cold dilute acetic acid, but when precipitated from this solution by ammonia, or left in contact with or boiled with water or dilute alcohol, it is converted into an insoluble substance like fibrin. Gliadin forms a solution in alcohol which resembles varnish; on evaporating the alcohol it is obtained in a form resembling animal gelatin. It is more soluble in hot than cold water, and is precipitated by tannic acid, basic lead acetate, and mercuric chloride. The analyses of crude gluten, and of glutin, give approximately the same percentage composition as other proteids (Ritthausen, J. pr. 74, 193, 384). Gunsberg (J. pr. 85, 213) regards mucedin as

Gunsberg (J. pr. 85, 213) regards mucedin as consisting simply of fragments of suspended fibrin; he states that gliadin is also not a distinct proximate principle, for cold water extracts from it a brown substance containing nitrogen and sulphur, and the residue has nearly the same composition as animal gelatin. Martin (Brit. Med. Jour. 1886, ?, 104) has shown that gluten does not exist in flour as such, but is formed by the action of water (perhaps also by a ferment action) on the proteids pre-existent in the flour. The doctrine of a ferment action is supported by the fact that washing flour with water at a low temperature (2°C.) does not lead to the formation of gluten. Johannsen (Ann. Agronom. 14,

420) has advanced evidence against the ferment theory. Gluten is insoluble in cold water, and in 10 to 15 p.c. sodium chloride solution. It dissolves partially in alcohol and in boiling water. Both these extracts contain the same substance, which is an albumose (insoluble phytalbumose), and it corresponds to Ritthausen's mucedin and gliadin. The insoluble residue, which is not sticky, may still be called gluten fibrin, and it is soluble in 0.2 per cent. hydrochloric acid. The flour itself contains two proteids: (1) A myosin coagulating between 55° and 60°, precipitated by sodium chloride and magnesium sulphate; and (2) a soluble phytalbumose. Both can be extracted from flour by 10–15 p.c. sodium chloride solution. They are considered to be the precursors of gluten, according to the following scheme:

Ginten = { Ginten-fibrin—precursor: myosin Insoluble albumose precursor: soluble albumose precursor: soluble albumose the more wheaten flour has been extracted with a 10 or 16 p.c. sodium chloride solution the less is the yield of gluten when it is subsequently treated with water.

The proportion of gluten in wheat flour varies considerably according to climate, soil, temperature, &c.; the best flour containing 10-11 p.c., inferior kinds 8-9 p.c. In the moist state gluten weighs about three times as much as when dry. The flours of barley, ryc, and oats contain only a trace of gliadin, or albumose, as it may now be regarded; hence these flours, containing mostly gluten-fibrin or its precursor, cannot be made into such a sticky paste as can be made with wheat flour. Gliadin also does not exist in leguminous seeds; it is said to be present in the juice of the grape and other fruits, and is held in solution there by tartario or other vegetable acids.

APPENDIX A.—Proteids in urine. Normal urine contains no proteid. The chief facts concerning proteids in morbid urine are treated fully in medical works (MacMunn's Clin. Chem. of Urine, Halliburton's Chem. Physiol.), but may be here briefly summarised as follows:

When urine contains blood (which may be detected by the microscope or spectroscope) or pus (which may be also detected microscopically), it of necessity contains a certain amount of proteid derived from these contaminations. In paroxysmal hemoglobinuris, the urine may contain hemoglobin or methemoglobin independently of the presence of blood corpuscles. In the various forms of Bright's disease, the unhealthy kidney allows the proteids of the blood to diffuse into the urine, the most common and abundant being serum albumin. Serum globulin is usually also present, and is recognised by the fact that saturation with magnesium sulphate in the neutralised urine precipitates it (A. Ott, C. C. 1886, 540). A crystalline globulin was found in urine by Paton, Lab. Rep. R. Coll. Phys. Edin. 4, 47.

Clinical observers do not as a rule attempt to distinguish, however, between the various forms of proteid that occur in urine, but speak of them all under the name of albumin. The most commonly applied tests for its detection are:—(1) To boil the upper part of a test tube full of urine; any cloudiness produced is then seen in contrast to the clear urine below. If any precipitate occurs it is insoluble in acetic acid, so distin-

guishing it from phosphates. If the urine is neutral or alkaline it is necessary always to acidify with acetic acid either before or after boiling, in order to obtain a precipitate. The clinical method of estimating the proteid quantitatively has been already described. (2) Nitric acid causes a precipitate in the cold. If urine contains but little proteid, it may be detected by pouring the urine on to the surface of some nitric acid in a narrow test tube, the ring of precipitate at the junction of the two liquids is then clearly seen (Heller). The difficulty of carrying nitric acid about has led to the adoption more recently of methods in which test papers saturated with various reagents, picric acid, potassio-mercuric iodide, &c., are added to the urine. A committee of the Clinical Society have recently presented a report in which the relative advantages of various methods of detecting albumin in urine are discussed (Clin. Soc. Trans. 19, 339). They have investigated Dr. Oliver's test papers just mentioned; Dr. Pavy's pellets of citric acid and potassium ferrocyanide; Dr. Johnson's picric acid solution; Sir W. Roberts's acid brine test; acetic acid and boiling nitric acid; and a solution of potassio-mercuric iodide with citric acid. The last named is the most delicate reagent in the list; the test papers and pellets are not so delicate but are more convenient; the pieric acid test has the advantage of being also applicable for recognising (after the addition of potash) sugar as well as albumin.

Besides albumin and globulin in urine, other proteids may sometimes occur; viz. (1) egg albumin—this occurs after a very large ingestion of eggs as food; (2) Bence-Jones albumin, so called after its first observer, has been shown to be a form of hemi-albumose—it occurs in cases of osteomalacia; (3) peptones or deutero-albumose occurs in many suppurative diseases, and doubtless originates from the disintegration of pus cells; (4) casein has been stated to occur in chylous urine, but there are considerable doubts as to the accuracy of this statement; (5) mucin occurs not only in suspension in the mucus from the urinary tract, but it appears to be occasionally present dissolved in the urine—it is precipitable therefrom by acetic acid. It is probably not true mucu, but a nucleo-albumin.

APPENDIX B .- Proteids as poisons. For effects on blood pressure, &c., of albumoses and pentones, v. Pollitzer, J. Physiol. 7, 283. The poison of venomous snakes has also been shown to depend on the proteids contained therein (Weir Mitchell), and not to any alkaloid, ptomaine, or cobric acid (W. Blyth, An. 1, 204) Wolfenden has separated a globulin, albumin, syntonin, and albumose from the venom of the cobra and daboia; for the action of these v. J. Physiol. 7, 827; see also Kanthack, *ibid.* 13, 272. The poisonous principle abrin of Abrus or Jequirity is also proteid (Martin, *Pr.* 42, 331). The subject of proteid poisons has recently risen into prominence, as it is found that the micro-organisms of many diseases produce these toxalbumoses. Koch's tuberculin owes its activity to similar substances. The poisons produced in anthrax, diphtheria, &c., are also proteid in nature. For references see Halliburton's Chem. Physiol. German translation; Martin, Brit. Med. Journal, March and April 1892. On the other hand

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sertain proteids (globulins or nucleo-albumins) are protective and destroy micro-organisms. They are termed alexines by Daremberg, Buchner, and Hankin. For Hankin's most recent paper, see *Centr. Bacteriol.* 12, Nos. 22 and 23.

APPENDIX C.—Albuminoids. The term 'albuminoid' is still used by some synonymously with proteid; it will be here restricted to a number of substances which resemble proteids in many points, but which differ from them in others.

Collagen. This is the substance of which the white fibres of connective tissue are composed, and which by the action of boiling water is converted into gelatin. Collagen is prepared from tendons by Rollett's process as follows: the finely-divided tissue is soaked in water to remove proteids, and then for some days in lime water to dissolve the mucin-holding cementing substance between the fibres. The insoluble matter is washed first with water, then with weak acctic and then again with water. The residue consists of collagen, mixed, however, with small quantities of elastin and nuclein. With very dilute acids or alkalis collagen swells and becomes transparent.

The organic material which composes onethird of the substance of bone consists mainly of a substance identical with collagen, and which has been termed ossein by some writers. The organic basis of dentine (but not of the enamel of teeth) is also collagenous.

Gelatin. When the white fibres are subjected to the action of boiling water, or of water heated under pressure, as in a Papin's digester, or to the long-continued action of dilute acids at the ordinary temperature, they dissolve, and the solution contains a substance called gelatin. Gelatin may be similarly prepared from bones. Isinglass is gelatin prepared from the swimming bladder of the sturgeon; an inferior kind is made from fish bones. Glue is the crude product obtained by boiling down hides, hones, &c. (v. Ure, Dictionary of Arts, &c., [2] 324, 376). Pure gelatin is prepared from commercial gelatin by soaking the latter in distilled water for some days to remove salts; it is then dissolved in hot distilled water, and filtered while hot into 90 p.c. alcohol. The gelatin separates in the form of white thready masses, which can be subsequently dried. Thus prepared it contains only 0.6 p.c. of ash.

Gelatin is insoluble in cold, but soluble in hot water; on cooling the hot watery solution it sets into a jelly (gelatinises); this property is possessed by solutions as weak as I p.c., it is lost by prolonged boiling, or instantly by heating to 140° in sealed tubes. Gelatin is insoluble in alcohol, ether, and chloroform. Aqueous solutions are powerfully hevorotatory, the rotatory power being influenced by the temperature and reaction of solution; at 30° [a] p = -130 (Hoppe-Seyler). Gelatin is not precipitated by acetic acid nor by a solution of lead acetate; it may be thus distinguished from chondrin. It is not precipitated by acetic acid and potassium ferrocyanide, nor by the majority of metallic salts which precipitate proteids. Tannic acid even in very dilute solutions precipitates it; it is on the formation of the last-named precipitate that the conversion of hides into leather is brought about.

Schützenberger and Bourgeois ascribe to gelatin the formula $O_{18}H_{124}N_{24}O_{29}$. Hofmeister (H. 2, 315) finds that by heating gelatin it loses water, and is converted into collagen, which he therefore considers an anhydride of gelatin; his formula for celatin is $C_{12}H_{11}N_{12}O_{22}$.

formula for gelatin is C_{10} . $H_{151}N_{31}O_{35}$.

By the action of boiling water, gelatin loses after 25 hours its power of gelatinising, and it is split up into two peptone-like bodies, semiglutin (sparingly soluble in 70-80 p.c. alcohol and precipitated by platinum tetrachloride) and hemicollin (soluble in 70-80 p.c. alcohol, not precipitated by platinum tetrachloride). Similar substances are formed by the action of the peptic or pancreatic ferment, but ultimately true gelatin peptones (not precipitable by saturation with ammonium sulphate), leucine, glycocine, and volatile fatty acids are formed. (The foregoing account of gelatin is very largely taken from Gamgee's Physiol. Chem., p. 252.) Many bacteria liquefy gelatine. On digestion of gelatin see Chittenden, J. Physiol. 12, 23, 34. The most recent work on the decomposition products of gelatin has been done by Schützenberger. On heating gelatin at 200° with barium hydroxide, one-fifth of the total nitrogen is converted into ammonia; carbonic and oxalic acids are also formed, these products being in the ratio of the products of decomposition of urea and oxamide. The other products are amidoacids of the acetic series, the most important being glycocine, alanine, amido-butyric acid and leucine, and acids of an homologous series $C_nH_{2n}N_2O_{2n}$ the value of n varying from 8 to 10. These latter acids are difficult to isolate; at 100°-120° they are converted into anhydrides; they do not yield derivatives with acetic anhydride, but with ethyl iodide in the presence of an alkali they yield di-ethyl derivatives. general results lead to the conclusion that gelatin is formed by the combination with elimination of water of 1 mol. urea or oxamide with 2 groups $C_nH_{2n}N_iO_i$ and 4 groups $C_nH_{2n}N_iO_i$ and 4 groups $C_nH_{2n}N_iO_2$, n being 2, 3, 4, or 6, with a mean value of 3.5 (v. Schützenberger a. Bourgeois, C. R. 82, 262; Schützenberger, C. R. 102, 1296) Both gelatin and albumin yield on treatment with alcoholic hydrochloric acid a diazo-compound C. H. N.O. (Buchner a. Curtius, B. 19, 850)

The question of the part played by gelatin, which is an easily-digestible substance in nutrition, is very important practically, jellies especially being given to invalids. The question was first investigated by J. Etzinger (N. R. P. 23, 535), and subsequently by Voit (Z. B. 8, 297). Voit's chief result showed that gelatin will not entirely replace proteids, but that animals rapidly waste which are fed on it alone, but, in conjunction with a certain small amount of proteid, it is capable of maintaining nitrogenous equilibrium as well as if the only nitrogenous food taken was proteid in nature. These results have been since very generally confirmed (v. S. Pollitzer, Pf. 37, 301). Voit distinguishes between circulating and organic albumin; gelatin can never yield the latter, but it may replace the former in so far as it prevents the conversion of organic into circulating albumin. Gelatin also diminishes the waste of fat in the body.

Mucin. This body forms the chief constituent of the ground substance of connective tissue, the other organic constituent being a globulin very like serum globulin. Mucin is especially abundant in the 'jelly like' tissue of the umbilical cord, and in the vitreous humour. The cement-substance of epithelia behaves similarly to microscopic reagents (especially silver nitrate, by which it is stained brown owing to a deposit of metallic silver), and is probably of the same chemical nature as the ground substance of connective tissue; both are soluble in alkalis. Mucin forms the chief constituent of mucus, and gives the sliminess to the secretion of mucous membranes. In mucus it is suspended in an alkaline exudation from the blood and mixed with the debris of epithelium cells, and a lew white blood corpuscles. The mucin itself is here formed by the protoplasm of certain cells of the epithelium becoming altered, so that it becomes swollen and brightly refracting; the globule of mucin so formed is discharged, leaving a so-called goblet cell. In mucous glands, such as the submaxillary salivary gland, a very similar replacement of protoplasm by mucin (or mucigen, as it is called when inside the secreting cells) takes place. Mucin is also largely contained in the surface secretion of several invertebrate animals, e.g. the snail. Mucin is contained in submaxillary saliva; the metalbumin and paralbumin (q, v) of ovarian cysts is a very similar substance. The substance which confers sliminess to the bile and the synovial fluid. formerly considered to be mucin, has been shown to consist of a nucleo-albumin (q. v.).

The methods of preparation of mucin from its various sources differ; from tendon (v. Rollett, Sitz. W. 30, 308; Löbisch, H. 10, 40); from submaxillary gland (Obolensky, Pf. 4, 336; Hammarsten, H. 12, 163); from bile (Gautier, Chimie Appliquée à la Médecine, 2, 126; Paijkull, H. 12, 196). Eichwald, Hammarsten, and others have prepared it from snails (Pf. 36, 373), and Giacosa (H. 7, 40) from the membranes of frog's eggs. These methods depend upon the fact that mucin is soluble in weak alkalis, e.g. lime water or dilute baryta water, and can be precipitated from this solution by acetic acid, in excess of which it is not soluble. Hammarsten finds, however, that submaxillary mucin is easily decomposed by lime water and similar weak alkaline fluids; he, therefore, uses water to extract the mucin. Hammarsten has shown that considerable differences exist in mucin according to its origin; this was previously suspected from the divergencies in elementary composition. Tendon mucin (C, 48.3; H, 6.44; N, 11.75; S, 0.81 p.c., Loebisch) and submaxillary mucin (C, 48.84; H, 6.8; N, 12.32; S, 0.8, Hammarsten) are very much alike in elementary composition, but differ in their reactions; e.g. tendon mucin is not easily decomposed by weak alkalis, nor is it so easily soluble in weak hydrochloric acid as submaxillary mucin. These forms of mucin differ still more from those obtained from Helix pomatia; Hammarsten, indeed, has shown that two distinct varieties of mucin, from the foot and mantle respectively, can be obtained from

Mucin gives the xanthoproteic, Millon's, and the Adamkiecwicz reactions: it is precipitated.

but not rendered insoluble, by saturation with sodium chloride or magnesium sulphate, and by alcohol. It is precipitated by acetate of lead, but by no other metallic salt (except the submaxillary mucin, which is precipitated by several), it is not precipitated by tannic acid nor by boiling; acetic acid gives a characteristic stringy precipitate. Mucin yields, when boiled with strong sulphuric acid, leucine and tyrosine, and when boiled with caustic soda pyrocatechin (Obolensky). When boiled with dilute sulphuric acid for a few hours, mucin yields a reducing sugar, but one which is not capable of the alcoholic fermentation, and albumin is also formed. Landwehr regards mucin as a compound of a proteid and a non-reducing carbohydrate (C.H.,O.) which has most of the properties of plant gum; he calls it animal gum (Pf. 39, 193). At one time this carbohydrate was regarded as a variety of glycogen which gave no colour with iodine (achrooglycogen).

Met-albumin and paralbumin. These two proteid-like substances are fairly constantly found in the fluids removed from ovarian cysts (Scherer), and occur occasionally in other cysts and in ascitic fluid also. Metalbumin is a form of mucin (pseudomucin); paralbumin differs from metalbumin by giving a precipitate when it is boiled; it is probably a mixture of pseudomucin with albumin, and can indeed be prepared by mixing these two substances. Both yield reducing sugars when boiled, and both contain animal gum (D. Hammarsten, Maly's Jahresb. 11, 11; Landwehr, H. 8, 114; Pf. 39, 193; Ocrum, Maly's Jahresb. 14, 459).

Ocrum, Maly's Jahrsb. 14, 459).

Nuclein. This is the name given to the substance which composes the nuclei of cells. It was prepared by Lauder Brunton from the red blood corpuscles of birds and snakes : the nuclei were freed from adhering stroma and homoglobin by repeated agitation with ether and water (Journ. of Anat. and Physiol. 2nd series, 3 91). Nuclein resembles mucin in its solubilities. Plosz found, however, that it contained phosphorus (Hoppe-Seyler, Med. Chem. Untersuchungen, Heft 4, 460), and considered it was identical with the nuclein which Miescher separated from the nuclei of white corpuscles (ibid.). Miescher separated the nuclein from the other constituents of the cells by subjecting them to artificial gastric digestion, nuclein, like mucin, being indigestible by pepsin. Miescher ascribes to it the formula C₂₂H₄₀N₂P₃O₂₂. Nuclein has also been separated from the brain (Jaksch, Pf. 13, 469) to the amount of 0.14 p.c. (Geoghegan, H. 1, 330), and from the liver; it is probably present in all parts where nucleated cells occur. Miescher has also described nuclein as occurring in the yolk of hens' eggs; it has also been described in milk. A. Kossel (H. 10, 248) has shown that the nuclein of volk and milk differ from that of cell nuclei in containing iron, and by not yielding guanine and hypoxanthine when decomposed at a high temperature by weak acids. Adenine C,H,N, is described by Kossel as being an intermediate product between cell nuclein and hypoxanthine. Nuclein is present in vegetable cells also, and adenine can also be obtained from this. It is present in yeast (Hoppe-Seyler) and mildew; in tea leaves (Kossel), in poppy, earth nut, rape and cotton

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cake; also in palm nut, but the proportion P:N is different in the nuclein prepared from this source (Klingenberg a. A. Stutzer, B. C. 1883, 204). Miescher's formula for nuclein must, indeed, be received with caution; there are either several varieties of nuclein-for elementary analyses show great discrepancies—or else, as Worm Müller (Pf. 8, 190) supposes, it is no definite chemical individual, but the different nucleins are mixtures of an organic phosphorus compound with varying quantities of proteids. Recent work on nuclein has shown that this phosphorus compound is nucleic acid (Altmann, Arch. f. Anat. u. Phys. 1888. 524). For artificial nuclein made by adding phosphoric acid to albumin see Liebermann, B. 21, 598; Pohl, H. 13, 292; Malfatti, B. d. Naturwiss. Med. Ver. Innsbruck, 1891-2; Kossel, Verh. physiol. Ges. Berlin, Oct. 21, 1892. See also numerous papers by Kossel, Krüger, and others on adenine and nuclein bases in last few volumes of H. For iron compounds of nuclein see Bunge's Physiol. Chem. This haematogen is probably the normal iron-containing food. The chromatin and plastin of histologists are respectively phosphorus-rich and phosphorus-poor nucleins. For iron in the nucleus see Macallum, P. 49, 488.

Nucleo-proteids. Nucleo-albumin. E. Merck (D. P. J. 261, 316) calls nucleo-proteids substances which, when boiled with water under pressure or treated with acids, alkalis, or ferments, are resolved into nuclein and albumin; for instance, vitellin and casein (v. also Lubavin. Hoppe-Seyler, Med. Chem. Unters. p. 447), Hammarstengives the name nucleo-albumin to a class of proteid-like bodies which are very like globulins, being precipitated from their solutions by saturation with sodium chloride or magnesium sulphate; they are also precipitated by acetic acid, but, unlike mucin, are soluble in excess. On gastric digestion of a clear solution, an insoluble phosphorus-containing substance, like nuclein, is formed. Many nucleo-albumins have the physical characters of mucin, and the sliminess of bile and synovia is due to such bodies (Hammarsten, H. 12, 173, on synovia; Maly's Jahrsber. 12, 1882, on bile-mucin; Paijkull, H. 12, 196). The chief proteid constituent of all protoplasm is nucleo-albumin (Halliburton's Goulstonian Lectures, Brit. Med. Journ., March 1893). Wooldridge's tissue fibrinogens are also nucleo-albumins (for ref. see above lectures).

Chondrin. This is the substance obtained from cartilage by boiling; the mother substance of chondrin in the matrix of the cartilage is termed chondrigen. Hot aqueous solutions of chondrin gelatinise on cooling like those of gelatin. Aqueous solutions are precipitated by the same reagents that precipitate solutions of gelatin and of mucin. It is strongly lawor otatory; its rotatory power in solutions of different strengths has been studied by de Bary (Med. Chem. Unters. i. 71). Very great discrepancies exist between the results of various analyses (see table comparing analyses by Mulder, Fischer a. Bödecker, Schützenberger a. Bourgeois, and v. Mehring in Gamgee's Physiol. Chem. p. 270), hence considerable doubts have been entertained of its being a chemical individual. It gives the reactions both of mucin and gelatin; on being boiled with dilute acids it

yields a lævogyrate reducing augar, called by de Bary chondriglucose (v. also Fischer a. Bödecker, A. 117, 111), but is now regarded as identical with that obtained from mucin, Landwehr considering that animal gum is contained in chondrin as in mucin (Pf. 39, 204, 40). Morochowitz was the first to arrive at the conclusion that chondrin is a mixture of gelatin and mucin (Verhandl, d. naturhist, med. Vereins zu Heidelberg, 1, Heft 5); mucin can be extracted from it with lime or baryta water, and pure gelatin is left behind. On this assumption chondrigen collagen + mucin. It must, however, be mentioned, in opposition to this view, that Hoppe-Seyler (J. pr. 56, 129) and Otto (Z. [2] 4, 628) state that on treating chondrin with dilute sulphuric acid it yields leucine, but no tyrosine or glycosine. The most recent work on chondrin shows that it is chondroitic acid rather than mucin which is present (C. T. Mörner, H. 12, 396; Skand, Arch. Physiol. 1, 210; Krukenberg. Z.B. 20, 307; Schmiedeberg, Arch. exp. Path. u. Pharm. 1891, 355).

Elastin. This substance is the very insoluble material of which the clastic fibres of connective tissue are composed. It may be prepared from the ligamentum nuchee by boiling it with ether and alcohol to remove fatty matters, then for 36 hours with water to remove the collagen. The residue is boiled with strong acetic acid, and afterwards with concentrated caustic soda till the fibres begin to swell; it is then treated with weak acetic acid, water, and lastly for 24 hours with hydrochloric acid. The acid is removed by washing with water, and the residue has still all the characters of fresh clastic tissue, and has the following percentage composition: C, 55-45; II, 7-41; N, 16-19; O. 20-80 (Müller, Zeit, f. Nat. Med. 3, 10, Heft 2). For recent analyses see Chittenden, Z. B. 25, 368.

Elastin is not soluble in any liquid which does not decompose it. It is soluble in boiling concentrated caustic potash, in concentrated nitric and sulphuric acids. It is digestible by both pepsin and trypsin; the former ferment being the more active (A. Ewald a. W. Kühne, Die Verdanung als histol. Methode). Peptones are ultimately formed; there are also intermediate bodies of the nature of albumoses (Horbaczewski, C. C. 1885, 843). Elastin when treated with sulphuric acid yields leucine but no tyrosine.

Keratin. This substance replaces the protoplasm in the cells of certain epidermal structures, viz. the superficial layer of the epidermis itself, nails, horns, hoofs, feathers, and the cuticle and fibrous substance of hairs. It is prepared by successively boiling the tissue with ether, alcohol, water, and dilute acids; the insoluble residue is keratin.

Subjected to the prolonged action of water under pressure at 150°-200° it yields a turbid solution. It is also dissolved by boiling with alkalis, and on the addition of acids to this solution sulphuretted hydrogen is given off, the sulphur in keratin, which varies considerably in amount, being very loosely combined. Horn swells in dilute acetic acid, dissolves in boiling glacial acetic acid, and in nitric acid; it yields aspartic acid, volatile fatty acids, leucine and tyrosine when boiled with dilute subhuric acid.

when burnt it gives off a characteristic smell. The following are the chief analyses that have been made (Hoppe-Seyler, *Physiol. Chem.*, Th. 1, p. 90):—

_	Hair	Nails	Horn	Hoof
	(r. Laer)	(Mulder)	(Tilanus)	(Mulder)
O	50·60	51·00	51·03	51·41
H	6·36	6·94	6·80	6·96
N	17·14	17·51	16·24	17·46
O	20·85	21·75	22·51	19·49
S	5·00	2·80	3·42	4·23

Neurokeratin. This is a substance which forms an irregular framework in the medullary sheath of nerve fibres, which resembles keratin in its general behaviour, but differs from it in being less easily soluble in boiling solutions of caustic potash (Ewald a. Kühne, Verhandl. d. naturnist. med. Vereins zu Heidelberg, 'vol. i. Heft 5; Kühne a. Chittenden, Z. B. 26, 291). This substance is interesting, as both the epidermis and the nervous system are derived from the epiblast of the embryo.

Chitin. This substance forms the chief constituent of the skeletal octodermal tissues of invertebrate animals, especially arthropoda. list of situations in which it has been described is given in Gamgee's Physiol. Chem. p. 299; to these must be added the pen of cuttlefishes (Krukenberg), the cartilages and other mesodermal tissues of sepia and the king-crab (Halliburton, Pr. 88, 75). In crustacea it is often impregnated with calcareous matter, and in the odontophore of molluses with silica. It is prepared from the wing-cases or shells by boiling them with caustic soda. The chitin remains insoluble. It may be dissolved in cold concentrated hydrochloric acid, and the solution precipitated by the addition of water. It is colourless, amorphous, insoluble in water, alcohol, ether, acetic acid, dilute mineral acids, and solutions of the alkalis. It is dissolved by concentrated mineral soids. (On the solubilities of chitin v. Krukenberg, Z. B. 22, 480.)

The formula for chitin is C₁₃H₁₈N₂O₁₆ (Led-

The formula for chitin is C₁₃H_mN₂O₁₀ (Ledderhose, H. 2, 213; 4, 139). Berthelot (C. R. 47, 227) stated that it yields a fermentable sugar on boiling it with sulphuric acid; and Sandwick considered it to be an amine derivative of a carbohydrate with the formula N(C₁₂H_mO₁₀). Ledderhose showed, however, that the reducing substance is a nitrogenous body, glucosamine; and when chitin is heated with acids it takes up the elements of water, and yields glucosamine

and acetic acid,

 $2C_{19}H_{28}N_2O_{16} + 6H_1O = 4C_6H_1NO_5 + 2C_1H_1O_2$. Glucosamine is an amido- derivative of grape sugar $(C_6H_1O_4 - OH + NH_2 = C_4H_1NO_5)$; it forms salts, of which the hydrochloride is formed by boiling chitin with hydrochloric acid; this is a crystalline substance soluble in water, and in solution dextrorotatory $(a_D = +70^{\circ}6^{\circ})$. The pure base prepared by the action of barium hydrate on the sulphate of glucosamine crystallises from alcohol in the form of needles. It is not fermentable. (The foregoing account of elastin, keratin, and chitin is largely taken from Gamgee's *Physiol. Chem.*, which see for fuller details.)

Skeletins. This term is applied by Krukenberg (Z. B. 22, 241) to a number of nitrogenous but sulphur-free substances, including conchiolin, spongin, &c., found in the skeletal tissues of invertebrates; they are probably all like chitin amido-derivatives of carbohydrates. The substances are all very insoluble.

Conchiolin (C₂₀H₄₈N₃O₁₁) forms the organic basis of the shells of mussels and snails. On decomposition it yields leucine, perhaps glycocine, but no tyrosine nor reducing substance. It does not give the xanthoproteic, Millon's, nor the Adamkiewicz reactions. The cementing substance between the eggs of various mollusces, whose shells and egg capsules contain conchiolin, is coloured red by heating with Millon's reagent, and contains a body allied to keratin. Cornein (from corals) (C₂₀H₄₄N₃O₁₃) differs from conchiolin by giving a red colour with Millon's test.

Spongin, the organic basis of the common sponge, yields as decomposition products leucine and glycocine (Stüdeler), but no tyrosine. It does not give any of the colour reactions mentioned above; it also resembles conchiolin by yielding on digestion peptone-like substances which differ from true peptones and albumoses by not giving the three colour reactions just mentioned; they thus differ from keratin, which is not digestible.

Fibroin, the chief constituent of insects' cocoons and spiders' threads, behaves to all three tests like an ordinary proteid, and on decomposition yields leucine, glycocine, and tyrosine. Fibroin is soluble when heated in sealed tubes in glacial, acetic, and other organic acids (A. Ledow, Maly's Jahrsbericht, 13, 32). For silk see Weyl, B. 21, 1407, 1529.

Hyalins and Hyalogens. The term 'hyalin' is applied to the chief constituent of the walls of hydatid cysts. Krukenberg states (Z. B. 22, 261) that the substance is present in the cyst wall as hyalogen, an insoluble substance which by the action of alkalis is changed into hyalin, which is easily soluble in water. Hyalogen is also converted into hyalin by heating with water (under pressure) at 150°C. (For elementary composition v. Lücke, Virchou's Archiv, 19, 189). By heating with sulphuric acid hyalin yields a sugar, probably glucose, which is dextrorotatory and capable of the alcoholic fermentation, and in this hyalin resembles muoin.

Krukenberg has extended the terms hyalogen and hyalin to other similarly related bodies obtained from various sources. The edible bird's nest has properties very like those of mucin (v. J. R. Green, J. Physiol. 6, 40), and is the result of the activity of certain glands described by Bernstein (Journ. Ornithologie, 1859. 111) as being remarkably developed in the nest-building season. Krukenberg finds that it is chiefly composed of a hyalogen (neossine), which yields as its hyalin, neossidine. Chondrosine is a hyalogen, obtained from the sponge Chondrosia reniformis. The vitreous humour from the eyes of oxen and pigs was found to contain a hyalogen, whereas the cornea did not yield one, but was found to consist chiefly of collagen, and a proteid allied to myosin. Spirographin, which largely composes the skeletal tissues of the worm Spirographis is also a hyalogen, but differs from others by yielding when acted on by alkalis

not only a hyalin, spirographidin, but also pyrocatechin. The hyalogens are not acted on by gastric juice; some are, some are not attacked by trypsin. W. D. H.

PROTEÏN v. PROTEÏDS. PROTEOSES v. PROTEÏDS. PROTO-ALBUMOSE v. PROTEÏDS.

s. C₁H₄O₄ ... [199°] 12, PROTOCATECHUIC ACID C4H3(OH)2.CO2H[4:3:1]. Mol. w. 154. (Hlasiwetz); [194°] (Barth a. Schmidt, B. 12, 1265). S. 1.9 at 14°; 10 at 60° (Tiemann a. Nagai, B. 10, 211). Occurs in the fruit of Illicium religiosum (Eykman, R. T. C. 4, 47).

Formation. - 1. By potash-fusion from piperic acid (Strecker, A. 118, 280), catechin (Kraut, A. 128, 285), maclurin (Hlasiwetz a. Pfaundler, A. 127, 351), guaiac resin (Hlasiwetz a. Barth, A. 130, 346), kino (Stenhouse, C. J. 28, 6), cafferd acid (Hlasiwetz, A. 142, 219), cinchona-red (Bembold, A. 143, 273), asafætida (Hlasiwetz a. Barth, A. 138, 61), angelica-resin (Brünner, N. R. P. 24, 641), many other resins, the methyl- derivative of sulpho-p-oxy-benzoic acid (Malin, A. 152, 109), sulpho-m- and sulpho-p-oxy-benzoic acids (Barth, C. J. 24, 829), and iodo-p-oxy-benzoic aldehyde (Tiemann a. Herzfeld, B. 10, 213).—2. By heating piperonylic acid with HClAq at 150° (Fittig a. Remsen, A. 159, 129).—3. By the action of Br and water on quinic acid (Hesse, A. 112, 52; 122, 221; Fittig, A. 168, 111).-4. By heating pyrocatechin with water and ammonium carbonate at 140° (Miller, C. J. 41, 400).

Properties.-Tufts of monoclinic needles (containing aq), sol. water, alcohol, and ether, nearly insol. boiling benzene. FeCl, colours its aqueous solution bluish-green, the colour changing to red on addition of alkalis. FeSO, colours pp., sol. acetic acid. Crystallises with p-oxybenzoic acid as (C,H₂O₃)C,H₄O₃ 2aq, which yields PbC₁₄H₁₀O₂ 2aq (Hlasiwetz, A. 134, 276). Reduces aqueous AgNO, on heating or on adding NH, Aq. Does not reduce Fehling's solution.

Reactions.—1. Split up by dry distillation into CO₂ and pyrocatechin.—2. Soda-fusion gives 55 p.c. of the theoretical amount of pyrocatechin .- 3. Bromine in the cold forms bromoprotocatechuic acid. Br at 100° yields tetra-bromo-pyrocatechin.—4. N₂O₃ passed into the ethereal solution forms oxalic acid (16.5 p.c.), carboxy-tartronic acid (10 p.c.), di-nitro-di-oxy-quinone (5 p.c.), trinitrophenol (4 p.c.), (a)-dintiro-phenol [114°] (3°5 p.c.), and nitro-phenol end of the process and of the process and the quantity of tetra-oxy-anthraquinone (ruflopin) (Nölting, Bl. [2] 37, 395).—6. Heating with As,O, at,160° or exposing a solution in Na,CO,Aq to the air forms catellagic acid C14H1.O,? which resembles ellagic acid and forms an orange solution in nitric acid.

Salts.—BaA', 5aq.—Ba₁(C,H₁O₁)₂ (dried at 130°) (Barth, A. 142, 246).—CaA', 4aq.—CaA', 3aq.—Pb_A',O₂.—PbA', 2aq.
Acetyl derivative O₂H₂(O_AO₂, CO₂H. [158°]. Crystals (Herzig, M. 6, 872).

Methyl ether MeA'. [134·5°]. Needles.
Ethyl ether Eth'. [184° cor.]. Prisms (Matemato R. 11.190).

(Matemoto, B. 11, 129).

m-Methyl derivative C.H.(OH)(OMe).CO.H [4:3:1]. Vanillie acid. [207°]. S. 12 at 14°; 2·5 at 100°. Formation (Tiemann, B. 8, 509, 1123; 9, 52, 419; 10, 59, 202; 11, 122).-1. By exposing moist powdered vanillin to the air.—2. By oxidising coniferin with dilute KMnO₄.—3. From its acetyl derivative, which is got by the action of KMnO, on acetyl-eugenol, acetyl-ferulic acid, and acetyl-creosol.—4. Together with isovanillic acid by heating C.H. (OMe) CO.H with HClAq at 140°. Properties. Needles (from water), v. e. sol. alcohol, m. sol. ether. Has no smell. May be sublimed. Gives no colour with FeCl. Reactions.—1. Split up by HClAq (S.G. 1·1) at 150° into protocatechuic acid and MeI.—2. Potashfusion yields protocatechuic acid.—3. By heating with MeI (2 mols.) and KOH (2 mols.) it is converted into C.H. (OMe) .CO.Me. -4. Yields guaia. col on distillation with lime.—5. The Ca salt yields vanillin on distilling with calcium formate.

Methyl ether of the m-Methyl deriva-

tive MeA'. [63°]. (286°).

Ethyl ether of the m-Methyl derivative EtA'. [44°]. (292°).

Acetyl derivative of the m-Methyl derivative C,H₂(OAO)(OMe).CO₂H. [142°]. Needles (from dilute alcohol).

Benzoyl derivative of the m-Methyl

derivative. [178°] (Tiemann, B. 15, 2068).

p-Methyl derivative
C.H.(OMe)(OH).CO.H [4:3:1]. Isovanillic acid.
[250°]. S. 06 at 15°; '7 at 100°. Formed with Isovanillic acid. other products by heating protocatechuic acid with MeI and KOH at 150°. Got also by heating hemipic acid with HClAq (Matthiessen a. Foster, A. Suppl. 2, 378), and, together with vanillic acid, by digesting C_aH₁(OMe)₂CO₂H with dilute HClAq at 140° (Tiemann). The acetyl derivative in the contract of the con tive is got by oxidation of the acetyl derivative of isoferulic acid (hesperetic acid) by KMnO₄ (Tiemann a. Will, B. 14, 963), and likewise by exidation of the acetyl derivative of betelphenol C.H.₃(OMe)(OH).C.₃H.₃(4:3:1] (Bertram a. Gildemeister, J. pr. (2) 39, 349). Prisms, v. sol. alcohol and ether. May be sublimed. Its aqueous solution is not coloured by FeCl. Yields a nitro- derivative [173°] and an acetyl deriva-tive C.H. (OMe) (OAc).CO.H [207°].

Di-methyl derivative C.H.(OMe), CO.H.
Veratric acid. [174°] (T.); [181°] (G.). S. 05
at 14°; 6 at 100°. Occurs in small quantity in
sabadilla seeds (Merck, A. 29, 188). Formed by
heating at 140° protocatechnic acid (1 pt.) with
MeI (4 pts.) and KOH (1 pt.) dissolved in MeOH
(KSI) A. 150 241. MeI (4 pts.) and KOH (1 pt.) dissolved in MeOH (Kölle, A. 159, 241). Produced also by oxidation of C.H.Me(OMe). (Tiemann, B. 8, 1138), of methyl-eugenol (Graebe, A. 158, 282), of papaverine (Goldschmidt, M. 6, 378), and of dimethyl-eaffele acid (Tiemann a. Will, B. 14, 962). Formed also by seponifying its amide, which is made by the action of Cl.CONH, on C.H.(OMe), in CS, in the presence of AlCl. (Gattermann, A. 244, 71). Veratric acid is a product of the action of alcoholic soda on pseudaconitine, on veratrine (Wright a. Luff. pseudaconitine, on veratrine (Wright a. Luff. C. J. 33, 160, 353), and on hexa-methyl-quercetin (Herzig, M. 5, 83), and of fused potash on papaveraldine (Goldschmidt, M. 7, 493). Veratric acid is also got by the action of KOH on pseudo-opianic acid (W. H. Perkin, jun., C. J. 57, 1068).

Properties.—Slender needles (containing aq). From hot solutions (above 50°) it separates in anhydrous crystals. V. e. sol. alcohol and ether. FeCl, gives no colour. Distillation with lime forms C,H,(OMe)₂. Potash-fusion yields protocatechuic acid. HIAq at 160° forms MeI and protocatechuic acid. HClAq forms vanillic and also iso-vanillic acids.—Salts.—NaA' 2aq.— BaA'₂ 6aq. — AgA'. — Ethers. — MeA' [60°] (c. 800°).—EtA'. [44°]. (296°).

Di-ethyl derivative C,H,(OEt), CO,H. [166°]. Formed by saponifying its ether, which is made from protocatechuic acid, alcoholic potash, and EtI (Kölle, A. 159, 240). Got also by heating hexa-cthyl-querectin with alcoholic potash at 150° (Herzig, M. 5, 78). Needles (from alcohol).—KA' 'aq.—BaA', 2aq.—AgA'.—Ethyl ether EtA'. [57°]. Crystals.

Methyl-ethyl derivative C,H,(OMe)(OEt).CO,H [3:4:1]. [194°]. Formed by oxidation of ethyl-vanillin (Tiemann, B: 8, 1130), of ethyl-eugenol (Wassermann, A. 179, 379; Balbiano, G. 11, 416), and of di-ethyl-curcumin (Jackson a. Mencke, Am. 4, 90). Needles, almost insol. cold water. - BaA', 4aq: needles.

Methyl-propyl derivative C.H. (OMe) (OPr).CO.H [3:4:1]. Formed by oxidation of the propyl derivative of eugenol (Cahours, Bl. [2] 28, 314). Needles.

Methyl-carboxymethyl derivative O₆H₈(OMo)(O.CH_CO₂H).CO₂H [3:4:1]. f256°1. Formed from C,H,(OMe)(O.CH, CO,H).CHO by oxidation (Elkan, B. 19, 3056). Yields CuA" as a green insoluble pp.

Methylene derivative

CH2:O2:C4H2:CO2H. Piperonylic acid. [228°]. Occurs in para-coto bark (Hesse a. Jobst, A. 199, Prepared by oxidation of piperonal (Fittig a. Mielck, A. 152, 40). Got by heating protocatechuic acid with potash and CH2I2 (Fittig a. Remsen, A. 168, 94). Piperonylic acid is also formed by the action of KMnO on cubebin, on methystic acid (Pomeranz, M. 8, 468; 10, 790), on safrole (Eykman, R. T. C. 4, 39; Poleck, B. 19, 1096), and on the (a)-dihydride of piperic acid (Regel, B. 20, 415). Needles (from alcohol). May be sublimed. Nearly insol. cold water, m. sol. boiling alcohol. FeCl, gives a brown pp. in neutral solutions. Dilute HClAq at 170° forms protocatechuic acid. HNO3 forms nitro-piperonylic acid [172°]. Salts.—NaA' aq.
—KA'aq.—BaA', aq.—CaA', 3aq. S. 625 at 15°.
—PbA', aq.—CuA', aq.—Agà'. Quinine salt
C,H,2,N,O,HA'aq: needles, sol. hot water. Cinchonidino salt O₁₀H₂₂N₂OHA': needles (Hesse, A. 243, 147). — Ethyl ether EtA'. Oil.— Nitrile CH₂O₃:C₈H₂CN. [95°]. Formed from the oxim of piperonal and Ac₂O (Marcus, B. 24, Alcabelli, h. 24, Alcabelli, h. 25, Alc 8656). Needles, v. sol. alcohol. Alcoholic hydroxylamine at 60° forms the amidoxim CH₂O₂:C₆H₄.C(NH₂):NOH [151°] which yields B'HCl [198°], and is converted by Ac₂O into $CH_2O_2:C_0H_3.C \stackrel{NO}{<}_N > CMe [110^\circ].$

Ethylene derivative C₂H₁O₂:C₆H₃:CO₂H. [184°]. Formed by heating protocatechuic acid with ethylene bromide and KOH (Fittig, Z. [2] 7, 289; A, 168, 99). Needles (from hot water). May be sublimed. PCl, yields a product whence water reproduces ethylene-protocatechuic acid.

PCl, at 130° followed by water yields the acid C,H,Cl,O,:C,H,.CO,H [121°].-BaA', 2aq.-CaA', 2aq: monoclinic crystals.—Ethyl ether EtA'. Õil.

Di-methyl-ethylene ether C2H4(O.C6H2(OMe).CO2H)2. Formed by oxidising the ethylene ether of eugenol with KMnO, (Cahours, Bl. [2] 29, 270). Amorphous.

Reference. - NITRO-PROTOCATECHUIC ACID.

Homo-protocatechuic acid v. DI-OXY-PHENYL-ACETIC ACID.

Diprotocatechuic acid C, H, (OH), (CO,H), Formed by potash-fusion from divanillin (Tiemann, B. 18, 3494). Amorphous, sl. sol. water and alcohol. Coloured bluish-green by FeCl₃.

PROTOCATECHUIC ALDEHYDE C.H.O. i.e.

C₀H₃(OH)...CHO [4:3:1]. Mol. w. 133. [150°].
Formation. 1. From piperonal by successive treatment with PCl₃ and water at 100° (Fittig a. Remson, Z. [2] 7, 100; A. 159, 148; 168, 97). 2. By heating piperonal with dilute HClAq at 200° (F. a. R.).—3. By heating a solution of pyrocatechin in dilute NaOH with chloroform (Tiemann, B. 9, 1269; 14, 2020). - 4. By heating vanillin with dilute HCl at 200° (Tiemann, B. 7, 620) .- 5. By heating opianic acid with dilute HCl at 170° (Wegscheider, M. 3, 792).

Properties .- Flat needles (from water), v. sol. alcohol, ether, and hot water. FeCl₃ colours the aqueous solution green, changing to red on addition of Na.CO₃. Oxidised by KMnO₄ and by potash-fusion to protocatechuic acid. Gives a mirror with ammoniacal AgNO2. Combines with NaHSO.

m-Methyl derivative. C_aH_aO₃ i.e. C_aH_a(OMe)(OH).CHO. Vanillin. Mol. w. 152. [81°]. (285°). S. 1 at 14°; 5 at 80° (Tiemann a. Nagai, B. 10, 211). The fragrant constituent of the pods of Vanilla aromatica (Gobley, J. 1858, 534; Stokkebye, J. 1864, 612). Occurs also in the seeds of Lupinus albus (Campani a. Grimaldi, G. 17, 545), in raw beet-root sugar (Weger, D. P. J. 237, 146; Scheibler, B. 13, 335; Lippmann, B. 13, 662), in gum benzoïn from Siam (Jannasch a. Rump, B. 11, 1635), and in small quantity in wood (Singer, M. 3, 409). Formation.-1. Together with isovanillin, by heating guaiacol with chloroform and NaOIIAq (Reimer, B. 9, 424; Tiemann, B. 14, 2023). 2. By oxidation of coniferin or coniferyl alcohol with chromic acid mixture (Tiemann, B.7, 613).-3. By oxidation of eugenol by KMnO, (Erlenmeyer, B. 9, 273).—4. By heating calcium vanillate with calcium formate (Tiemann, B. 8, 1124) .-5. By the action of chloroform and potash on vanilie acid (Tiemann, B. 9, 1280).—6. By the action of emulsin or of boiling dilute acids on glucovanillin (Haarmann a. Reimer, C. J. 46, 1343). -7. From C₆H₃(OMe)(NO₂).CHO by reduction followed by the diazo- reaction (Ulrich, B. 18, 2573). Properties.—Monoclinio needles, v. sol. alcohol, other, CHCl₃, and CS₂; v. sl. sol. cold, v. sol. hot, ligroin. Smells and tastes like vanilla. May be sublimed. Acid in reaction, and decomposes carbonates. FeCl, gives a blue colour. Boiling aqueous HgCl₂ containing KNO₂ gives a violet colour (Nickel, Fr. 28, 247). Reduces silver solution. Oxidised by moist air to vanillic acid C_sH_sO_s. Reactions.—1. Bromine forms C_sH_sBrO_s [161°].—2. Dilute HCl at 199°

yields MeCl and protocatechnic aldehyde.— 8. Potash-fusion gives protocatechnic acid.— 4. Sodium-amalgam reduces it in alcoholic solution to vanillyl alcohol C.H.O. as a yellowish oil, and also hydrovanilloin CisHisOs [c. 225°] (Tiemann, B. 8, 1123).—5. By heating with di-methyl-aniline and ZnCl₂ it is converted into $C_{21}H_{28}N_{2}O_{2}$ [136°] (Fischer a. Schmidt, B. 17, 1895)—6. Vanillin (1 mol.) mixed with pyrogallol (2 mols.) is converted by cone. HClAq into 'pyrogallo-vanillein' CaoH18O8, which forms colourless crystals, insol. water, v. sol. alcohol, giving isomeric bluish-violet crystals by the further action of HCl (Etti, M.3, 637) .-7. Vanillin (1 pt.) boiled with diacetonamine acid oxalate (1 pt.) forms the oxalate of vanillodiacetonamine C₁₄H₁₈NO₃ (v. vol. i. p. 28).—8. Heating with Ac,O forms the acetyl derivative of vanillin, and also C6H3(OMe)(OAc).CH(OAc),[89°]crystallising in six-sided tables (Tiemann a. Nagai, B. 8, 1143) .- 9. Boiling aqueous FeCl, forms divanillin C₁₆H₁O₃ (304°), whence NaOEt and MI form C₆H₂(OMe)₂(CHO).C₆H₂(OMe)₂(CHO) [138°] (Tiemann, B. 18, 3493).—10. Chloro-acetic acid and KOHAq form C₆H₃(OMe)(OCH₂CO₂H).CHO [188°] (Elkan, B. 19, 3055). Salts.—*C₈H,NaO₃. Needles (from alcohol), sl. sol. NaOHAq.— $Hg(C_nH_1O_3)_2$: crystals, sl. sol. cold water, insol. alcohol.— $Zn(C_nH_1O_3)_2$: crystalline pp. Estimation .- Vanilla pods are extracted with ether, the extract shaken with a nearly saturated solution of NaIISO3, the aqueous layer decomposed by H.SO,, the vanillin thence extracted by ether, and the extract evaporated (Tiemann a. Haarmann, B. 8, 1115).

Acetul Acetul derivative of vanillin C₆H₂(OMe)(OAc).CHO. [77°]. Formed slowly by the action of an ethereal solution of Ac.O on sodium-vanillin in the cold (Tiemann a Nagai, B. 11, 646). Flat needles. Combines with bi-

sulphites.

Oxim of vanillin C.H. (OMe)(OH).CII:NOII. [1227] (Tiemann a. Kees, B. 18, 1661; cf. Lach, B. 16, 1786).

Phenyl-hydrazide of vanillin C_oH₃(OMe)(OH).CH:N.HPh. [105°]. Plates.

Glucoside of vanillin C,H,(OMe)(OC,H,,O,).CHO. Glucovanillin. $[192^{\circ}]$. $[a]_{\rm p} = -88.63$ at 20°. Prepared by slowly adding CrO, (8 pts.) in water (100 pts.) to coniferin (10 pts.) dissolved in water (200 pts.), and leaving the mixture to stand for 5 days (Tiemann, B. 18, 1596, 1661). Colourless needles (containing 2 aq), v. sol. water, m. sol. alcohol, insol. ether. Readily split up by dilute H.SO. or by emulsin into vanillin and glucose. Does not reduce Fehling's solution in the cold. Yields C_eH₂(OMe)(OC_eH₁₁O_s).CH:N₂HPh [c. 195°] and a lavorotatory oxim [152°], crystallising in slender yellow needles (containing aq).

p-Methyl-derivative C_sH₂(OMe)(OH).CHO[4:3:1]. Isovanillin. [116°]. Formed by oxidising acetyl-isoferulic acid with KMnO, and saponifying the resulting acetyl derivative (Tiemann a. Will, B. 14, 968). Formed also by heating opianic acid (4 pts.) with water (30 pts.) and HClAq (8 pts. of S.G. 1-17) (Wegscheider, M. 3, 789). Monoclinic pyramids, sl. sol. cold water, v. sol. alcohol and ether. May be sublimed. When warm it smells somewhat like vanillin. Its alkaline solutions are yellow.

FeCl. does not colour the aqueous solution. Reduces boiling ammoniacal AgNO. very soluble compound with NaHSO.

Di-methyl derivative C.H. (OMe). CHO.

Methyl-vanilin. [43°]. (c. 283°). Formed
from potassium vanillin and MeI (Tiemann, B. 8, 1135), and also by distilling opianic acid with soda-lime (Beckett a. Wright, C. J. 29, 164). Needles, v. sl. sol. hot water, v. sol. alcohol and ether. Smells like vanilla.

Methyl-cthyl derivative

C_sH_s(OMe)(OEt),CHO. [65°]. Formed by boiling potassium-vanillin with EtI and alcohol (Tiemann, B. 8, 1129). Prisms, v. sl. sol. hot water. Smells like vanilla.

Methylene derivative C_xH_xO₃ i.e. CH_xO₂:C_aH_x.CHO. Piperonal. Mol. w. 150. [37]. (263°). S. 2 in the cold. Formed by oxidation of piperic acid in neutral solution by KMnO, (Fittig . Mielek, A. 152, 35). Formed also by oxidation of the (a)-dihydride of piperic acid by alkaline KMnO, (Regel, B. 20, 415). Transparent prisms (from water), m. sol. hot water, v. sol. alcohol and ether. Smells much like coumarin. Forms a crystalline compound with NaHSO₃. Not affected by aqueous alkalis. Reactions.—1. By oxidation, or by boiling with alcoholic potash, it is converted into piper-onylic acid CH₂O₂:C₆H₃.CO₂H.—2. Reduced by water and sodium-amalgam to piperonyl alcohol C₈H₅O₈, hydropiperoïn C₁₆H₁₄O₈ [202], and isohydropiperoïn [138°]. AcCl converts the hydrohydropperoins into C₁₄H₁₂Cl₁O₁ [198°] (Remson a. Fittig, Z. [2] 6, 97; A. 159, 129).—3. An alcoholic solution of KCy forms piperonyloin CH₂O₂C₆H₄,CH₄(OH).CO.C₆H₄;O₂CH₂ [120°], separating from alcohol in yellow crystals [F. M. Perkin, C. J. 59, 164).—4. Very dilute HClAq at 200° forms protocatechuic aldehyde.—5. PCl, forms liquid CH₂O₂:C₈H₄.CHCl₂ (c. 235°) and C.H.(Cl,O₂, whence cold water forms dichloropiperonal C₈H₄(Cl,O₄, [90°].—6. Gaseous HCl, passed into a mixture of phenyl mercaptan and piperonal, forms CH₂O₂C₈H₄CH(SPh)₂ [48°] (Baumann, B. 18, 886).—7. Alcoholic ammonia, in presence of some HCy, forms $C_{24}H_{18}N_2O_{6}$, crystallising in prisms [213°], insol. alcohol and ether. Piperonal, heated with alcoholic NH, at 70°, forms an isomeric body [172°], crystallising in yellow needles, sol. hot alcohol, insol. water and ether (Lorence, B. 14, 791).— 8. Aqueous HCy at 65° forms a compound whence an alcoholic solution of NH, yields CH_O.C.H.CH(NH_).CN, converted by boiling HClAq into C_bH₀O_s.-9. Aniline forms, on heating, C_iH₁NO_s, crystallising in colourless needles [65°] (L.).-10. p-Phenylene-di-methyl-diamine gives C_sH₁(O_sCH_s).CH:N.C_sH_sNMe₂[110°] (Nuth, B. 18, 75°). B. 18, 575).

Oxim of piperonal CH,O,:C,H,.CH;NOH. [110°]. Needles, v. sol. alcohol (Marcus, B. 24,

Phenyl-hydrazide of piperonal CH_O,C,H_CH.N_HPh. [100°] (M,); [103°] (Rudolph, A. 248, 103). Yellow needles. PROTOPINE C₂₂H₁₂NO₂. [202°]. An alkaloid occurring in very small quantity in opium,

and obtained from the mother-liquors after the separation of morphine by Gregory's process (Hesse, Z. [2] 7, 653; A. Suppl. 8, 318). rated from cryptopine by ppn. of the solution of

the mixed hydrochlorides with conc. HClAq, the protopine salt adhering to the sides of the vessel. Crystalline powder (from alcohol), insol. water, sl. sol. hot alcohol, m. sol. chloroform. The alcoholic solution is alkaline in reaction. Sl. sol. ether, separating in spherical groups of prisms. Sl. sol. KOHAq and NH, Aq. FeCl, gives no colour. HNO, forms a colourless solution, which turns yellow on warming. H₂SO₄ containing ferric sulphate gives a dark-violet solution, turned dirty brownish-green at 150°. The salts have a bitter taste, and do not gelatinise .-

B'_H_PtCl, 2aq: yellow crystalline pp.
PRUSSIAN BLUE v. FERRIC FERRICYANIDE, vol. ii. p. 834; and Potassium-ferrous ferri-

CYANIDE, vol. ii. p. 339.

PRUSSIC ACID v. CYANHYDRIC ACID, vol. ii. p. 300.

PSATYRIN v. HARTIN.

PSOROMIC ANHYDRIDE O.H.O.? [264°]. Occurs in Psoroma crassa, a lichen growing in Sicily (Spica, G. 12, 431). Needles, sol. alcohol and ether, insol, benzene. Yields C. H13 AgO10 as a flocculent pp

PSYCHOSINE. A substance got, according

to Thudichum (J.m. [2] 25, 19), from brain. PTEROCARPIN $C_{20}H_{10}O_{s}$. $[152^{\circ}]$. $[a]_1 = -211^{\circ}$ in 46 p.c. chloroform solution. Obtained by mixing powdered sandal wood (Pterocarpus santal line). talinus) with slaked lime, and extracting with ether. The residue is crystallised from alcohol, and the homopterocarpine dissolved in CS2, which leaves the pterocarpine (Cazencuve a. Hugounenq, A. Ch. [6] 17, 115). Square tables (from CHCl₂), insol. water, m. sol. hot alcohol and hot CS₂. Insol. acids and conc. KOHAq, even on boiling. Bromine forms C₂₀H₁₃BrO₈, crystallising in yellowish needles.

Homopterocarpin carpin $C_{24}H_{24}O_6$. [82°-86°]. Obtained as above (C. a. H.). $[\alpha]_1 = -199^{\circ}.$ Long needles (from boiling alcohol), insol. water,

sol. ether, v. sl. sol. cold alcohol.

Reactions.—1. Bromine gives C₂₄H₂₃BrO₄ and C₂₄H₁₈Br₆O₆ [270°].—2. On distillation it is largely split up into phenols resembling creosote, and a small quantity of pyrocatechin. - 3. Distillation over zinc-dust gives benzene, toluene, ethylene, and CO.—4. HCl gives MeCl and a resin.—5. HI gives MeI.—6. Potash-fusion gives phloroglucin. - 7. Fuming HNO, gives oxalic acid and tri-nitro-orcin [162°]. Not acted upon by sodium-amalgam, phenyl-hydrazine, and Ac.O.

PTOMAINES. The name 'ptomaines' was first applied to poisonous organic bases obtained from dead bodies (πτῶμα, a corpse), but is now usually given to poisonous organic bases formed in the putrefaction of any kind of animal matter. In extracting ptomaines no reagents that would decompose proteids may be used. The bases may be extracted by alcohol, and purified by ppn. with phosphomolybdic acid. In presence of a little HCl the ptomaines are fairly stable, and the solution can then be evaporated and the hydrochlorides extracted from the syrupy residue by absolute alcohol. By this method neuridine

CH(OH), CH, NMe,OH (vol. iii. p. 444), a base isomeric with ethylene-diamine, neuridine C.H., N2, gadinine C,H,, NO2, triethylamine, dimethylamine, and trimethylamine. Garcia (H. 17, 543) got hexamethylene-diamine C.H. Herring-pickle contains choline, NMe, and NH, Me. By the putrefaction of the herring NMe, NH2Me, cadaverine C.H16N2, putrescine C4H12N2, and gadinine C,H₁,NO₂ are formed (Bocklisch, B. 18, 1922). Gautier and Etard (C. R. 94, 1600) from putrid mackerel and putrid horse-flesh obtained a collidine dihydride C,H12N, parvoline CoH13N, and a base C17H38N. In the putrefaction of proteids poisonous bases are formed in the first five or six days, and are destroyed by further progress of putrefaction. The highly poisonous methyl-guanidine is formed by the action of putrefactive bacteria on beef-broth at 38° (Bocklisch, B. 20, 1441). From human corpses Brieger obtained tri-methyl-oxyethyl-ammonium hydroxide C₃H₁₅NO₂ or CH₂(OH).CH₂NMe₃.OH (choline or neurine, vol. iii. p. 498), neuridine (choine or netrine, vol. iii. p. 498), neuridine $C_3H_{11}N_{2}$, cadaverine $C_3H_{12}N_{2}$, putreseine $C_4H_{12}N_{2}$, saprine $C_3H_{12}N_{2}$, trimethylamine, methyl-guanidine, tetanine $C_1H_{22}N_{2}O_4$, mydiatoxin $C_4H_{13}NO_2$, and mydaleine (Brieger, loc. cit.; cf. Selmi, Rend. Accad. Sci. Bologna, 1872; Schwanert, B. 7, 1332; Guareschi a. Mosso, J. pr. [2] 27, 428; 28, 504; G. 13, 493; Rockurte Ar. El. (314, 1041). Petominas are Beckurts, Ar. Ph. [3] 14, 1041). Ptomaines are often produced in animal bodies which, after brief exposure, have been excluded from the air ; e.g. corpses, sausages, and tinned meat. A crystalline ptomaine can be obtained from the body after arsenical poisoning (Husemann, Ar. Ph. [3] 16, 169; 19, 415). The alcoholic solution of hydrochlorides of ptomaines may be ppd. by an alcoholic solution of HgCl2; after twenty-four hours' standing, the pp. is boiled with a large quantity of hot water, which leaves the compounds of peptones and albuminates undissolved.
The hot filtrate deposits the mercury double salt of choline (neurine) while the mother-liquor contains the remaining bases. Picric acid added to an aqueous solution of the hydrochlorides ppts. neuridine picrate, while the mother-liquor deposits, on evaporation, broad needles of choline picrate C₅H₁₃NOC₆H₂(NO₂)₃OH. Cadaverine and putrescine can be separated by means of their aurochlorides. Saprine is isolated by means of its platinochloride. To distinguish a ptomaine from a vegetable alkaloid, Brouardel a. Boutmy (C. R. 92, 1056; cf. Tanret, C. R. 92, 1163) add a few drops of the solution of the sulphate of the alkaloid to potassium ferricyanide mixed with FeCl₃: a dark-blue pp. is formed if a pto-maine be present, while the vegetable alkaloids (except morphine, veratrine, eserine, aconitine; and ergotinine) have no action. The test is, of course, given by many other reducing agents. This ptomaine reaction is given (slowly) by a poisonous liquid alkaloid extracted by Stas's method from the intestines of persons who died of cholera (Villiers, C. R. 100, 91). Pouchet (C. R. 97, 1560; cf. Gautier, B. C. 1882, 710; Béchamp, C. R. 94, 973) obtained from urine and faces some alkaloids closely resembling by absolute alcohol. By this method neuridine hydrochloride can readily be obtained. By the putrefaction of proteids Brieger (Two monographs: Ueber Ptomaine, Berlin, 1885; cf. Gautier, Bl. [2] 48, 10) obtained tri-methylographs: Gautier, Bl. [2] 48, 10) obtained from urine and fæces some alkaloids closely resembling the ptomaines got by putrefaction of proteids of accompanies of alcohol, the lead being finally removed by H2S, and the liquid dialysed. C.H.NO. is liquid and dialyses with difficulty; it exhibits the alkaloidal reactions, is resinified by HCl, and reduces platinic chloride. The base C.H., N.O. or C,H, N,O2 is crystalline, and passes through the membrane; it is insol. ether, nearly insol. alcohol, is feebly alkaline and yields crystalline salts. From the dialysate the platinochlorides of two crystalline unstable bases C, H12N2O, and C,H, N,O, can be got. Urine which had a tendency to deposit cystin and the fæces of the same patient contained cadaverine and putrescine (Baumann, H. 13, 562; cf. Dupré a. Bence-Jones, Pr. 15, 73; Stadthagen a. Brieger, Ar. pathol. Anat. 115, pt. 3). These diamines appear to be absent from normal urine, but present in cholera.

Cadaverine is Pentamethylene-diamine, vol. iii. p. 805.

Putrescine is Tetramethylene-diamine.

Mydaleïne is extremely poisonous, while

gadinine is not poisonous.

Mydine C,H, NO. Occurs in putrid corpses (Brieger, Ptomaine, iii. 25). Has an ammoniacal odour and reduces gold chloride. Not poisonous. -B'C,H,N,O,. [195°]. Broad prisms.

Base C,H,NO,. Occurs in decaying horse-

flesh, four months old (Brieger). Acid in reaction. Poisonous. Does not form a picrate.—B'HAuCl., [176°]. Needles or plates.

Typhotoxin C, H1, NO2. Formed by the action of the typhus bacillus on muscle (Brieger, Ptomaine, iii. 86). Poisonous base.—B'HAuCl. [176°]. Prisms.

Mydatoxin C_bH₁₃NO₂. Occurs in decaying horse-flesh and corpses (B.). Poisonous. Strongly

alkaline.—B'_H,PtCl, [193°]. V. e. sol. water.

Tetanine C₁H₃N₂O₄. Occurs in decaying corpses (Brieger, B. 19, 3120), and is formed by the action of the tetanus bacillus on beef. Very

poisonous base.—B'H,PtCl_s. Plates.

Base C,H₁₁N. (c. 100°). Accompanies tetanine, and also produces convulsions (B.). Volatile liquid. Its hydrochloride is crystalline [205°].—B'HAuCl₄. [130°].—B'₂H₂PtCl₆. Plates, decomposed at 240°.

Base C₃₂H₃₁N. Oily ptomaine, smelling like hawthorn (Delezinier, Bl. [3] 1, 178). In prosence of air it acts chemically and physiologically like veratrine. Insol. water, sol. alcohol and ether. Its salts are deliquescent.

Base C₃H₁₁NO₂. [156°]. Occurs in putrid flesh and putrid fibrin (E. a. H. Salkowski, B. 16, 1192). Crystalline powder, v. e. sol. water. Not poisonous. - B'HCl: crystals, v. e. sol. water.

-B'HAuCl, aq: yellow crystals.

Base C₁₁H₁₂NO₂. Erysipeline. Occurs in urine in erysipelas (Griffiths, C. R. 115, 667). Prisms, sol. water. Very poisonous.

Base C₁₂H₁₃NO. Occurs in urine in puerperal fever (G.). Crystalline and poisonous.

Base C₁₂H₁₃N. A product of the decomposition of albumen by Bacterium allii, which is found in decaying onions (A. B. Griffiths, C. R. 110, 416). Minute deliquescent needles (from water), smelling like hawthorn.-B'₂H₂PtCl₄: crystalline, sol. hot water.

Base C, J.H., N.O. Occurs in urine of victims to glanders (A. B. Griffiths, C. R. 114, 1382). White crystals. Poisonous. Forms crystalline salts.

Base C₂₀H₂₆N₂O₅. Occurs in urine in cases of pneumonia (G.). Minute needles, forming an

alkaline aqueous solution [a]₀ = 23.5°.

Base C_sH₁₁N. (202°). S.G. 2 9865. Extracted, together with a base CieHisN from putrid cuttlefish (De Coninck, C. R. 106, 858, 1604; 108, 58, 809; 110, 1339; 112, 584). Mobile, stronglysmelling liquid, v. sol. water, alcohol, and ether. Turns brown in air. Appears to be a propylpyridine, as it yields nicotinic acid on oxidation by dilute KMnO, at 90°.—B'HCl: deliquescent radiating flass.—B'_HPtCl_e. Converted by hot water into B'_PtCl_e, a nearly insoluble brown b'₂H₁H₃Cl₈. B'HBr. B'₂H₁H₃Cl₈. B'₂H₁H₃Cl₈. B'₄H₁N₂Cl₈. B'₄McI. Needles, v. e. sol. alcohol. Base C₁₀H₁₃N. (230°). Formed as above. Liquid, smelling like furze. Resinified by air.—

B'HBr. White deliquescent needles .- B'HCl. --B'₂H₂PtCl₄. — B'₂PtCl₅. [206"]. — B'HAuCl₄: yellow pp., decomposed by hot water.

. Base C₁₀H₁₃N. (200°). Extracted by Stas's method from fibrin that has putrefied for two months (Guareschi a. Mosso, J. pr. [2] 27, 428; J. Th. 1887, 487). Yields the alkaloidal reactions. Smells like pyridine. Acts physiologically like curare.—B'2H_PtCl₂: rose-red crystals.

Base C₁₄H₂₀N₂O₄. [250°]. Formed in the putrefaction of fibrin, from which it can be extracted, together with the liquid alkaloid C10H13N, by chloroform and ether (Guarcschi, G. 17, 509). Tables (from alcohol), sol. water and alcohol, v. sl. sol. chloroform. Its aqueous solution is neutral. Griffiths (Bl. [2] 7, 250; C. R. 113, 656) got, from urine of patients suffering from erysipelas, a crystalline ptomaine 'erysipeline' C11 K13 NO3, sol. water, and very poisonous. gives the alkaloidal reactions.

The term leucomaines (λεύκωμα, white of egg) is applied by Gautier (Sur les Alcaloïdes des Tissus Animaux, Paris, 1886) to alkaloids occurring in the tissues of living animals. From fresh beef and Liebig's extract of beef he obtained xanthocreatinine $C_2H_{10}N_1Q$, crysocreatinine $C_2H_1N_1Q$, amphicreatinine $C_2H_1N_1Q$, pseudoxanthine $C_1H_1N_1Q$, and two feeble bases $C_{11}H_{12}N_{12}Q_3$ and $C_{12}H_{12}N_{11}Q_4$, both crystallising in tables.

Xanthocreatinine C5H10N4O. Thin sulphuryellow tables, v. e. sol. water, sol. boiling alcohol. Gives an odour of roast meat when heated. Resembles creatinine.

Chrysocreatinine C.H.N.O. Orange crystals, with feebly alkaline reaction. Sl. sol. water, Resembles creatinine.

Amphicreatinine C₀H₁₀N,O₄. Yellow prisms, sl. sol. water. A weak base, resembling crea-

Pseudoxanthine C.H.N.O. Yellow orystalline powder, sl. sol. cold water, sol. HClAq and NaOĤAq. Reacts with HNO, and KOH like vanthine.

Carnine v. vol. i. p. 710.

PTYALIN v. vol. ii. p. 545.
PTYCHOTIS OIL. The essential oil got from the seeds of Ptychotis ajowan, an umbelliferous plant growing in Central India, contains thymoland a terpene C₁₀H₁₈ (172°) S.G. ¹² ·854 (Stenhouse, C. J. 9, 234; cf. Haines, C. J. 8, 289).
PULEGIUM OIL. The essential oil of Puls-

gium micranthum, growing on the Steppes of Southern Russia, contains oily C. H. O (227°) S.G. 11 .932 (Butlerow, J. 1854, 594). It yields acetic and valeric acid when fused with potash. The oil of Mentha pulegium is described under

PULVIC ACID $C_{18}H_{12}O_{5}$ i.e. $CO_{2}H.CPh; C < \stackrel{C(OH):CPh}{O} \stackrel{CO}{CO}$. [215°]. Prepared

by the action of cold NaOHAq on a solution of the anhydride in acctone, and also by boiling vulpic acid with milk of lime (Spiegel, B. 13, 1630, 2219; 14, 1686; 15, 1550; A. 219, 1). Orange crystals or yellow plates (containing EtOH), sol. alcohol and ether, sl. sol. water. Decomposed by baryta-water into phenyl-acetic and oxalic acids. Alkaline KMnO, oxidises it to phenyl-glyoxylic and oxalic acids. On reduction by zinc-dust and NH3Aq it gives a mixture of carboxy-cornicularic acid (C1, H1,O3), cornicularic carboxy-cornicularic acid (C₁,H₁₁O₃), cornicularic acid (C₁,H₁₀O₃), and the two dihydrides of cornicularic acid (C₁,H₁₀O₃).

Salts.—BaA" and; golden plates.—AgHA"; small prisms.—Ag,A" aq: long needles.

Methyl ether v. Vulpic acid.

Ethyl ether Eth'. [128°]. Prepared by

dissolving the anhydride in alcoholic potash.

Methyl derivative of the methyl ether $C_{1s}H_{1o}Me_2O_3$. [139°]. Colourless needles. An hydride $C_{1s}H_{1d}O_4$ i.e.

CO.O.C:CPh CO. [221°]. Formed, together with MeOH, by heating vulpic acid at 200°. Colourless needles, sl. sol. alcohol, insol. water. Converted by ammonia into C₁₈H₁₁(NH₂)O₄ [220°] crystallising in yellow prisms.

PUNICIN. The purple of the ancients. Extracted from Purpura capillus and other shell-

fish which yield a colourless secretion which becomes purple on exposure to sunlight (Schunck, C. J. 35, 589; 37, 613). Obtained in Central America from Purpura patula. Yarn dyed by the Indians is warmed with HCl and then with ether. The colouring matter is then extracted with aniline, which on cooling deposits punicin as a crystalline powder, insol. boiling alcohol and ether, sl. sol. benzene and HOAc. Its solution in aniline shows an absorption band between C and D, with a sharp edge towards C. The band resembles that of indigo, but it disappears sooner on standing. In phenol it forms a sky-blue solution. Its solution in conc. H.SO. shows an absorption band between D and E this disappears on standing, the liquid becoming bright green. Water precipitates the purple from this solution, so that a sulphonic acid is not formed. Punicin begins to sublime at 190°. It is hardly attacked by HNO₄ (S.G. 1·2) or by aqueous CrO₃. With bromine it reacts, forming a body which crystallises from alcohol in yellow needles. Punicin dissolves in aqueous SnCl, but is deposited again on exposing the solution to air.

PURPLE OF CASSIUS. A purple-coloured solid, obtained by adding SnCl,Aq to AuCl,Aq in presence of a reducing agent; v. Tin, oxides or, in this volume.

PURPURIC ACID C,H,N,O,. Not known in the free state.

Salts. - (NH4)HA" aq. Murexide. Formed by heating ammonium dialurate; by oxidising uranil with HgO; and by adding ammonia or ammonium carbonate to a mixture of

alloxan and alloxantin (Prout, A. Ch. 11, 48; Kodweiss, P. 19, 12; Liebig a. Wohler, A. 26. 319; Fritzsche, J. pr. 16, 380; 17, 47; Beilstein, A. 107, 176; Laurent, C. R. 35, 629; Gregory, A. 33, 334). Garnet-red four-sided prisms with golden-green lustre; when dried in vacuo it forms a brown powder. M. sol. hot water, forming a purple solution, insol. alcohol and ether. Decomposed by acids with formation of uranil and alloxan. The absorption spectrum has been studied by Hartley (C. J. 51, 199) .- KHA". Crystals resembling murexide, forming in cold KOHAq a blue solution decolourised by heat.— NaHA".—BaA" 3aq; dark.green powder.— AgHA" 1 aq: brownish-red powder.—Ag2A".

Isopurpuric acid v. TRI-NITRO-PHENOL, Re-

action 5.

Metapurpuric acid v. (a)-DI-NITRO-PHENOL,

PURPUREO CHROMIUM SALTS v. CHROM-AMMONIUM SALTS, vol. ii. 159-60.

PURPUREO-COBALT SALTS v. COBALT-AMINES, vol. ii. pp. 227-8. PURPUREO-RHODIUM SALTS

DIUM-AMMONIUM COMPOUNDS.

PURPURIN v. TRI-OXY-ANTHRAQUINONE.

PURPURIOR 2. IRI-OXY-ANTHIBAGOINOSE.

PURPUROGALLIN C. H. 10. Pyrogalloguinone. [256]. Formed by the slow oxidation of pyrogallol (Struve, A. 163, 162; Girard,
Z. 1870, 86; Wichelhaus, B. 5, 848; De Clermont a. Chautard, C. R. 94, 1362; 102, 1072,
Victoria C. 100, 1077; Lagy J. 27 Nietzki a. Steinmann, B. 20, 1277; Loew, J. pr. [2] 15, 322). Formed also by the action of aqueous KNO2 on gallic acid (Hooker, B. 20, 3259). Obtained also from pyrogallol and quinone (Wichelhaus, B. 5, 847; Nietzki, B. 18, 1278). Prepared by adding a solution of K_a FeCy_g (87 g.) in water (330 c.c.) to pyrogallol (20 g.) dissolved in cold water (330 c.c.), and filtering after half an hour; the yield is small (3 g.). Dark-brown needles (from alcohol). May be sublimed. V. sl. sol. water, sl. sol. alco-hol, m. sol. ether. Reduces AgNO, and Fehling's solutions. H.SO, forms a crimson solution changed to violet by HNO, Ammonia forms a blue solution, changing through green to dark rellow. Yields naphthalene on distillation with zinc-dust. According to De Clermont and Chautard purpurogallin yields Na,A' os crystal-lising in deliquescent needles, Ba,A' os crystalline plates, C₂₀H₁₂Br₄O₀ as red needles [204°] and C₂₀H_{1.}Ac₄O₀ [186°]. By heating with H₂SO₄ these chemists obtained SO2 and C20H12O10, which crystallised in brown needles forming a blue solution in KOHAq.

PURPUROXANTHIN v. m-DI-OXY-ANTHRA-

PURREIC ACID v. EUXANTHIC ACID. PUTREFACTION v. FERMENTATION.

PUTREFACTIVE ALKALOIDS v. PTOMAÏNES. PUTRESCINE v. TETRA-METHYLENE-DIAMINE.

PYKNOMETER. This name is sometimes given to various forms of the specific gravity bottle, for determining the relative densities of

liquids (cf. Densities, relative, vol. ii. p. 373).
PYRANIL-PYROIC ACID C₁₀H₁₀NO(CO₂H). [165°]. Formed by heating phenyl-amido-pyrotartaric acid CO.H.CH, CMe(NHPh).CO.H a little above its melting point for some time (Reissert a. Tiemann, B. 19, 622; 21, 1942, 3257; 22, 2281; 24, 314). Crystalline powder, sl. sol.

water, alcohol, and ether. Converted by heating strongly into the phenyl-imides of citraconic acid and of phenyl-amido-pyrotartaric acid. According to Anschütz (B. 21, 3252; 22, 731; 23, 895, 2979; A. 246, 115; 248, 269), pyranilpyroïc acid is the mono-anilide of mesaconic

PYRAZINE. This name is used to denote the ring NCH:CH>N.

Pyrazine hexahydride C4H10N2 NH CH₂CH₂ NH. Piperazine. Di-ethylenediamine. [104°-107°]. (137° uncor.). Formed from ammonia and ethylene bromide (Cloez, Instit. 1843, 213) or ethylene chloride (Natanson, A. 92, 48; 98, 291; Hofmann, Pr. 10, 224; 11, 278; B. 23, 3297). Formed also by boiling NO.C. H. N. CH. CH. N. N. With alcoholic potash (Bischler, B. 24, 717). According to Majert a. Schmidt (B. 24, 241), it is not identical with spermine. Glittering tables (from water). May be sublimed. Strongly alkaline and absorbs CO₂ from the air.

Reactions .- 1. Aqueous NaOCl, saturated with Cl, forms ClN CH₂·CH₂·NCl [71°], crystallising in prisms, v. sl. sol. water, v. sol. alcohol (Schmidt a. Wichmann, B. 24, 3243). This body explodes at 80°-85°. Bromine water forms the corresponding di-bromo-piperazine, which is very unstable. -2. Diazobenzene chloride and NaOHAq form Ph.N. N:C, H. N.N. Ph [129°] (S. a. W.). - 3. Beneoic aldehyde yields the compound (N:C,H,:N):CHPh [247] (Schmidt a. Wichmann, B. 24, 3212). - 4. Quinone forms an amorphous violet-brown body, almost insol. alcohol. -5. Hydroquinone in alcoholic solution forms $C_4H_{10}N_2C_4H_0O_2$, crystallising in needles [195°].—6. Phenol forms $C_4H_{10}N_2$ PhOH [101°], crystallising from spirit in prisms, v. sol. water.-7. Oxalic ether at 110° reacts forming the ether CO₂Et.CO.N.C.H.; N.CO.CO₂Et [124°] crystallising in broad needles (S. a. W.).—8. p-Chloro-nitro-benzene at 150° gives the compound NO₂, C., H., N.C., H., NO₂ [248°] (Schmidt a. Wichmann, B. 24, 3240).

Salts.—B"H,Cl, aq: needles, v. sol. water.— B"H,PtCl, -B"2HAuCl, -B"H,HgCl, : stellate Britin.—D Zimudi.—D Halleri, Sociale groups of needles (Sieber, B. 23, 326).—
B"C,H.(NO₂),OH: yellow needles.—Carbonate: [162°-165°].—Urate: B"C,H,N₄O₃. The phosphate and the bismutho-iodide are crystalline.

Di-acetyl derivative [138.5°]. (above 310°). Formed from piperazine and Ac₂O. Needles, v. e. sol. water and alcohol.

Nitrosamine NO.N:C,H,:N.NO. (Ladenburg, B. 24, 2640; Schmidt, B. 24, 3245; HOAc to NH, N.C.H, N.NH, which crystallies in needles [c. 100°] (228°), and yields B'HCl, B'C,H,N,O,, an amorphous di benzoyl derivative, and reacts with benzoic aldehyde, forming CHPh:N.N:C,H,:N.N:CHPh [205], which crystallises in pearly plates.

PYRAZOLE C,H,N, i.e. CH:CH>NH. [70°]. (187°). Formed by heating the tri-carboxylic acid produced by saponification of the product slowly adding H,SO, to aqueous KNO, under an

of direct addition of diazoacetic ether and of direct addition of diszoncesic etner and accetylene dicarboxylic ether (Buchner, B. 22, 2165). Formed also by heating hydrazine hydrate (10.8 g.) with epichlorhydrin (10 g.) and ZnCl₂ (11 g.) (Balbiano, B. 23, 1193). Needles, v. sol. cold water, forming a neutral solution, sol. alcohol and ether. Gives a white pp. with HgCl., and also with ammoniacal AgNO.

Salts .- B'HCl. Hygroscopic prisms. B',H,PtCl, 2aq. At 210° it is split up into HCl and $(C_3H_3N_2)_2PtCl_2$, a light-yellow powder. — AgC₃H₃N₂ sl. sol. water. — B'C₆H₂N₂O₇. [160°]. PYRAZOLE BLUE C20H18N,O2 i.s.

N.NPh.CO CO.NPh.N -CMe. Formed by oxidation С́Ме — С́=С _ of di-oxy-di-phenyl-di-methyl-dipyrazyl (Knorr, A. 238, 172; B. 25, 765). Sol. chloroform, conc. H₂SO, and HOAc. Its spectrum resembles that of bodies of the indigo group. Decomposes about 230°. Its sulphonic acid, got by the action of Br on di-oxy-di-phenyl-di-methyl-dipyrazyl disulphonic acid, is destroyed by excess of bromine (Möllenhoff, B. 25, 1949).

o-PYRAZYL-BENZOIC ACTD C10H8N2O2 i.e. CH:N CH:CH>N.C.H..CO.H. [139° cor.]. Formed by oxidising o tolyl pyrazole with KMnO, (Balbiano, G. 19, 123). Yellow needles (from dilute alcohol) .- BaA' ...

Ethyl ether EtA'. (309° i.V.). p-Pyrazyl-benzoic acid. [265°]. Got in like manner from p-tolyl-pyrazole.—NaA'. BaA'. Ethyl ether EtA'. [62°]. Tables.

202. [149°]. (above 360°). S. (alcohol) 1:87 at 16°; 3:08 at 78°; S. (toluene) 16:5 at 18° (Bechi, B. 12, 1978). Occurs in coal tar (Graebe, A. 158, 285). Monoclinic tables (Fittig a. Hintz, 1978). B. 10, 2143), v. e. sol. CS2 and ether. Yields pyrene-quinone and pyrenic acid on oxidation. ShCl, at 360° forms CCl4, C15Cl10 [above 800'], C1,Cl10 [above 300°], and other bodies (Merz a. Weith, B. 16, 2880). Bromine forms crystalline C_{1e}H_zBr₄ and C_{1e}H_zBr₅ (Graebe).

Picric acid compound C, H, O, H, N,O, [222]. Red needles (from alcohol), v. sl. sol.

cold alcohol, m. sol. ether, v. sol. benzene. Hexahydride C₁₀H₁₀. [127°]. Formed by heating pyrene with HIAq and P at 200°. Needles, v. e. sol. ether and boiling alcohol. alcoholic solution is not ppd. by picric acid.

Chloropyrenes. The following chloro-pyrenes are formed by passing Cl into a solution of pyrene in chloroform. They are separated by fractional crystallisation from alcohol, chloroform, and xylene (Goldsch.niedt a. Wegscheider, M. 4, 237).

C_{1c}H_cCl. [119°]. Golden needles, forming in H₂SO, a solution with violet fluorescence. Yields C_{1c}H_cClC_cH₁N₁O₁. [177°].
C_{1c}H_cCl₂. Two di-chloro-pyrenes [156°] and

[196°]. C16H,Cl. [257°]. White needles. ClaH.Cl. [above 830°]. Needles.
Nitropyrene ClaH.NO. [150°]. Formed by ethereal solution of pyrene (Goldschmiedt, M. 2, 580). Yellow needles (from alcohol), sl. sol. cold alcohol.

Dinitro-pyrene C_{1*}H₃(NO₂)₂. Formed from pyrene and MNO₃ (S.G. 1·45). Yellow needles (from HOAc). Reduced by tin and HCl to diamido-pyrene (Jahoda, M. 8, 449).

Tetra-nitro-pyrene C_{1*}H₄(NO₂)₄. [above 800°]. Yellow needles (from HOAc), nearly insol. alcohol.

insol. alcohol.

Amido-pyrene C₁₈H₂.NH₂. [116°]. Got by reducing nitropyrene. Needles, sl. scl. water.—
B'₂H₄SO₄ (dried at 100°).—B'HCl. Its solution dyes fir wood red.

PYRENE CARBOXYLIC ACID $C_{16}H_{9}.CO_{2}H$. [287°]. Formed by fusing its nitrile with potash (Goldechmiedt a. Wegscheider, M. 4, 256). Needles, sl. sol. water. Resolved by heat into pyrene and CO.—CaA'₂ aq.—BaA'₂ 2\(\frac{1}{2}\) aq.

Nitrile C₁₈H₂CN. [150°]. Formed, together with the privale of the discripacytic gold.

gether with the nitrile of the dicarboxylic acid, getner with the nitrie of the disarboxylic acid, by heating potassium pyrene disulphonate with KOy or K, FeCy_s. Needles (from alcohol). The solutions of this body show green fluorescence.— (O₁,H_{*}N₂,C_{*}H_{*}N₃O_{*}. [134°]. Red needles, decomposed by alcohol.

Fyrene dicarboxylic acid C_{1s}H_s(CO₂H)₂.

[above 300°].

Nitrile [above 300°]. C_{1e}H_s(CN)₂. Formed as above. Yellow powder. Its solutions show green fluorescence.

PYRENE-KETONE C13H8O i.s.

[1:1] $C_{10}H_s < CH > CO$. [142°]. Formed by

distilling pyrenic acid with slaked lime (Bamberger a. Philip, B. 19, 1996, 3040; 20, 371; A. 240, 178). Golden tables (from dilute alcohol), volatile with steam. Reduced by zinc and HCl to C₁₂H_s(CH.OH). Oxidised by KMnO₄ to naphthalene (1,1')-dicarboxylic acid.

PYRENE-QUINONE C, H,O, i.e.

(Bamberger a. Philip, B. 20, 369; A. 240, 166). [c. 282]. Formed by oxidation of pyrene by chromic acid mixture (Graebe, A. 158, 295; Goldschmiedt, M. 4, 309). Red needles (from HOAc), sol. aqueous NaHSO₃, v. sl. sol. alcohol and ether. Yields pyrene on distillation with zinc-dust. Bromine forms C₁₄H₂Br₁O₂ and the control of the control o C16H2Br3O2. Its alcoholic solution is turned claret-colour by a little NaOH. Reduced by zinc-dust and ammonia to hydropyrenequinone or pyrene-hydroquinone C18H10O2, which forms golden crystals exhibiting a dark-blue fluorescence in alcoholic solution, and yielding C18H8Ac2O2 [167°].

PYRENE SULPHONIC ACID C, H, SO, H. Got by fusing the disulphonic acid with potash (Goldschmiedt a. Wegscheider, M. 4, 242).— KA'aq: minute needles (from dilute alcohol).

PYRENE DISULPHONIC ACID C,H,(SO,H). Formed by heating pyrene with H,SO. Sticky mass, v. sol. water, sl. sol. alcohol, insol. ether.—K,A"2½aq.—BaA"8½aq.— CaA"2aq : yellow powder.

Formed by the oxidation of pyrene or pyrenequinone by chromic acid (Bamberger a. Philip, quinone by chromic acta (Damberger at 1 https://dx.1995.3036; 20, 369; A. 240, 168). Pale-yellow plates, blackened above 250°. V. sl. sol. alcohol. H₂SO, forms an orange solution. Oxidised by KMnO, to naphthalene tetra-carboxylic acid. Reacts with hydroxylamine. Phenyl-hydrazine forms C₁₅H₈O₄(N₂HPh) 2aq, crystallising in yellow prisms. - BaA"aq. Ag, A": amber-yellow pp.

 $C_{13}H_6O<_{CO}^{CO}>0.$ Anhydride Yellow needles, formed by boiling the acid with HOAc.

Imide C₁₃H₆O CO NH. Yellow plates,

got by dissolving the acid in NH₃Aq.

PYRENOLINE C₁₀H₁₁N. [153°]. Formed by heating amido-pyrene hydrochloride with nitrobenzene, glycerin, and H₂SO₄ (Jahoda, M. 8, 442). Golden scales (from alcohol), v. sol. water,

442). Golden scales (from alconol), v. sol. water, forming solutions which exhibit green fluorescence.—B'HCl. [270°].—B',H,P'tCl., [above 290°].—B'HSQ., aq. [246°].—B'C,H,N,O,. Decomposes at 260°.—B'MeI. [212°].

PYRIDANTHRILIC ACID C,H,N,O, i.e. [2:1]CO,H,C,H,N,H,CO,C,H,N(CO,H), [265°].

Formed by the action of alkaline KMnO, on solutions the scale of t cyclothraustic acid derived from a-diquinoline (Weidel a. Strache, M. 7, 289; 8, 197). Micaceous plates, sl. sol. hot water. Yields isocinchomeronic and anthranilic acids on oxidation.

PYRIDAZINE. The ring CH CH.CH CH. (Ach, A. 253, 46; cf. Knorr, A. 236, 295).

PYRIDINE C₃H₅N i.e. N CH:CH CH. Mol. w. 79. (116°) (Schiff, B. 19, 566); (114°) Mol. W. 79. (116°) (Schiff, B. 19, 566); (114°) (Ladenburg, A. 247, 4); (116·5°) (Perkin, C. J. 55, 701). S.G. 21·0033 (L.); \(\frac{1}{16}\) -9855; \(\frac{3}{2}\) -9778 (P.). M.M. 8·761. H.F. p. -19,370 (Thomsen); 7,117 (Ramsay, C. J. 35, 696). H.F. v. -20,530 (Thomsen, Th.). S.H. 418 (Colson, A. Ch. [6] 19, 408). S.V. 89·4 (Schiff); 91·6 (Ramsay). Occurs in bone oil, in coal-tar, and in target by distilling hituminous shele and reactions. got by distilling bituminous shale and peat (Anderson, Tr. E. 16, 4; 20 [2] 247; P. M. [4] 2, 257; A. 80, 55; 96, 200; 105, 335; Greville Williams, P. M. [4] 8, 24; Church a. Owen, C. N. 2, 146; P. M. [4] 20, 110; Schulze, B. 20, 409). Occurs also in tobacco smoke, and, in small quantity, in fusel oil (Haitinger, M. 3, 688).

Formation .- 1. By heating isoamyl nitrate with P.O. (Chapman a. Smith, A. Suppl. 6, 329). 2. By distilling its carboxylic acids with lime .-3. By distilling oxytrialdine and oxytetraldine with soda-lime (Schiff, A. Suppl. 6, 21).-4. With other bases by heating glycerin with ammonium other cases by neating giverin with ammonium phosphate (Stöhr, *J. pr.* [2] 45, 23).—5. By passing ethyl-allyl-amine over PbO at 450° (Koenigs, *B.* 12, 2344).—6. By heating piperidine with H.SO, at 300° (K.), with nitro-benzene (4) pts.) at 260° (Lellmann a. Geller, *B.* 21, 1921). or with AgOAc and 10 p.c. HOAc at 180° (Tatel, B. 25, 1621) .- 7. Together with mono- and disubstitution products by the action of Br on

acetyl-piperidine (Hofmann, B. 16, 587).—8. By heating sodium-pyrrole with NaOMe and CH₂I₂ in sealed tubes at 200° (Dennstedt a. Zimmermann, B. 18, 8316).—9. From anhydroegonine, by treatment with conc. HCl and distillation of the product with zinc-dust (Einhorn, B. 22, 1365).

Purification.—By ppg. the crude base (20 g.) dissolved in (100 g. of) a 10 p.c. solution of HCl by adding HgCl₂ (135 g.) dissolved in hot water (1,00 g.). The crystalline double salt is distilled with NaOHAq (Ladenburg, 4. 247, 4).

Properties.—Colourless liquid with powerful odour, miscible with water. Fumes with HCl. Strong poison. Should not be inhaled (Marcus a. Oechsner, Bl. [2] 38, 97; cf. Kendrick a. Dewar, Pr. 22, 432; 23, 290). Forms a hydrate B'Saq. (93°), S.G. 1-0219, V.D. 1-17, which is a colourless liquid (Goldschmidt a. Constam, B. 16, 2976). Not attacked by boiling HNO₃ or CrO₂. Pyridine ppts. the hydroxides of Fe, Al, and Cr from their salts. With CuSO₄ it gives a pale-blue pp. dissolving in excess, forming a deep-blue liquid. Pyridine passes unchanged into the urine (O. de Coninck, Compt. rend. Soc. Biol. 4, 755). Pyridine does not mix with liquid CO₂ (Ditte, C. R. 105, 612). It gives no reaction with hot alkaline NaOBr (Denigès, C. R. 107, 662)

Reactions.—1. Dry chlorine forms di-chloro-pyridine [72°]. Chlorine passed into a solution of pyridine in CHCl, forms B'Cl, a white powder (Bally, B. 21, 1772). Chlorine-water ppts. a white powder. KOCl completely decomposes pyridine, forming N, CO₂, CHCl₃, and chloro-acetic acid (Keiser, Am. 8, 308). -2. Bromine added to a solution of the hydrochloride ppts. C. H. NBr., which is split up by heat into pyridine and bromine. Bromine acting in the cold on pyridine and water gives rise to (C,H,NBr,),HBr [126°] (Grimaux, Bl. [2] 38, 127). Pyridine hydrochloride heated with Br at 200° forms mono- and di-bromo-pyridine.-3. at 200 forms more and alt-promoto-pyrionic—3. HIAq at 300° yields n-pentane and NH, (Hofmann, B. 16, 590).—4. Sodium at 80° yields (γ)-dipyridyl C₁₀H₁N₂, idipyridine C₁₀H₁₀N₂, isonicotine C₁₀H₁N₂, and two nitrogenous oils (240°–250°) and (300°–310°) (Weidel a. Russo, M. 3, 884). - 5. Its alkylo-iodides are converted by distillation with solid KOH into volatile bases .- 6. Excess of AcCl forms dehydracetic acid (Dennstedt a. Zimmermann, B. 19, 75).—7. acid (Dennstedt a. Zimmermann, B. 19, 75).—7. Unites with CH_Cl.OH (the product of the union of formic aldehyde and HCl), and the product in aqueous solution gives with HgCl, a pp. of (C,H,N)(CH,ClOH)HgCl, [162°], with platinic chloride a pp. of (C,H,N),(CH,ClOH),PtCl, [216°], and with picric acid the compound (C,H,N)CH,(OH),C,H,(NO₂),0 [c. 200°]. Treatment with AgNO₂ forms (C,H,N)CH,(OH)NO₂ errystallising from alcoholectic in prisms (Hom. erystallising from alcohol-ether in prisms (Hemmelmayr, M. 12, 533). -8. Alloxan and aqueous SO, form triclinic crystals of B'C, H, N,O, H, SO, (Pellizzari, A. 248, 150).—9. Glycollic chlorhydrin forms the base C₂H₂NO (Coppola, G. 15, 831). Glycerin chlorhydrin reacts with forma-tion of O.H.NCl.C.H. (OH). [107°] separating from alcohol in hexagonal crystals and yielding (C.H., NO, CI), PtCI, [180°] and C.H., NO, CIAuCi, [122°] [Krüger, J. př. [2] 44, 130).—10. Chlorosectic acid at 100° forms C.H., NCI. CH., CO.H.

and B'.CdCl, [107°].
Salts. — B'HCl. Deliquescent mass. B'₂H₂PtCl₆. [242°]. Orange triclinic prisms. The aqueous solution is converted by long boiling into crystalline B',H2Cl2PtCl, and B',PtCl, a yellow insoluble powder .-- B', PtCl, Yellow tables, almost insol. cold water (Jörgensen, J. pr. [2] amost insol. cold water (Jorgensen, J. pr. [2] 33, 504). An isomeride crystallises in needles.

—B',PtCl, 3aq.—B',Pt,Cl,.—B'₂(NH₂),PtCl,.—B'(NH₃)PtCl,.—B'₂(NH₃),PtCl,.—B'(NH₃),PtCl,.—B',(NH₃),PtCl,.—B',(NH₃),PtCl, aq.

colourless prisms.—B',HHg,Cl,. [178°]. Needles (from water).—B'₂3HgCl,.—B',HAuCl,. [285°].

Prisms, sl. sol. water.—B',ZhCl,. short prisms. Needles, sl. sol. water. -B', ZnCl,: short prisms, very soluble in cold water (Lang, B. 21, 1578).—B',ZnCl, 2aq (Lachovitch, M. 9, 516).-1578).—B', ZnCl, 2aq (Lachovitch, M. 9, 516).—
B', ZnBr,: prisms, v. sol. pyridine.—B', H, ZnCl,
—B', CuCl, [180°—190°].—B'CuSO, 8aq.—
B', Cu, Cl, —B', Cu, Cl, —B', CuBr, —B', Cu, L,
—B', Cu, Cy, —B', L, CuCl, —B', CdCl, : needles, almost insol. alcohol, sol. water.—B', CdBr,
—B', CdL, —B'CdL, (Monari, J. 1884, 629).—
B'IgCl, —B', HgCy, —B', CaCl, : white powder.—
B', NiBr, —B'AgBr: white needles, sol. cold pyridine.—B'Agl.—B'AgCy: prisms (Varet, B).

(31 5, 843)—B', CuCy: vellow lamelles, sol. [3] 5, 843).—B',CuCy: yellow lamelle, v. sol. warm pyridine (Varet, C. R. 112, 391). Loses pyridine on warming.—B'H.SO,: deliquescent mass.—B'HI: tables, v. sol. water, but not deliquescent.—B'HI, [89°]. Green crystalline powder (Dafert, M. 4, 508).—B'HBr. Deliquescent needles.—B'_HBr, [126°]. Red tables.—B'_2Cl, Waxy mass (Keiser, Am. 8, 312).—B'HNO,.—B'_AgNO, [87°] (Jörgensen, J. pr. [2] 33, 502).—B'_AGNO,—B'_GUSO,—B'CuSO, 48aq.—B',CuS,O,-B',SiCl, Anorphous (Harden, C. J. 51, 47).—B'_SiF, (Corney e. Smith, Am. 10, 294).—B'_2SiF,—B',H,FeCy, 2aq: monoclinio prisms (Mohler, B. 21, 1015).—B'ICl. [133°]. Needles (Pictet a. Krafft, Bl. [8] 7, 72).—B'ZHC,HCl. [180°]. Long yellow needles (from water).—B'_RhCl,HCl 2aq (Jörgensen, J. pr. [3] 27, 478).—B',RhCl,HCl 2aq (Jörgensen, J. pr. [3] 27, 478).—B',RhCl,HCl, Gl., B',RhCl,Br.—B',RhCl,NO) (dried at 100°).—B'_gRh_cl,SO₄ (dried at 100°). pyridine on warming .- B'H,SO, : deliquescent (dried at 100°) Acetate B',3HOAo. (140°). Miscible with

water, forming an acid solution (Gardner, B. 23, 1588).—Formate B'3CH₂O₂. (149°). Liquid, v. sol. water.—Propionate B'3C,H₆O₂. (149°). Liquid. -- Cupric oxalate compound B'CuC.O.: minute prisms (Seubert a. Rauter,

B. 25, 2825).

White Methylo-chloride B'MeCl. needles (Ostermeyer, B. 18, 591). Converted by hot aqueous solution of pieric acid into B'MeOC, H2(NO2)2 2 aq, which crystallises in B'₁Me₂PtO₃, [188] (0.); [207°] (B.). — B'₂Me₂PtO₃, [188°] (0.); [207°] (B.). — B'MeAuCl., [253°].—B'MeClTCl. [82°] (0.); [90°] (B.). Yellow plates.—B'MeClTCl., [180°]. Unstable yellow crystals (Bally, B. 21, 1774).

Methylo-perbromide B'MeBr, [48°]. Methylo-iodide B'MeI. Converted Converted at 290° into methyl-pyridine hydriodides. On heating with alcoholic potash at 45° it yields a brown resin, forming a deep-red solution in alcohol, turned bright-red by HCl, orange-red by acetic acid, and ruby-red by ammonia (O. de Coninck, C. R. 102, 1479). Chlorine forms B'MeICl, [90°] (v. supra). Oxidised by alkaline K₃FeCy, to oxy-methyl-pyridine or v-methyl-pyridone CH CH:CH NMe (250°), a liquid miscible with water (Decker, J. pr. [2] 47, 28; cf. Pechmann, B. 24, 3144).

Ethylo-iodide B'EtI. Silvery tables Anderson, A. 94, 364). At 300° it yields pyridine, NH., (a) and (γ)- ethyl-pyridine, and di-ethyl-pyridine (Ladenburg, B. 16, 2059; 18, 2961). Yields B' Et. PtCl.. Oxidised by alkaline

K₃FeCy₆ to CH≪CH:CO NEt (250°).

Ethyleno-iodide B'C.H.I. Prisms (Coppola, G. 15, 332). Ag.O yields a base C.H.NO. By heating pyridine with ethylene bromide and some alcohol at 100° there is found B'2C2H4Br2, which yields B'2C2H4PtCla (Davidson, A. 121, 254).

Benzylo-chloride B'PhCH,Cl. Reduced by sodium-amalgam to the unstable C21H21N2 (Hofmann, B. 14, 1503).—(B'PhCH,Cl),PtCl,

Nitro-benzylo-chlorides B'C,H,(NO,).CH,Cl. o [c. 76°], m [70°-100], p [90°-100°]. These bodies are reduced by tin and HClAq to B'C,H,(NH,Cl).CH,Cl, which are

Phenacylo-bromide B'BzCII, Br. Prisms (Bamberger, B. 20, 3344).—B'₂(BzCH₂)₂Cr₂O₂.

References.—Bromo-, Chloro-, Oxy-Amido-,

Dipyridine C₀H₁₆N₂ v. DIPYRIDYL DIHYDRIDE.

Dipyridine C₀H₁₆N₂. (275°). S.G. ¹² 1·124.

Is probably a dipyridyl dihydride. Formed by and Oxy. PYRIDINE.

heating nicotine with KOH and K.FeCy, and also by heating the product of the action of S on nicotine at 150° with finely-divided copper (Cahours a. Etard, Bl. [2] 34, 452).
Inactive liquid.—B'HHgCl,—B',HLPtCl, 2aq.—
B',H,FcCy, 2aq: brownish-green tables.

(a) PYRIDINE CARBOXYLIC ACID

C.H.NO. i.e. CH:CH.C.CO.H. Picolinic acid. [136°]. Formed by oxidation of (a)-methylpyridine with KMnO, (Weidel, B. 12, 1994), and by oxidation of (a)-phenyl-pyridine (Skraup, M.

4, 477). Obtained also, together with its herahydride, from comenamic acid by successive treatment with PCl, and H,SO, the resulting di-chloro-picolinic acid being reduced by heating for three days at 155° with HI dissolved in HOAc (Ost, J. pr. [2] 27, 285).

Preparation.—The three acids got by oxida-

tion of crude methyl-pyridine from animal oil are converted into copper salts. Cupric pyridine (a)-carboxylate is extracted by hot water. residue is treated with H.S. and the difficultlysoluble (γ) -acid separated from the (β) -acid (Ost,

J. pr. [2] 27, 286).

Properties .- Needles, v. sol. water and alcohol, almost insol. ether, benzene, CHCl₃, and CS. May be sublimed. FeSO, gives a red colouration with picolinic acid and with all the carboxylic acids of pyridine that contain CO₂H in the (x)-position (Skraup, M. 7, 210). The absorption of the ultra-violet spectrum has been

studied by Hartley (C. J. 41, 45).

Reactions.—1. Yields pyridine on distillation with lime or with alcoholic potash at 240°. The Cu salt on distillation gives pyridine and (a)-dipyridyl [70°] (Blau, M. 10, 375; B. 21, 1077). 2. Sodium-amalgam forms δ-oxy-adipic acid (Weidel, M. 11, 522). 3. Fuming HI at 170° forms (a)-methyl-pyridine and piperidine (Seyfferth, J. pr. [2] 34, 241) .- 4. Zinc-dust and HOAc reduce it to (a)-methyl-pyridine.

Constitution.—This may be deduced from its

formation from (3)-naphthoquinoline via (3)phenyl-pyridine carboxylic acid (Skraup a. Co-

benzl, M. 4, 436).

Salts. - HA'HCl: unstable crystals. H.A',H.PtCl, 2aq: orange-red crystals.—NH,A': triclinic tables.—KA'.—BaA', ½aq.—CaA', aq.— MgΛ', 2aq.

Hexahydride C.H. N.CO.H. Piperidine (a)-carboxylic acid. The chief product of the action of HI at 160° on mono- or di-chloropicolinic acid (Ost, J. pr. [2] 27, 287). Got also by reducing picolinic acid (Ladenburg, B. 24, 640). Syrup, v. sol. water. Salts.—B'HCl. [264°]. Nodules.—B',H,PtCl. [184°] (L.).—B',H,PtCl. 2aq.—B'McCl. [191°]. Needles.

By Hiller (1) archaeolic acid

Pyridine (\$)-carboxylic acid CH:CH.C.CO.H. Nicotinic acid. [230°].

CH: N.CH Formation .- 1. By oxidising nicotine with HNO, (Weidel, A. 165, 330), Cro, (Huber, A. 141, 271; B. 3, 849), or KMnO, (Laiblin, A. 196, 129).—2. A product of oxidation of coal-tar bases (Weidel; Mohler, B. 21, 1003).—3. By heating quinolinic acid at 160° or with HCl at 180° (Ost, J. pr. [2] 27, 286; Lippmann a. Fleissner, M. 8, 315).—4. By oxidation of (β)-methyl-pyridine (Weidel, B. 12, 2004), (β) ethylicidal (Black). pyridine (Stochr, J. pr. [2] 43, 155) or (8)-phenyl-pyridine (Skraup, M. 4, 453).—5. By saponifica-tion of its nitrile, which is got by distilling sodium-pyridine sulphonate with KCy (Fischer, B. 15, 63). - 6. By heating three of the pyridine D. 10, 03).—U. By nearing three of the pyriame dicarboxylic acids (Hoogewerff a. Van Dorp, R. T. C. 1, 1, 107; A. 204, 117; 207, 226; Weidel a. Herzig, M. 1, 16).—7. By heating berberonic acid at 215° (Fürth, M. 2, 420).—8. By the action of Zn and HClAq on chloro-nice.

tinic acid (Pechmann a. Welsh, C. J. 47, 145).

Properties.—Needles, st. sol. cold water, sol. alcohol, nearly insol. ether. May be sublimed.

Reactions.—1. Yields pyridine on distillation with lime.—2. Sodium-amalgam yields a mixture of 8-oxy-a-methyl-glutaric acid and its lactone, which, on treatment with alcohol and HCl, yields a mixture of two ethers. One of these, C₁₀H₁₁ClO₄, is converted by sodium-amalgam into a methyl-glutaric acid, and the other, C₄H₁₄O₄, is also converted by successive treatment with PL₂ and with Zn and dilute H₂SO₄ into a-methyl-glutaric acid (Weidel, M. 11, 502) .-3. Bromine and water at 120° yield CO, pyridine, and bromoform.—4. The K salt heated with MeI at 150° forms C.H.,NMeI.CO,Me, which on saponification yields C.H., NMe(OH).CO.H [130°], converted at 100° into trigonellin C₃H₄NMe<0

[218°], which occurs in the seeds of Trigonella fænum græcum (Jahns, B. 18, 2521; Hantzsch, B. 19, 31). This anhydride forms the salts C,H,NO,HCl, B',H,PtCl, aq, B'HAuCl, [198°], and B',3HAuCl, [186°].

Constitution .- This may be deduced from its formation from (a)-naphthaquinoline vid (a)-

phenyl-pyridine carboxylic acid.

Salts.— HA'HCl. Colourless prisms.— H.A',H.PtCl_a 2aq.—B',H.AuCl₃.—B'HNO₃ aq.— NH,A': needles.—KA'.—MgA'₂: needles.— CaA', 5aq: monoclinic crystals; $a:b:c=1\cdot537:1:\cdot629$; $\beta=62^\circ50^\circ$. — Cu(OH)A' (De Coninck, BL, [2] 42, 100).—AgA': needles (from

Nitrile C,H,N.Cy. [40°]. Formed by distilling sodium pyridine sulphonate with KCy (Fischer, B. 15, 63). Needles or prisms, sol. water.— B'HCl.—B'_H_P(Cl_e: yellow soluble needles. Tables (by sublimation). Converted by means of hydroxylamine into the amidoxim C₃H₁N.C(NH₂):NOH [128°], which yields an acetyl derivative [143°] and a benzoyl derivative [190°], and is converted by phonyl cyanate into $C_*H_*N.C(NOH).NH.CO.NHPh$ [167°], by phonyl thiocarbimide into $C_*H_*N.C < \stackrel{N.S}{N} > C.NHPh$ [241°], and by succinic anhydride at 100° into $C_{*}H_{*}N \stackrel{N.O}{\leqslant} C.CH_{*}CH_{*}.CO_{*}H$ [178°]. acetyl and benzoyl derivatives are converted by heating into $C_3H_4N \stackrel{N.O}{\swarrow} CMe$ [109°] and $C_sH_sN \leqslant_N^{N.O} > CPh$ [139°] respectively (Michaelis, B. 24, 3439).

Hexahydride C, H, N(CO, H). Nipecolinic acid. [250°]. Got by reducing nicotinic acid in alcoholic solution by Na (Ladenburg, B. 25, 2768). Crystals, v. e. sol. water, insol. alcohol and ether.— HA'HCl. [240°].—H_AA'H_aPtCl. [218° cor.].— HA'HAuCl. [197° cor.].— HA'HCl5HgCl_s. [231°].—MeA'HCl [208°].— Me₂A'₄H_aPtCl_s.— Nitrosamine C₆H₁₆N₂O₆. [112°].

Pyridine (γ)-carboxylic acid

N CH.CH C.CO.H. Isonicotinic acid. [805°]

(S.); [806] (B. a. H.); [309-5°] (W. a. H.).

Formation.—1. By heating pyridine s-tricarboxylic acid (Skraup, B. 12, 2331) and three of the pyridine di-carboxylic acids (Hoogewerff a. Van Dorp, A. 204, 112; Weidel a. Herzig, M. 1, 38; Böttinger, B. 15, 68).—2. By the action of KMnO, on (γ)-methyl-pyridine (Behrmann a. Vor. IV. Hofmann, B. 17, 2696; Ladenburg, B. 21, 287). 8. By heating di-chloro-pyridine carboxylic acid [210°] with HI (B. a. H.).

Properties.—Needles, sl. sol. cold water, in-sol. alcohol. Yields pyridine on distilling with lime and 8-oxy-ethyl-succinic acid on reduction with sodium-amalgam (Weidel, M. 11, 517).

Salts.—NH,A': needles.—CaA'₂4aq: silky needles, m. sol. water.—HA'HCl: monoclinio

needles, m. sol. water.—Ha hor. inductions.—H.A',H.PtCl, 2aq: monoclinic crystals.

Hexahydride C₃H₁₀N(CO,H). Got by reducing the zeid in alcoholic solution by Na (Ladenburg, B. 25, 2773). Branching groups of needles, v. e. sol. water, insol. alcohol. Blackens at 300°, but is not melted at 320°.—HA'HCl. [228°]. Trimetric crystals; a:b:c:-922:1: 979.
—HA',H,PtCl_s. [239°]. — Aurochloride; [197°]. Nitrosamine C_sH₁₀N₁O_s. [101°].

Pyridine (ac)-dicerboxylic acid

CH CH.C(CO.H) N. Dipicolinic acid. [226°] (L. a. R.; S.); [237°] (E.); [236° cor.] (Collie, C. J. 59, 179). Formed by oxidation of (aa)-dimethyl-pyridine [145°] (derived from acetoacetic ether or from coal-tar) by KMnO, (Epstein, A. 231, 26; Ladenburg a. Roth, B. 18, 52; 19, 790; 20, 130; A. 247, 32; Lange a. Rosenberg, B. 20, 132; cf. Dewar, C. N. 23, 18). Got also by oxidation of (α)-methyl-(α)-ethyl-pyridine by dilute (2 p.c.) KMnO, (Schultz, B. 20, 2724).

Properties .- Hair-like needles (containing 1 aq) or anhydrous scales; sl. sol. cold alcohol, water, and ether. On heating at 245° in a curwater, and etner. On neuting at 225 in a current of H it yields pyridine and pyridine (a)-carboxylic acid. PCl, forms a chloride [61°], (284°). FeSO, gives a reddish-yellow colour. Salts. — CAA" 2aq: minute prisms. —

CuA" 2aq : dark-blue prisms.

Pyridine (aB)-dicarboxylic acid

C(CO,H).C(CO,H) N. Quinolinic acid. [281°]. S. .55 at 6.5°. Formed by the oxidising action of KMnO, on quinoline (Hoogewerff a. van Dorp, B. 12, 747; R. T. C. 1, 107; A. 204, 117), on cinchonine (H. a. D.), on o and p methylquinoline (Skraup, M. 2, 157), on o oxyquinoline, on quinoline o-sulphonic acid (O. Fischer a. Renouf, B. 17, 755), and on (α)-oxy-quinoline carboxylic acid (La Coste a. Valeur, B. 20, 103).

Properties. - Monoclinic needles, a:b:c = .542:1: .607; $\beta = 64° .54'$; sl. sol. water and alcohol, insol. ether. Begins to decompose at 140°, and forms nicotinic acid. Yields pyridine when distilled with limo. Reduced by sodium-amalgam to the δ-lactone of butane aβγ-tricarboxylic acid CH., CH., CH.CO., H (Perimutter, M. 13, 840).

Salts.—KHA" 2aq: triclinic plates (Lippmann a. Fleissner, M. 8, 311).—K_AA" 2aq.—BaA" aq.—Ag,A": crystalline.—AgHA" aq.

Anhydride C.H.N CO O. [185°]. Got from the acid and Ac₂O (Bernthsen a. Mettegang, B. 20, 1208). Prisms. Converted by benzene and AlCl₂ into C₂H₄BzN.CO₂H [147°], converted by heat into the ketone C₃H₄BzN (307° uncor.), which yields a crystalline phenyl-

hydrazide [143.5°].

Pyridine (a7) dicarboxylic acid

CO₂H.O CH:C(CO₂H) N. Luti Lutidinic acid.

[240°] (V.); [235°] (B.; L. a. R.). Formed by the oxidising action of KMnO, on (ay)-dimethyl-pyridine (Ramsay, P. M. [5] 4, 241; 6, 19; Weidel a. Herzig, M. 1, 20; Ladenburg a. Roth, B. 18, 915; A. 247, 37), on (a)-methyl-cy)-ethyl-pyridine (Schultz, B. 20, 2726), on distribution of the distribution of the control o ethyl-pyridine, on (aa)-di-methyl-dipyridyl (Heuser a. Stochr, J. pr. [2] 44, 409), and on the methyl-pyridine carboxylic acid obtained from uvitonic acid (Böttinger, B. 14, 68; 17, 93; Voigt,

Properties.—Needles (containing aq), m. sol. cold water, sol. alcohol, insol. ether. Gives a blood-red colour with FeSO. Yields pyridine on distillation with lime. Converted by heat into CO2 and isonicotinic acid. PCl, yields a

chloride [203°]

Salts.-KHA" jaq. Crystals.-(NH4)2A".-CuA" 4aq (B.).—Ag₂A" 2aq: white pp.

Pyridine (ab')-dicarboxylic acid

CH\(C(CO_2H).CH\) N. Isocinchomeronic acid.

Formation.-1. By oxidation of lutidine rormation.—1. By oxidation of intidine (150°-170°) with KmO, (Ramsay, P. M. [5] 4, 246; Weidel a. Herzig, M. 1, 1; Lange a. Rosenberg, B. 20, 135).—2. By oxidising (B)—methyl-(a)-ethyl-pyridine (Ladenburg, A. 247, 44).—8. By oxidation of quinine (Ramsay a. Dobble, C. J. 33, 102; B. 11, 324).—4. By heating the dishydride of profession purisions treath ing the dihydride of potassium pyridine tricarboxylate (Weiss, B. 19, 1311).-5. By the action of alkaline KMnO, on cyclothraustic acid and on pyridanthrilic acid (Weidel a. Strache, M. 7, 290). - 6. By oxidising (β)-ethyl-(α)-stilbazole (Plath, B. 22, 1062).

Properties .- Small prisms (containing aq), almost insol. cold water, alcohol, and benzene, sol. hot HClAq. On heating with HOAc at 220° it is split up into CO, and nicotinic acid [230° On heating with lime it gives pyridine. PCl. yields a chloride [61°] converted by NH, into an amide [297°]. FeSO, gives a reddish colour.

colour.

Salts.—(NH₁)HA" aq. [253°]. Triolinic prisms, sl. sol. cold water.—(NH₁)₂A".—
KHA" aq: needles.—K₁A" aq.—CaA" 2aq.—
Ca(HA"), 3aq.—MgA" 5aq.—CuA" aq.—Ag.A".

Methyl ether Me.A". [117:5°] (R.).

Pyridine (8B')-dicarboxylic acid

CH ⟨C(CO,H).CH⟩N. Dinicotinic acid. [822°]. Formed by heating pyridine (2,3,5)-tri-carboxylic acid and pyridine (2,3,5,6)-tetra-carboxylic acid (Riedel, B. 16, 1613; Hantzsch a. Weiss, B. 19, 286; Weber, A. 241, 12). Formed also by heating di-chloro-pyridine di-carboxylic acid with conc. HIAq at 180° (Guthzeit, A. 262, 130).

Properties.—Small prisms (from HOAc), split up by heat into CO₂ and nicotinic acid.

Salts.—PbA" 2aq.—Ag.A" aq.—Ag.A" 1½aq.

-HA'HCl 2aq: needles, decomposed by water.

-H.A',H.PtCl_s: orange-red needles.
Pyrldine (β_{γ}) -dicarboxylic acid

CO,H.C $\stackrel{C(CO_2H):CH}{CH}$ N. Cin Cinchomeronic

acid. [259°].

Formation.-1. By oxidation of cinchonine or cinchonidine by HNO, of S.G. 1.4 (Weidel, A. 173, 76). -2. By oxidation of quinine by HNO, the yield being 28 p.c. (Weidel a. Schmidt, B. 12, 1146).—3. By heating apophyllenic acid with conc. HClAq at 240° (Von Gerichten, B. 13, 1635). - 4. By heating pyridine tricarboxylic acid (formed from cinchonic acid) at 190° (Hoogewerff a. van Dorp, B. 13, 61; Skraup, M. 1, 184; Weidel a. Brix, M. 3, 604) .- 5. By the action of KMnO, on methyl-pyridine carboxylic acid and on isoquinoline (Hoogewerff a. van Dorp, R. T. C. 2, 23; 4, 285,—6. By heating pyridine pentacarboxylic acid (Weber, A. 241, 16).—7. By oxidation of methyl-nicotinic acid, derived from (B)-collidine (Oechsner de Coninck, Bl. [2] 43, 106). -8. By boiling berberonic acid with HOAc (2 pts.) and Ac.O (1 pt.) for six hours (Mayer, M. 13, 344; cf. Fürth, M. 2, 426).

Properties.—Prisms (from HClAq), v. sl. sol. water and ether, sl. sol. alcohol. Yields isonicotinic and some nicotinic acid on heating (Hoogewerff a. van Dorp, A. 207, 217). Gives pyridine on distillation with lime. Sodiumamalgam yields NH, and cinchonic acid C,H,O, i.e. $CO_2H.CH < CH_2.CO_2 > 0$ (Weidel a. Hoff, M.

CO.H

13, 578). Cinchonic acid [169°] forms monoclinic crystals, v. sol. hot water and alcohol, and yields BaC,H₀O₆ 3aq, Ba₃(C,H₁O₇)₂ 3aq, CaA'' 2aq, Ca₃(C,H₁O₇)₂ (dried at 190), and oily Et₄A'', whence PCl₃, followed by alcohol, yields CO₂Et.CH(CH₂Cl).CH(CO₂Et).CH₂CO₂Et, which is a heavy oil. Cinchonic acid is reduced by HI to butane tricarboxylic acid C, H10O6 [184°], whence Ca, A", 8aq, accompanied by an isomeric butane tricarboxylic acid [133°]. FeSO, gives no colour.

Salts .- Na, A" 2aq: tables.-NaHA".-BAITS.—Na₂A 2aq: BOIES.—NAITA', — RAA'' 1₃aq: needles, sl. sol. water.—CaA'' 3₃aq: prisms. — CaA'' 3aq. — CuA'' 3₃aq: small blue crystals.—Ag₂A'': white pp.—AgHA''.— HA'HCl: monoclinic prisms, decomposed by

water.—H.A'₂H.PtCl₃: golden prisms.

Anhydride (C,H₂N).C.O₃. [77°]. Formed by boiling the acid with Ac₂O (Goldschmiedt a. Strache, M. 10, 156). Plates. May be sublimed. Converted by NH, gas into C,H,N(CO,NH,).CONH, [229°], which is converted by heat into a yellow powder [130°], and which yields the amic acid C₄H₄N(CO₂H).CONH₂ [237°], orystallising in needles.

Mono-ethyl ether HEtA". [133°]. Formed from the anhydride and EtOH. Plates (from benzene).-AgEtA": long needles.

Mono-methyl ether HMeA". [154°]. Anhydride of the Methylo-hydroxide C₃H,NO₄ i.e. C₄H₂NMc(CO₂H) CO Apophyllenic acid [242°]. Formed by oxidation of cotarnine by HNO, (Wöhler, A. 50, 24; Anderson, Tr. E. 23, 347; C. J. 5, 257; Gerichten, B. 13, 1635). Formed also by heating cinchomeronic acid with MeI and MeOH at 100° (Roser, A. 234, 116). Needles (anhydrous) or octahedra (containing aq), sol. hot water, insol. alcohol and ether. HClAq at 250° decomposes it, forming cinchomeronic acid and McCl. — BaA'. AgA'.-Ag,A'(NO,).-H,A',H,PtCl, aq.

Bromo-spophyllenic acid C.H.BrNO, 2aq. [205]. Formed by oxidation of bromo-tarconine. Yields BaA', 3aq and H2A'2H.PtCl. (Gerichten, A. 210, 91).

Pyridine (aa'8)-tricarboxylic acid

CH < C(CO,H), C(CO,H) > N. Formed by oxidising di-methyl-nicotinic acid with KMnO, (Weiss, B. 19, 1309). Crystallises from alcohol in plates B. 19, 1909). Crystamses from arcono in places (containing 2aq), v. e. sol. water. Decomposes at 160° into CO₂ and isocinchomeronic acid. FcSO₄ colours its neutral solution red.—

KII₄A''', 5aq: needles.—Ca,A''', 4aq.—Pb₃A'''₂ 5aq. Pyridine (aa'\gamma)-tricarboxylic acid

 $CO_zH.C \stackrel{CH.C(CO_zH)}{\leqslant} N.$ Trimesitic acid. Carbolutidinic acid. [244°]. Formed by oxidation of uvitonic acid (Böttinger, B. 13, 2048; 14, 69), and by oxidation of the tri-methyl-pyridine obtained from acetoacetic ether and aldehyde-ammonia (Voigt, A. 228, 31). Tables or spheroidal groups of needles (containing 2aq), sol. hot water, sl. sol. alcohol and ether. Yields isonicotinic acid on sublimation. FeSO, gives a violet-red colour.

For each colour. So alts.— $K_1A'''_5aq$: needles.— $Ca_2A'''_24aq$.—Ba, A'''_26aq .—Ba $H_1A'''_24aq$.— $Mg_2A'''_212aq$.— $Cu_2A'''_212aq$.— $Ag_3A'''_14aq$.

Ethylether Et,A'''. [127-5°].

Amide. [above 280°].

Pyridine (aBB') tri-carboxylic acid

CH C(CO,H):C(CO,H) N. Carbodinicotinic acid. [323°]. Formed by oxidation of quinoline (Py. 2)-carboxylic acid (Riedel, B. 16, 1615), methyl-pyridine (BB)-dicarboxylic (Weber, A. 241, 11), and of the parvoline got by heating propionic aldehyde ammonia with propionic aldehyde at 200° (Dürkopf, B. 21, 832, 2707; 23, 689). Spherical aggregates (containing 1 aq), v. sol. hot water. At 155° it is split up into CO, and dinicotinic acid,—Ba,A''', 5aq, -- Ag, HA''' 1 aq : rosettes of plates. Pyridine (αβγ)-tri-carboxylic acid

 $CO_2H.C \leqslant \begin{array}{c} C(CO_2H):C(CO_2H) \\ CH \end{array} > N. \quad [250^\circ] \text{ (H. 8.}$ D.; S.); [257°] (D. a. R.). S. 1.2 at 15°.

Formation. -1. By the action of KMnO, on quinine, cinchonine, cinchonidine, quinoïdine, and einchonic acid (Dobbie a. Ramsay, C. J. 35, 189; Hoogewerff a. van Dorp, B. 12, 158; 13, 152; A. 201, 84; Skraup, A. 201, 312; Strache, M. 10, 642).—2. By oxidation of cinchonine by HNO, (Weidel, A. 173, 101; B. 12, 415).—3. By oxidation of methyl-pyridine (αβ)-dicarboxylic acid (Hoogewerff a. van Dorp, R. T. C. 2, 18), of di-methyl-pyridine carboxylic acid (Michael, B. 18, 2027), of (a)-oxy-cinchonic acid (Weidel a. Cobenzl, M. 1, 865).—4. By oxidation of papaverine (Goldschmiedt, M. 6, 397). Trimetric plates (containing 1 aq), v. sol. hot water, m. sol. alcohol, nearly insol. ether. Blackens at 200°. FeSO, gives a reddish colour. H2S forms by long heating at 180°, or by boiling with HOAc into CO₂ and cinchomeronic acid. Yields pyridine on distilling with lime. MeI and MeOH at 100° form CO, and apophyllenic acid. Sodium-amalgam gives NH, and cinchonic acid. PCl, forms a chloride (206° at 40 mm.). Salts. — K₁A'''3aq. — Ba₂A''', 16aq. —

Pyridine $(a\beta'\gamma)$ -tricarboxylic acid $CO_{\cdot}H.C \stackrel{CH.C(CO_{\cdot}H)}{<}N.$ Berberonic acid. [243°]. Formed by oxidising berberine with nitric acid (Weidel, B. 12, 410; Fürth, M. 2, 416). Triclinic prisms (containing 2nq), sol. hot water, v. sl. sol. hot alcohol, insol. ether. Yields pyridine on distillation with lime. FeSO, gives a red colour. At 215° it is split up into CO. and nicotinic acid; above 243° it yields isonicotinic acid.

Salts. — K₃A" 4\aq. — K₂HA" 8aq. — KH₂A" 1\quad qq. — Cd₃A" 2\aq. — Cd₃A" 4aq. — Ag,A": white pp., insol. water.

Pyridine (\$\beta B'. 9) tricarboxylic acid

CO₂H.C $\stackrel{C}{<}$ C(CO₂H).CH $\stackrel{N}{>}$ N. (8) - Carbocinchomeronic acid. [261°]. Formed by heating dipotassium pyridine pentacarboxylate at 220° (Weber, A. 241, 17). Plates (containing 3aq), v. sol. hot water. Yields cinchomeronic acid when heated. Gives no colour with FeSO. - Cu,11,4", 24aq. -- Ag,4"' 2aq: crystalline pp.

Pyridine $(a\beta\beta'\gamma)$ -tetra-carboxylic acid

 $C_0H_0NO_0$ i.e. $CO_2H_0C < C(CO_2H_0) < C(CO_2H_0) > N$. Formed by oxidising $(\alpha \gamma)$ -di-methyl-pyridine $(\beta \beta')$ -dicarboxylic acid (Weber, A. 241, 23). Prisms (containing 2aq or 3aq). At 120° it loses CO, forming (B)-carbocinchomeronic acid. FeSO, gives a dark-red colour. - Ba, Aiv 4aq. -

Ag, ΠΛ¹ν, nq: crystalline.

Pyridine (αα'ββ')-tetracarboxylic acid
CII C(CO, H).C(CO, H)
C(CO, H):C(CO, H)
N. Formed by oxidisdicarboxylic di-methyl-pyridine (Hantzsch, B. 19, 286; Weber, A. 241, 4). Needles (containing 2aq), v. sol. water. Decomposes at 150° into CO2 and dinicotinic acid .-CaH_Aiv 2aq: needles, v. sol. water.—Cu,Aiv 5aq. - Ag, Aiv 2aq : bulky pp.

Pyridine $(\alpha\alpha'\beta'\gamma)$ -tetra-carboxylic acid $CO_{\cdot}H.C \ll_{C(CO_{\cdot}H)\cdot C(CO_{\cdot}H)}^{CII} \gg N$. Formed by oxidation of tri-methyl-pyridine carboxylic acid and of di-methyl-pyridine di-carboxylic acid (Michael, A. 225, 142). Formed also by oxidation of flaveriol by alkaline KMnO, (Fischer a. Täuber, B. 17, 2927). Slender needles (containing 2aq), v. sol. water, v. sl. sol. alcohol and ether. Not decomposed at 150°. FeSO gives a brownish-red colour. - Ba, Aiv 2 aq. - Ba, Aiv aq. -Cu₂A" 2½aq. - Ag,Alv aq.

Pyridine penta-carboxylic acid NC (CO.H), Formed from potassium tri-methyl-pyridine dicarboxylate and KMnO, (Hantzsch, A. 215, 62; Weber, A. 241, 15). Crystalline mass of minute needles (containing 2aq), extremely sol. water, v. sl. sol. ether. Acid to litmus and to taste. Loses 2aq at 120° and decomposes, without having melted, at 220°. The neutral alkaline salts are very soluble, but the acid alkaline salts are sl. sol. water. The acid does not combine with HCl. Distilled with lime it gives pyridine. FeSO, gives a dark-red colour.

water, forming an acid solution (Gardner, B. 23, 1588).—Formate B'3CH₂O_x. (149°). Liquid, v. sol. water.—Propionate B'3C_xH₂O_x. (149°). Liquid. — Cupric oxalate compound B'₂CuC₂O₄: minute prisms (Seubert a. Rauter, B. 25, 2825).

Methylo-chloride B'MeCl. needles (Ostermeyer, B. 18, 591). Converted by a hot aqueous solution of picric acid into B'MeOC₆H₂(NO₂)₃ ¹/₂aq, which crystallises in greenish-yellow explosive needles [34°]. — B'2Me,PtCl₄. [188°] (O.); [207°] (B.). — B'MeAuCl₄. [253°].—B'MeCllCl. [82°] (O.); B'MeAuCl., [253°].—B'MeClICl. [82°] [0.], [90°] (B.). Yellow plates. B'MeClICl., [180°]. Unstable yellow crystals (Bally, B. 21, 1774).

Methylo-perbromide B'MeBr. [48°

Methylo-iodide B'MeI. Converted at 290° into methyl-pyridine hydriodides. On heating with alcoholic potash at 45° it yields a brown resin, forming a deep-red solution in alcohol, turned bright-red by HCl, orange-red by acetic acid, and ruby-red by ammonia (O. de Coninck, C. R. 102, 1479). Chlorine forms B'MeICl₂ [90°] (v. supra). Oxidised by alkaline K₃FeCy₈ to oxy-methyl-pyridine or v-methyl-pyridone CH CH.CO NMe (250°), a liquid miscible with water (Decker, J. pr. [2] 47, 28; cf. Pechmann, B. 24, 3144).

Ethylo-iodide B'EtI. Silvery tables Anderson, A. 94, 364). At 300° it yields pyridine, NH₃, (a) and (\gamma)- ethyl-pyridine, and diethyl-pyridine (Ladenburg, B. 16, 2059; 18, 2961). Yields B' Et. Pt. Co. Oxidised by alkaline

K,FeCy, to CH CH:CH NEt (250°).

Ethyleno-iodide B'C.H.I. Prisms (Coppola, G. 15, 332). Ag.O yields a base C.H.NO. By heating pyridine with ethylene bromide and some alcohol at 100° there is found B',C,H,Br., which yields B',C,H,PtCl, (Davidson, A. 121, 254).

Benzylo-chloride B'PhCH,Cl. Reduced by sodium-amalgam to the unstable C21H21N2 (Hofmann, B. 14, 1503) .- (B'PhCH2Cl)2PtCl4.

Nitro benzylo-chlorides
B'O.H.(NO₂).OH₂Cl. o [0.76°], m [70°-100°], p
[90°-100°]. These bodies are reduced by tin and HClAq to B'C,H,(NH,Cl).CH,Cl, which are split up by heat into pyridine hydrochloride and C₄H₄ < NH₂Cl (Lellmann a. Pekrun, A. 259, 54).

Phenacylo-bromide B'BzCH2Br. Prisms (Bamberger, B. 20, 3344).— $B'_2(BzCH_2)_2Cr_2O_7$.

References .- BROMO-, CHLORO-, OXY-AMIDO-, and Oxy- PYRIDINE.

Dipyridine $C_{10}H_{10}N_2$ v. Dipyridyle dihydride. Dipyridine $C_{10}H_{10}N_2$. (275°). S.G. 13 1·124. Is probably a dipyridyl dihydride. Formed by heating nicotine with KOH and K.FeCy, and also by heating the product of the action of S on nicotine at 150° with finely-divided copper (Cahours a. Etard, Bl. [2] 34, 452). Inactive liquid.—B'HHgCl,.—B',H.PtCl, 2aq.—

B',H,FeCy,2aq: brownish-green tables.
(a)-PYRIDINE CARBOXYLIC ACID

C_eH_bNO₂ i.e. CH:CH.C.CO₂H Picolinic acid. [186°]. Formed by oxidation of (a)-methyl-pyridine with KMnO, (Weidel, B. 12, 1994), and by oxidation of (a)-phenyl-pyridine (Skraup, M.

4, 477). Obtained also, together with its hexa-hydride, from comenamic acid by successive treatment with PCl₂ and H₂SO₄, the resulting di-chloro-picolinic acid being reduced by heating HOAc (Ost, J. pr. [2] 27, 285).

Preparation.—The three acids got by oxida-

tion of crude methyl-pyridine from animal oil are converted into copper salts. Cupric pyridine (a)-carboxylate is extracted by hot water. The residue is treated with H.S. and the difficultlysoluble (y)- acid separated from the (\$\textit{\textit{g}}\)- acid (Ost, J. pr. [2] 27, 286).

Properties.—Needles, v. sol. water and alco-

hol, almost insol. ether, benzene, CHCl₃, and CS₂. May be sublimed. FeSO₄ gives a red colouration with picolinic acid and with all the carboxylic acids of pyridine that contain CO_2H in the (2)-position (Skraup, M. 7, 210). The absorption of the ultra-violet spectrum has been

studied by Hartley (C. J. 41, 45).

Reactions.—1. Yields pyridine on distillation with lime or with alcoholic potash at 240°. The Cu salt on distillation gives pyridine and (α)dipyridyl [70°] (Blau, M. 10, 375; B. 21, 1077). 2. Sodium-amalgam forms δ-oxy-adipic acid (Weidel, M. 11, 522). -3. Fuming HI at 170° forms (a)-methyl-pyridine and piperidine (Seyfferth, J. pr. [2] 34, 241).—4. Zinc-dust and HOAc reduce it to (a)-methyl-pyridine.

Constitution.—This may be deduced from its

formation from (β)-naphthoquinoline via (β)phenyl-pyridine carboxylic acid (Skraup a. Co-

benzl, \hat{M} . 4, 436).

Salts. - HA'HCl: unstable crystals. -H₂A'₂H₂PtCl₆ 2aq: orange-red crystals.—NH₄A': triclinic tables.—KA'.—BaA'₂ ½aq.—CaA'₂ aq.—

MgA'2 2aq.

Hexahydride C₅H₁₀N.CO₂H. Piperidine (a)-carboxylic acid. The chief product of the action of HI at 160° on mono- or di-chloropicolinic acid (Ost, J. pr. [2] 27, 287). Got also by reducing picolinic acid (Ladenburg, B. 24, 640). Syrup, v. sol. water. Salts.—B'HCl. [264°]. Nodules.—B'₂H₄PtCl₆. [184°] (L.).—B'₂H₄PtCl₆ 2aq.—B'MeCl. [191°]. Needles.

Pyridine (B)-carboxylic acid CH.CH.C.CO.H. Nicotinic acid. [230°].

Formation .- 1. By oxidising nicotine with HNO, (Weidel, A. 165, 330), CrO, (Huber, A. 141, 271; B. 3, 849), or KMnO. (Laiblin, A. 196, 129).—2. A product of oxidation of coal-tar bases (Weidel; Mohler, B. 21, 1009).—3. By heating quinolinic acid at 160° or with HCl at 180° (Ost, J. pr. [2] 27, 286; Lippmann a. Fleissner, M. 8, 315).—4. By oxidation of (β) methyl-pyridine (Weidel, B. 12, 2004), (B)-ethylpyridine (Stoehr, J. pr. [2] 43, 155) or (β)-phenylpyridine (Skraup, M. 4, 453).—5. By saponification of its nitrile, which is got by distilling sodium-pyridine sulphonate with KCy (Fischer, B. 15, 63). -6. By heating three of the pyridine dicarboxylic acids (Hoogewerff a. Van Dorp, R. T. C. 1, 1, 107; A. 204, 117; 207, 226; Weidel a. Herzig, M. 1, 16).—7. By heating berberonic acid at 215° (Fürth, M. 2, 420).—8. By the action of Zn and HClAq on chloro-nico-tinic acid (Pechmann a. Welsh, C. J. 47, 145).

Properties. - Needles, sl. sol. cold water, sol. alcohol, nearly insol. ether. May be sublimed.

Reactions.—1. Yields pyridine on distillation with lime.—2. Sodium-amalgam yields a mixture of 8-oxy-a-methyl-glutaric acid and its lactone, which, on treatment with alcohol and HCl. yields a mixture of two ethers. One of these, C10H17ClO4, is converted by sodium-amalgam into a-methyl-glutaric acid, and the other, C_sH_{1,1}O₄, is also converted by successive treat-ment with PI₂ and with Zn and dilute H₂SO₄ into a-methyl-glutaric acid (Weidel, M. 11, 502).-8. Bromine and water at 120° yield CO₂, pyridine, and bromoform.—4. The K salt heated with MeI at 150° forms C.H.NMeI.CO.Me. which on saponification yields C.H.NMe(OH).CO.H [130°], converted at 100° into trigonellin C₅H₄NMe<

[218°], which occurs in the seeds of Trigonella fænum græcum (Jahns, B. 18, 2521; Hantzsch, B. 19, 31). This anhydride forms the salts C,H,NO,HCl, B',H,PtCl, aq, B'HAuCl, [198°], and B',3HAuCl, [186°].

Constitution.—This may be deduced from its formation from (a)-naphthaquinoline vid (a)-

phenyl-pyridine carboxylic acid.

Salts. - HA'HCl. Colourless Saits.—HA'HO!. Colourless prisms.— $H_2A'_2H_2PtCl_0$ 2aq.— $B'_2H_2AuCl_3$.— $B'HNO_3$ aq.— NH_A' : needles.—KA'.— MgA'_2 : needles.— CaA'_2 5aq: monoclinic crystals; a:b:c=1:537:1::629; $\beta=62^\circ$ 50'.—Cu(OH)A' (De Coninck, Bl. [2] 42, 100) .- AgA': needles (from hot water).

Nitrile C,H,N.Cy. [49°]. Formed by distilling sodium pyridine sulphonate with KCy (Fischer, B. 15, 63). Needles or prisms, sol. water. — B'HCl. — B'₂H₂PtCl₆: yellow soluble needles. Tables (by sublimation). Converted by means of hydroxylamine into the amidoxim C₃H₁N.C(NH₂):NOH [128°], which yields an acetyl derivative [143°] and a benzoyl derivative [190°], and is converted by phenyl cyanate into C_bH₄N.C(NOH).NH.CO.NHPh [167°], by phenyl thiocarbimide into $C_sH_sN.C \leqslant N \lesssim C.NHPh$ $C_{a}H_{a}N \leqslant_{N}^{N.O} \geqslant CPh$ [139°] respectively chaelis, B. 24, 3439).

Hexahydride C, H, N(CO, H). Nipecotinic acid. [250°]. Got by reducing nicotinic acid in alcoholic solution by Na (Ladenburg, B. 25, 2768). Crystals, v. e. sol. water, insol. alcohol 2706). Crystais, v. e. soi. Water, insoi. alcohol and ether.—HA'HCl. [240°].—H_A',H_2PtCl., [213° cor.].— HA'HCl5HgCl., [231°].—MeA'HCl [208°].— Me,A',H,PtCl., — Nitrosamine C.,H₁₈N₂O₃. [112°].

Pyridine (γ) -carboxylic acid

N CH.CH C.CO.H. Isonicotinic acid. [305°]

(S.); [306] (B. a. H.); [309-5°] (W. a. H.). Formation.—1. By heating pyridine s-tri-carboxylic acid (Skraup, B. 12, 2331) and three of the pyridine di-carboxylic acids (Hoogewerff a. Van Dorp, A. 204, 112; Weidel a. Herzig, M. 1, 28; Böttinger, B. 14, 68).—2. By the action of KMnO, on (γ)-methyl-pyridine (Behrmann a. Vol. IV. Hofmann, B. 17, 2696; Ladenburg, B. 21, 287). 8. By heating di-chloro-pyridine carboxylic acid

[210] with HI (B. a. H.).

Properties.—Needles, sl. sol. cold water, insol. alcohol. Yields pyridine on distilling with lime and 8-oxy-ethyl-succinic acid on reduction with sodium-amalgam (Weidel, M. 11, 517).

Salts.-NH,A': needles.-CaA', 4aq: silky needles, m. sol. water .- HA'HCl: monoclinic prisms.—H₂A'₂H₂PtCl₆ 2aq: monoclinic crystals.

Hexahydride C,H,ON(CO,H). Got by reducing the acid in alcoholic solution by Na (Ladenburg, B. 25, 2773). Branching groups of needles, v. e. sol. water, insol. alcohol. Blackens at 300°, but is not melted at 320°.—HA'HCl. [228°]. Trimetric crystals; a:b:c = 922:1: 979. [228]. Trimetric crystals; a.b.c - 922:1: 979.

-H.A'₂H₂PtCl_e. [239°]. — Aurochloride:
[197°]. Nitrosamine C₆H₁₉N₂O₃. [101°].

Pyridine (ac)-dicarboxylic acid

CH CH.C(CO.H) N. Dipicolinic acid. [226°]

CH.C(CO.H) N. Dipicolinic acid. [226°] (L. a. R.; S.); [237°] (E.); [236° cor.] (Collie, C. J. 59, 179). Formed by oxidation of (ac)-dimethyl-pyridine [145°] (derived from acetoacetic ether or from coal-tar) by KMnO, (Epstein, A. 231, 26; Ladenburg a. Roth, B. 18, 52; 19, 790; 20, 130; A. 247, 32; Lange a. Rosenberg, B. 20, 132; cf. Dewar, C. N. 23, 18). Got also by oxidation of (a) methyl-(a)-ethyl-pyridine by dilute (2 p.c.) KMnO, (Schultz, B. 20, 2724). Properties.—Hair-like needles (containing

1 aq) or anhydrous scales; sl. sol. cold alcohol. water, and ether. On heating at 245° in a current of H it yields pyridine and pyridine (a)-carboxylic acid. PCl_s forms a chloride [61°], (284°). FeSO, gives a reddish yellow colour.

Salts. - CaA" 2aq: minute prisms. -CuA" 2aq: dark-blue prisms.

Pyridire (aB) dicarboxylic acid

C(CO₂H).C(CO₂H) N. Quinolinic acid. [231°]. S. .55 at 6.5°. Formed by the oxidising action of KMnO, on quinoline (Hoogewerff a. van Dorp, B. 12, 747; R. T. C. 1, 107; A. 204, 117), on cinchonine (H. a. D.), on o- and p- methyl-quinoline (Skraup, M. 2, 157), on o-oxy-quinoline, on quinoline o-sulphonic acid (O. Fischer a. Renouf, B. 17, 755), and on (α)-oxy-quinoline carboxylic acid (La Coste a. Valeur, B. 20, 103).

Properties. — Monoclinic needles, a:b:c=542:1:607; $\beta=64°54'$; sl. sol. water and alcohol, insol. ether. Begins to decompose at 140°, and forms nicotinic acid. Yields pyridine when distilled with lime. Reduced by sodium-amalgam to the δ-lactone of butane aβγ-tricarboxylic acid CH. CH. CH. CO. H (Perlmutter, M. 13, 840).

Salts.—KHA" 2aq: triclinic plates (Lippmann a. Fleissner, M. 8, 311).—K₂A" 2aq.— BaA" aq.—Ag2A": crystalline.—AgHA" aq.

Anhydride C,H,N $<_{CO}^{CO}>0$. [135°]. Got from the acid and Ac₂O (Bernthsen a. Mettegang, B. 20, 1208). Prism... Converted by benzene and AlCl, into C₂H₂BzN.CO₂H [147°], converted by heat into the ketone C₂H₃BzN (307° uncor.), which yields a crystalline phenylhydrazide [143·5°].
Pyridine (a_γ)-dicarboxylic acid

CO'H'C CH CHO'H) N' Lutidinic acid.

A A

[240°] (V.); [285°] (B.; L. a. R.). Formed by the oxidising action of KMnO, on (eq)-dimethyl-pyridine (Ramsay, P. M. [5] 4, 241; 6, 19; Weidel a. Herzig, M. 1, 20; Ladenburg a. Roth, B. 18, 915; A. 247, 87), on (a)-methyl-(γ)-ethyl-pyridine (Schultz, B. 20, 2726), on di-ethyl-pyridine, on (αα)-di-methyl-dipyridyl (Heuser a. Stochr, J. pr. [2] 44, 409), and on the methyl-pyridine carboxylic acid obtained from nvitonic acid (Böttinger, B. 14, 68; 17, 93; Voigt, A. 228, 54).

Properties.—Needles (containing aq), m. sol. cold water, sol. alcohol, insol. ether. Gives a blood-red colour with FeSO. Yields pyridine. on distillation with lime. Converted by heat into CO2 and isonicotinic acid. PCl, yields a

chloride [203°]

Salts.-KHA" aq. Crystals.-(NH4)2A".-Salts.—KHA" kaq. Crystals.—(NH₄)A".—(NH₄)HA" aq: hygroscopic needles.—CaA" 3aq. CaA" aq.—CaA" &q.—CaA" &q.—BaA" aq.—BaA" aq.—BaA" aq.—BaA" aq.—BaA" aq.—BaA" aq.—BaA" aq.—CuA" aq. (Waage, M. 4, 727).—MgA" 5aq.—CuA" 3aq.—CuA" 4aq (B.).—Ag.A" 2aq: white pp. Pyridine (ab')-dicarboxylic acid. CH<CH:C(CO₂H)>N. Isocinchomeronic acid.

Formation.—1. By oxidation of lutidine (150°-170°) with KMnO₄ (Ramsay, P. M. [5] 4, 246; Weidel a. Herzig, M. 1, 1; Lange a. Rosenberg, B. 20, 135).—2. By oxidising (B')-methyl-(a)-ethyl-pyridine (Ladenburg, A. 247, 13) with the state of the control of the co 44).—3. By oxidation of quinine (Ramsay a. Dobbie, C. J. 33, 102; B. 11, 324).—4. By heating the dihydride of potassium pyridine tricarboxylate (Weiss, B. 19, 1311).—5. By the action of alkaline KMnO, on cyclothraustic acid and on pyridanthrilic acid (Weidel a. Strache, M. 7, 290). - 6. By oxidising (β)-ethyl-(α)-stilbazole (Plath, B. 22, 1062).

Properties .- Small prisms (containing aq), almost insol. cold water, alcohol, and benzene, sol. hot HClAq. On heating with HOAc at 220° it is split up into CO, and nicotinic acid [230°]. On heating with lime it gives pyridine. PCl. yields a chloride [61°] converted by NII, into an amide [297°]. FeSO₄ gives a reddish

colour.

Colour.

Salts.—(NH.)HA" aq. [253°]. Triclini prisms, sl. sol. cold water.—(NH.)₂A".—KHA" saq: needles.—K₂A" aq.—CaA" 2aq.—Ca(HA")₂Baq.—MgA" 5aq.—CuA" aq.—Ag₂A".

Methyl ether Me.A". [1175°] (R.).

Pyridine (ββ')-dicarboxylic acid

CH C(CO₂H).CH N. Dinicotinic acid. [322°]. Formed by heating pyridine (2,3,5)-tri-carboxylic acid and pyridine (2,3,5,6)-tetra-carboxylic acid (Riedel, B. 16, 1613; Hantzsch a. Weiss, B. 19, 286; Weber, A. 241, 12). Formed also by heating di-chloro-pyridine di-carboxylic acid with

conc. HIAq at 180° (Guthzeit, A. 262, 130). Properties.—Small prisms (from HOAc), split up by heat into CO₂ and nicotinic acid.

Salts.-PbA" 2aq.-Ag.A" aq.-Ag.A" 11aq. -HA'HCl 2aq: needles, decomposed by water.

-HA'₂H₂PtCl₃: orange-red needles. Pyridine (β_7) -dicarboxylic acid (β_7) -dicarboxylic acid Cinchomeronic acid. [259°].

Formation.—1. By oxidation of einchonine or cinchonidine by HNO, of S.G. 1.4 (Weidel, A. 173, 76).—2. By oxidation of quinine by HNO, A. 115, (6).—2. By Ordanton of dinnine by mice, the yield being 28 p.o. (Weidel a. Schmidt, B. 12, 1146).—3. By heating apophyllenic acid with conc. HClAq at 240° (Von Gerichten, B. 13, 1635).-4. By heating pyridine tricarboxylic acid (formed from cinchonic acid) at 190° (Hoogewerff a. van Dorp, B. 13, 61; Skraup, M. 1, 184; Weidel a. Brix, M. 3, 604) .- 5. By the action of KMnO, on methyl-pyridine carboxylic acid and on isoquinoline (Hoogewerff a. van Dorp, R. T. C. 2, 23; 4, 285).—6. By heating pyridine pentacarboxylic acid (Weber, A. 241, 16) .- 7. By oxidation of methyl-nicotinic acid, derived from (B)-collidine (Oechsner de Coninck, Bl. [2] 43, 106). -8. By boiling berberonic acid with HOAc (2 pts.) and Ac.O (1 pt.) for six hours (Mayer, M. 13, 344; cf. Fürth, M. 2, 426).

Properties.—Prisms (from HClAq), v. sl. sol. water and ether, sl. sol. alcohol. Yields isonicotinic and some nicotinic acid on heating (Hoogewerff a. van Dorp, A. 207, 217). Gives pyridine on distillation with lime. Sodiumamalgam yields NH, and cinchonic acid C,H_aO_e, i.e. CO₂H.CH CH, CO (Weidel a. Hoff, M.

CO.H

13, 578). Cinchonic acid [169°] forms mono-10, 0/0). Cincionic acid [109"] forms monoclinic crystals, v. sol. hot water and alcohol, and yields BaC,H₂O₆ Baq, Ba₃(C,H,O,)₂ Saq, CaA" 2aq, Ca₃(C,H,O,)₂ (dried at 190), and oily Et₄A", whence PCl₃, followed by alcohol, yields CO₂Et.CH(CH₂Cl).CH(CO₂Et).CH₂CO₂Et, which is a heavy oil. Cinchonic acid is reduced by HI to butane tricarboxylic acid C,H10O, [184°], whence Ca3A"2 8aq, accompanied by an isomeric butane tricarboxylic acid [133°]. FeSO, gives no colour.

Salts.—Na₄A" 2aq: tables.—NaHA".—BaA" 1½aq: needles, sl. sol. water.—CaA" 3½aq: prisms. — CaA" 3aq. — CuA" 3½aq: small blue crystals.—Ag₂A": white pp.—AgHA".—HA'HCl: monoclinic prisms, decomposed by

water. $-H_2\Lambda'_2H_2PtCl_3$: golden prisms. Anhydride ($C_2H_3N)_2C_2O_3$: [77°]. Formed by boiling the acid with Ac_2O (Goldschmiedt a. Strache, M.10, 156). Plates. May be sublimed. Converted by NH₃ gas into C₅H₃N(CO₂NH₄).CONH₂ [229°], which is converted by heat into a yellow powder [130°], and which yields the amic acid C₅H₂N(CO₂H).CONH₂ [237°], crystallising in

Mono-ethyl ether HEtA". [183°]. Formed from the anhydride and EtOH. Plates (from benzene).-AgEtA": long needles.

Mono methyl ether HMeA". [154°].

Anhydride of the Methylo hydroxide

C_bH,NO, i.e. C_bH,NMe(CO₂H) CO

Apophyllenic acid [242°]. Formed by oxidation of cotarnine by HNO, (Wöhler, A. 50, 24; Anderson, Tr. E. 23, 347; C. J. 5, 257; Gerichten, B. 13, 1635). Formed also by heating cinchomeronic acid with MeI and MeOH at 100° (Roser, A. 234, 116). Needles (anhydrous) or octahedra (containing aq), sol. hot water, insol. alcohol and ether. HClAq at 250° decomposes it, forming cinchomeronic acid and MeCl. - BaA'. $AgA'.-Ag_2A'(NO_3).-H_2A'_2H_2PtOl_3 aq.$

Bromo-apophyllenic acid C.H.BrNO, 2aq. [205°]. Formed by oxidation of bromo-tarconine. Yields BaA', 3aq and H₂A',H.PtCl_s (Gerichten, A. 210, 91). Pyridine (αα'β)-tricarboxylic acid

 $\mathbf{CH} < \begin{matrix} \mathbf{C}(\mathbf{CO}_2\mathbf{H}).\mathbf{C}(\mathbf{CO}_2\mathbf{H}) \\ \mathbf{CH} & \mathbf{C}(\mathbf{CO}_2\mathbf{H}) \end{matrix} > \mathbf{N}. \quad \text{Formed by oxidis-}$ ing di-methyl-nicotinic acid with KMnO, (Weiss, B. 19, 1309). Crystallises from alcohol in plates (containing 2aq), v. e. sol. water. Decomposes at 160° into CO₂ and isocinchomeronic acid. FeSO₄ colours its neutral solution red.—

RH_aA'', 5aq: needles.—Ca₄A'', 2aq.—Pb₃A''', 5aq. Pyridine (aa'7)-tricarboxylic acid

CO₂H.C CH.C(CO₂H) N. Trimesitic acid. Carbolutidinic acid. [244°]. Formed by oxidation of uvitonic acid (Böttinger, B. 13, 2048; 14, 69), and by oxidation of the tri-methylpyridine obtained from acetoacetic ether and aldehyde-ammonia (Voigt, A. 228, 31). Tables or spheroidal groups of needles (containing 2aq), sol. hot water, sl. sol. alcohol and ether. Yields isonicotinic acid on sublimation. FeSO, gives a violet-red colour.

Violet-red colour.

S a l t s . — K_AA''' 5aq : needles. — Ca₃A'''₂4aq. —

Ba₂A'''₂0aq. — BuH_AA'''₂4aq. — Mg₃A'''₂12aq. —

Cu₃A'''₂12aq. — Ag₃A'''1₃aq.

Ethyl ether Et₃A'''. [127.5°].

Amide. [above 280°]. Pyridine $(\alpha\beta\beta')$ -tri-carboxylic acid

CH $\langle C(CO_2H):C(CO_2H)\rangle$ N. Carbodinicotinic acid. [323°]. Formed by oxidation of quinoline $(Py.\ 2)$ -carboxylic acid (Riedel, B. 16, 1615). methyl-pyridine (ββ')-dicarboxylic (Weber, A. 241, 11), and of the parvoline got by heating propionic aldehyde-ammonia with propionic aldehyde at 200° (Dürkopf, B. 21, 832, 2707; 23, 689). Spherical aggregates (containing 1 aq), v. sol. hot water. At 155° it is split up into CO₂ and dinicotinic acid.— Ba₃A'''₂5aq.—Ag₂HA'''1\2 aq: rosettes of plates.

Pyridine $(\alpha\beta\gamma)$ -tri-carboxylic acid $CO_2H.C \stackrel{C(CO_2H)}{\subset} \stackrel{C($

D.; S.); [257°] (D. a. R.). S. 1.2 at 15°.

Formation.-1. By the action of KMnO, on quinine, cinchonine, cinchonidine, quinoïdine, and cinchonic acid (Dobbie a. Ramsay, C. J. 35, 189; Hoogewerff a. van Dorp, B. 12, 158; 13, 152; A. 204, 84; Skraup, A. 201, 312; Strache, M. 10, 642).—2. By oxidation of cinchonine by HNO, (Weidel, A. 173, 101; B. 12, 415).—3. By oxidation of methyl-pyridine (αβ)-dicarboxylic acid (Hoogewerff a. van Dorp, R. T. C. 2, 18), of di-methyl-pyridine carboxylic acid (Michael, B. 18, 2027), of (α)-oxy-cinchonic acid (Weidel a. Cobenzl, M. 1, 865).—4. By oxidation of papaverine (Goldschmiedt, M. 6, 397). Trimetric plates (containing 1 aq), v. sol. hot water, in. sol. alcohol, nearly insol. ether. Blackens at 200°. FeSO, gives a reddish colour. H2S forms a red amorphous body (D. a. R.). Decomposed by long heating at 180°, or by boiling with HOAe into CO₂ and cinchomeronic acid. Yields pyridine on distilling with lime. MeI and MeOH at 100° form CO₂ and apophyllenic acid. Sodium-amalgam gives NH2 and cinchonic acid. PCl, forms a chloride (206° at 40 mm.).
Salts. — K₁A'''3aq. — Ba₂A'''₂16aq. —

Ba₃A", 12aq. — Oa₃A", 14aq. — Ca₄A", 15aq.—
CaHA" 2½aq. — Cu₄A", 9aq: light-blue pp. —
CuHA" 3½aq: hexagonal prisms. — CuH₄A", 2aq.
— Cd₄A", 6aq. — Ag₂HA" aq. — Ag₃A" 2aq; amorphous pp. — AgH₄A", 2½aq. — H₄A"HCl: crystalline powder (Roser, A. 234, 125).

Pyridine (2"), bringshamile of 2

Pyridine $(a\beta'\gamma)$ -tricarboxylic acid $CO_2H.C < CI.CO_2H > N$. Berberonic acid. [243°]. Formed by oxidising berberine with nitric acid (Weidel, B. 12, 410; Fürth, M. 2, 416). Triclinic prisms (containing 2aq), sol. hot water, v. sl. sol. hot alcohol, insol. ether. Yields pyridine on distillation with lime. FeSO, gives a red colour. At 215° it is split up into CO₂ and nicotinic acid; above 243° it yields isonicotinic acid.

Salts. — $K_1A''' 4_3$ aq. — $K_2HA''' 3$ aq. — $K_2HA''' 3$ aq. — $K_2A''' 1_3$ aq. — $Ca_3A'''_2 8$ aq. — $Cd_3A'''_2 4$ aq. — Ag_3A''' : white pp., insol. water.

Pyridine $(\beta\beta'.9)$ -tricarboxylic acid $CO_2H.C \ll C(CO_2H).CH \gg N$. (β) - Carbocinchomeronic acid. [9619] Formed by besting 3^2 .

meronic acid. [261°]. Formed by heating dipotassium pyridine pentacurboxylate at 220° (Weber, A. 241, 17). Plates (containing 3aq), v. sol. hot water. Yields cinchomeronic acid whon heated. Gives no colour with FeSO, Cu₃H₂A'''₄ 24aq.—Ag₃A''' 2aq : crystalline pp. Pyridine $(a\beta\beta'\gamma)$ -tetra-carboxylic acid

 $C_9H_3NO_8$ i.e. $CO_2H.C \ll C(CO_2H) - CH > N$. Formed by oxidising $(\alpha \gamma)$ -di-methyl-pyridine $(\beta \beta')$ -dicarboxylic acid (Weber, A. 241, 23). Prisms (containing 2aq or 3aq). At 120° it loses CO2, forming (β)-carbocinchomeronic acid. FeSO, gives a dark-red colour.—Ba₂A^{1v} 4aq.—Ag,HA^{1v}₂ aq: crystalline.

Pyridine $(aa'\beta\beta')$ -tetracarboxylic acid $CH \stackrel{C(CO_2H)}{\sim} \stackrel{C(CO_2H)}{\sim} \stackrel{C(CO_2H)}{\sim} N$. Formed by oxidisdicarboxylic di-methyl-pyridine (Hantzsch, B. 19, 286; Weber, A. 241, 4). Needles (containing 2aq), v. sol. water. Decomposes at 150° into CO2 and dinicotinic acid.-Call, Aiv 2aq: needles, v. sol. water. - Cu, Aiv 5aq. -Ag Aiv 2aq: bulky pp.

Pyridine $(a\alpha'\beta'\gamma)$ -tetra-carboxylic acid $CO_2H.C \ll \frac{CH}{C(CO_2H)} : C(CO_2H) \gg N$. Formed Formed oxidation of tri-methyl-pyridine carboxylic acid and of di-methyl-pyridine di-carboxylic acid (Michael, A. 225, 142). Formed also by oxidation of flavenol by alkaline KMnO, (Fischer a. Täuber, B. 17, 2927). Slender needles (containing 2aq), v. sol. water, v. sl. sol. alcohol and ether. Not decomposed at 150°. FeSO, gives a brownish-red colour. -Ba, Aiv 2 aq. -Ba, Aiv aq.

-Cu₂A" 2½aq. - Ag₁Aiv aq. Pyridine penta-carboxylic acid NC₃(CO₂H)₃. Formed from potassium tri-methyl-pyridine dicarboxylate and KMnO, (Hantzsch, A. 215, 62; Weber, A. 241, 15). Crystalline mass of minute needles (containing 2aq), extremely sol. water, v. sl. sol. ether. Acid to litmus and to taste. Loses 2aq at 120° and decomposes, without having melted, at 220°. The neutral alkaline salts are very soluble, but the acid alkaline salts are sl. sol. water. The acid does not combine with HCl. Distilled with lime it gives pyridine. FeSO,

gives a dark-red colour,

Salts.-KHA 2 or Saq. When heated swells up like Pharaoh's serpent.—K,H,A*8;aq.

— K,A*. — Ba,A*, 11aq. — Ca,A*, 12aq. —

CaH,A*;aq.—Mg,A*, 12aq.—Ca₂(NH,)A*ŏaq.—

Ag,HA*2aq.

Double salt with oxalic acid

KH,AvKHC,O, 5aq.

References. - BROMO- and OXY-PYRIDINE CARB-OXYLIC ACID.

PYRIDINE TETRAHYDRIDE C.H.N i.e. CH2 CH : CH NH. Piperidein. Formed by heating amido-valeric aldehyde with solid KOH (Wolffenstein, B. 25, 2782).—B'HAuCl,. [141°]. —B₂'H₂PtCl₄.—B'HCl. [230°].—B'HBr. [178°].

Pyridine hexahydride v. PIPERIDINE. PYRIDINE (B)-SULPHONIC ACID

C.H.N.SO.H. Formed by heating pyridine (1 pt.) with H.SO. (3 pts.) at 320° (O. Fischer, B. 15, 62; 16, 1183). Small needles or plates, sol. water, sl. sol. alcohol, insol. ether. Br added to its boiling aqueous solution forms dibromopyridine. Potrsh-fusion gives oxy-pyridine [123°]. On distillation with KCy it yields the nitrile of nicotinic acid. The K salt, heated with MeI at 150° forms crystalline C₅H₄NMe< SO₂

(Hantzsch, B. 19, 36).—BaA', 4aq: needles. Pyridine sulphonic acid? C₅H₅NSO₃. [155°]. Formed from pyridine and ClSO₃H (Wagner, B. 19, 1157). Crystalline, decomposed

by water into pyridine and H₂SO₄.

Pyridine disulphonic acid C₅H₃N(SO₃H)₂. Formed by heating piperidine (1 pt.) with H.SO. (10 pts.) (Königs, B. 16, 735; 17, 592). Needles (from HOAc), v. sol. water, nearly insol. alcohol and ether. PCl. at 200° forms tri-chloropyridine [48°]. — Na₂A" 4aq. — K₂A" 3aq. — PbA" 4 ag.

PYRIDONE v. OXY-PYRIDINE.

(aa)-DIPYRIDYL C₁₀H₂N₂ i.e. C₃H₄N.C₃H₄N. [70°]. (272·5°). V.D. 5·6. Formed by distilling cupric picolinate (Blau, B. 21, 1077; M. 10, 875). Crystals (from water), m. sol. water, v. sol. alcohol. Not hygroscopic. Strong base. FeSO, colours its aqueous solution red. Oxidised by KMnO, to picolinic acid.—B"H_PtCl..— B"H_FeCy..—B"C.H_N.O.. [155.5°]. Needles Hexahydride. Formed by reducing the

base with zino and HClAq. Alkaline oil.

Dodecahydride C₁₀H₂₀N₂. Dipiperidyl.

(259° cor.). Formed by reducing the base, dissolved in isoamyl alcohol, by Na. Powerful base. Very deliquescent. Not poisonous. Forms with

Very deliquescent. Not poisonous. Forms with OS₂ a compound [93°], and yields a nitrosamine [159°].—B'H₂PtCl₂ 2½aq.
(ββ).Dipyridyl C₁₀H₂N₂. [68°]. (287°) (L.
a. O.); (292° at 736 mm.) (S. a. V.). Formed by distilling its dicarboxylic acid with KOH (Skraup a. Vortmann, M. 4, 591), and by the dry distillation of pyridine disulphonic acid (Leone a. Oliveri, G. 15, 276). Extremely deliquescent needles, miscible with water and alcohol, sl. sol. ether. Yields nicotinic acid on oxidation.—B"_H_PtCl_s.—B"2C,H_N_sO_r. [232°].

Hexahudride C...H_s,N_x. Nicotidine.

C,0H,1N2. (288°). Got by warming the base with tin and conc. HClAq. Poisonous oil, v.e. sol. water and alcohol, m. sol. ether.—B"₂H₂PtCl₆: orange-red pp.—Picrate: [202°].

 $(\gamma\gamma)$ -Dipyridyl C₁₀H₈N₂. [114°]. (305° cor.). V.D. 5'9 (calc. 5'5). Formed by boiling pyridine with sodium (Anderson, A. 154, 274; Weidel a. Russo, M. 3, 854). Formed also by heating its (aa)-dicarboxvlic acid with HOAc at 180° (Heuser a. Stochr, J. pr. [2] 44, 407). Tables, sl. sol. cold water, v. sol. alcohol. Crystallises from water in tables (containing 2aq). [73°]. Tastes bitter. Yields isonicotinic acid on oxidation. Br forms C10H6Br2N2 crystallising from alcohol in needles. MeI and EtI form crystalline B"2MeI and B"2EtI respectively.

Salts. — B"H₂Cl₂. Monoclinic crystals; a:b:c=1.064:1:.595. $\beta=112^{\circ}$ 33'.—B"H₂ZnCl₄. Monoclinic tables; -- B"H₂HgCl₄. β=91° 3'. — B"H,PtCl₆. – = .673:1: .341;

action of Na on pyridine (Anderson, C. J. 22, 406; Weidel, M. 3, 879). Liquid, sol. water and alcohol.—B"H₂PtCl₈. — B"2MeI. — B"Me₂PtCl₆

(Ramsay, C. J. 36, 264).

Hexahydride $C_{10}H_{14}N_{2}$. Isonicotine. [78°]. (above 260°). Formed by reducing $(\gamma\gamma)$ -dipyridyl with tin and HClAq (W. a. R.). Deliquescent needles, sol. water, alcohol, and benzene. Has hardly any smell. Strongly alkaline and caustic. Poisonous, acting somewhat like curari. Its salts are much less poisonous. Oxidised by KMnO. to isonicotinic acid. -B"2HNO3. Deliquescent needles. - B"H_PtCl3 aq. - B"_H_Hg_3Cl10. -B"2MeI: triclinic prisms (from MeOH).

Dodecahydride $C_{10}H_{20}N_2$. [122°]. Formed by reducing $(\gamma\gamma)$ -dipyridyl in alcohol by Na (Ahrens, B. 21, 2929). Needles, insol. water, v. sol. alcohol and ether.—B"H_PtCl_s.—B"HAuCl_s. Picrate: needles, blackening when heated.

Dipyridyl C₁₀H₈N₂ (281°). Formed by passing pyridine vapour through a red-hot tube (Roth, B. 19, 360). Oil.—B"2HCl: hygroscopic needles.—B"H.PtCl.—Piorate: [208°].

(αβ) Dipyridyl C₁₀H₁N₂. (296° cor.). Formed by heating its carboxylic acid with lime (Skraup a. Vortmann, M. 3, 599; Blau, B. 24, 326). Oil, sol. alcohol and ether. — B"H_2PtCl₁ aq. — B"C₂H₃N₃O₇. [149·5°]. Yellow needles. Dodecahydride C₁₀H₂₀N₂. [69°]. (269°

cor.). Formed by reducing the base with isoamyl alcohol and Na (Blau, M. 13, 332). Hygroscopic crystalline mass. Not identical with nicotine hexahydride. Strongly alkaline, absorbing CO₂ from the air. V. e. sol. water, but much water gives a turbidity. V. sol. alcohol, m. sol. ether. CS₂ forms a compound [205°].—B"H₂Cl₂. V.e. sol. water, sl. sol. alcohol and ether.—B"H₂PtCl₂ 2aq. [238°]. — B"2HAuCl₄. [212°]. — B"2C₄H₃N₄O₇. [215°].

Bensene sulphonyl derivative. [157°]. Nitrosamine C₁₀H₁₈N₂(NO)₂ [88°]. Dipyridyl dodecahydride? C₁₀H₂₀N₂? (251°). S.G. 4 ·956. Is perhaps (αβ)-dipyridyl hexa-hydride (Blau). Formed by the action of Na on nicotine in alcoholic solution (Liebrecht, B. 18, 2970; 19, 2590). Lævorotatory liquid, v. sol. water, alcohol, and ether. Alkaline in reaction. Smells like piperidine. Readily unites with CS. Forms an oily nitrosamine and an oily di-acetyl derivative (c. 405°).—B"2HCl. Sol. alcohol.—B"H,PtCl. [202°].—B"H,I.: brown needles.— B"2HAuCi, [182°].—B"H₂Hg,Ci, —B"Me,PtCl, —O₁₀H₁₀MeN₂Me,PtCl, Blau (M. 13, 341) by reducing nicotine obtained a mixture of bases (235°-265°) yielding a sparingly soluble platinochloride [218°], which gave a base (244°), possibly methyl-nicotine hexahydride C11H22N2

(a)-PYRIDYL-ACRYLIC ACID C.H.NO. i.e. C,H,N.CH:CH.CO₂H. [203°]. Formed by heating a-oxy-tri-w-chloro-propyl-pyridine with alcoholic potash (Einhorn, B. 20, 1593; 23, 220; A. 265, 215). Got also by heating a-oxy-pyridylpropionic acid. Small transparent needles, v. sl. sol. cold water, v. sol. alcohol.

Reactions. - 1. Br in HOAc forms C.H.N.CHBr.CHBr.CO.H [127°], which melts at 146.5° when containing HOAc of crystallisation.-2. Hydrogen bromide in HOAc forms (C,H,N.CHBr.CH,CO,H)HBr [164°], crystallising in needles.—3. MeI yields HA'MeI [220°] converted by AgBr into HA'MeBr [242°].

Salts.—HA'HCl. [220°].—H₂A'₂H₂PtCl₂. [210°]. Red prisms.—HA'HAUCl₄. [195°].— HA'HBr. [223°].—CaA',.—AgA': ncedles.

Methyl ether MeA'.—MeA'HCl. [186°].—

MeA'HBr. [242°]. MeA'HI. [220°].

Ethul ether EtA'. Needles.

(a)-PYRIDYL-BUTYLENE C₅H₄N.CH:CHEt. (148° at 75 mm.). By distilling oxybutyl-pyridine C₅H₄N.CH₂.CH(OH).C₂H₅ with KÖH in vacuo or by heating it with HClAq at 165° (Matzdorff, B. 23, 2711). Colourless oil, smelling like conyrin. - Platinochloride:

[140°], - B'HAuCl, [130°], Small needles.
(αβ).DIPYRIDYL (β).CARBOXYLIC . ACID
C₁₁H₄N₂O₂ i.e. C₅H₁N.C₅H₂N.CO₅H. [183°]. Formed by heating the dicarboxylic acid at 200° (Skraup, B. 15, 896; M. 3, 597). Needles (containing 1 aq), sl. sol. cold water and alcohol. Gives a yellow colour with FeCl, -- CaA', 2aq .-AgA' jaq: prismatic needles.

 $(\alpha\beta)$ -Dipyridyl $(\beta\gamma)$ -dicarboxylic acid $\mathbf{CH} \leqslant_{\mathbf{N}}^{\mathbf{CH}:\mathbf{C}(\mathbf{CO}_{2}\mathbf{H})} \geqslant_{\mathbf{C}.\mathbf{C}} \leqslant_{\mathbf{N}}^{\mathbf{C}(\mathbf{CO}_{2}\mathbf{H}):\mathbf{CH}} \geqslant_{\mathbf{CH}} \mathbf{CH}.$

Formed by oxidation of phenanthroline by KMnO, (Skraup a. Vortmann, B. 15, 896; M. 3, 587). Triclinic prisms (containing 2aq), sl. sol. cold water, v. sol. alcohol. FeSO, colours its aqueous solution red. Salts.—KHA", aq. has aqueous souther test. Sarts.—AIA __aq.,—CaA'' Baq.—CuA'' Saq.—BaA'' 12aq. Crystals.—AgHA'' 4aq.—H₂A'' 2HCl.—H₂A''H₂PtCl₆ 3aq.—(H₂A'')₂H₂PtCl₆ 6aq : golden prisms.

(ββ)-Dipyridyl (αα)-dicarboxylic acid C₁₂H₈N₂O₄. [213°]. Formed by oxidation of pseudo-phenanthroline by KMnO (Skraup a. Vortmann, M. 4,583). Thick prisms (containrotanani, at. 2, 005). The prisms (containing \(\frac{1}{2}\) aq), sl. sol. cold water, alcohol, and ether. FeSO, gives an orange-yellow colour.—K_\(\Lambda \) "5aq.— KHA" 2aq.— CaA" 5aq.— CuA" 3\(\frac{1}{2}\) aq.—Ag_\(\Lambda \) "AgNO_\(\lambda \).—H_\(\Lambda \)" HCl aq. Monoclinic prisms; \(a; b:c = 1.27.1:2.29; \(\beta = 1.10^{\circ} \) 16'.—

H.A. H.PtCl₂ Saq: orange crystalline pp.
(γγ).Dipyridyl (αα).dicarboxylic acid.[247·5°].
Formed by oxidising (αα).di-methyl-dipyridyl by KMnO, (Heuser a. Stoehr, J. pr. [2] 44, 405).
Needles y all sol, water and alcohol. Fe8O. Needles, v. sl. sol. water and alcohol. FeSO gives a reddish-yellow colour. AcOH at 1800

gives (γγ)-dipyridyl.

Dipyridyl tetracarboxylic acid? [96°]. Got
by oxidising diquinolyl (Claus, B. 14, 1942). Needles (from hot water).—Pb.Aiv.—Ag.Aiv.

PYRIDYLENE-PHENYLENE-KETONE

PHENYLENE PYRIDYL KETONE.

Pyridylene-phenylene-ketone sulphonic acid $\begin{bmatrix} 3_2^1 \end{bmatrix} C_t H_s(SO_tH) < \begin{matrix} CO.U:N-CH \\ C-C:CH.CH \end{matrix}$ Formed by oxidising (8)-naphthoquinoline sulphonate with alkaline KMnO, (Immerheiser, B. 22, 408). Yellow plates (from water), v. sl. sol. alcohol and ether. Yields an oxim crystallising in yellow flakes and a phenyl-hydrazide crystal-lising in minute orange needles.—KA' aq.— BaA', 2nq.—PbA', 3aq.—AgA' aq.

PYRIDYL-ETHYLENE C,H,N.CH:CH, (160°). Formed by the action of NaOHAq on the hydrochloride of β-bromo-β-pyridyl-propionic acid (Einhorn, B. 23, 221; A. 265, 229). Liquid.—B'HAuCl4. [144°]. Yellow needles.

(a)-PYRIDYL ETHYL KETONE C.H.NO i.s. C₅H₄N.CO.C₂H₅. (205°). Formed by distilling calcium picolinate with calcium propionate (Engler a. Bauer, B. 24, 2530). Oil, sol. alcohol. Sodium-amalgam forms a pinacone [136° Phenyl-hydrazine sulphonic acid vields a crystalline compound [268°].—B'HgCl2: crystalline.— B'EtI. [160°].

Oxim C.H.N.C(NOH).C.H. Needles. Yields an acetyl derivative [46°] and

a benzoyl derivative [69°].

(β)-Pyridyl ethyl ketone C,H,N.CO.C,H, Formed by distilling calcium nicotinate with calcium propionate (Engler, B. 24, 2539). Yields a phenyl hydrazide [145°] and a phenyl-hydrazide sulphonate [235°] which forms B'2H2PtCl2. $B'C_0H_3N_4O_n$, and $B'HgCl_2$ [130°]. $Oxim C_5H_4N.C(NOH).C_2H_3$.

(a) PYRIDYL METHYL KETONE C₅H₄N.CO.CH₃. (192°). Formed by distilling calcium picolinate with calcium acetate (Engler a. Rosun.off, B. 24, 2527). V. sol. alcohol and ether. Readily volatile with steam. Yields an oxim [120°], a phenyl-hydrazide [155°], and a phenyl-hydrazide sulphonate which is not melted at 300°.—B'C.H.N.O.. [131°].—B'HgCl., [150°].—B'MeI. [161°].—B'EtI. [205°]. (β)-Pyridyl methyl ketone C.H., N.CO.CH.,

(220°). Formed by distilling calcium nicotinate with calcium acetate (Engler a. Kiby, B. 22, 597). Oil, v. sol. acids. Yields an oxim [112°], which yields B'HCl [204°]. The phenyl-hydrazide [137°] crystallises from alcohol in yellow needles.—B'HgCl,. [158°]. White needles.

DI-(a)-PYRIDYL-PROPANE C13H11N2 i.e. CH (CH, C, H, N), (323°). S.G. 1.0281 Formed by heating picoline with methylal and ZnCl₂ for 10 hours at 290° (Ladenburg, B. 21, ZnCl₂ for 10 hours at 290° (Ladenburg, D. 21, 3100). Yellow oil, v. sol. alcohol and ether.—Salts: B"H₂PtCl_e. [215°]. - B"2HAuCl₄ 1½aq. -B"H₂Hq,Cl₉. [161°]. Large plates.

Dodecahydride C₁₃H₂₆N₂. Dipipecolylmethane. [54°]. (195° at 26 mm.). Formed by reducing the base with Na and alcohol.

Crystalline mass, sl. sol. water .- B"2HCl: very hygroscopic needles. - B"2MeCl. [171°]. C₁₃H₂₁Me₂N₂2MeI. Crystals, v. e. sol. water.

(a) PYRIDYL PROPYL KETONE

O.H.N.CO.Pr. (216°-220°). Formed by distilling calcium picolinate with calcium butyrate (Engler a. Majmon, B. 24, 2536). Oil. Yields an oxim [48°] which forms a benzoyl derivative [57°]. Forms a phenyl-hydrazide [82°] and a phenyl-hydrazide sulphonic acid [251°]. ketone is reduced, in dilute alcoholic solution, by sodium-amalgam to a pinacone $C_{18}H_{21}N_2O_2$ [146°]. The chloro-iodide melts at 85°.

Salts.— $B'_2H_2PtCl_8$.— $B'HgCl_2$. [c. 78°].

B'MeI. [79°].

(8) Pyridyl propyl ketone C₃H₄N.CO.Pr.
(246°-252°). Formed by distilling calcium nicotinate with calcium butyrate (Engler, B. 24, 2541). Yellow needles, sol. alcohol. Yields a phenyl-hydrazide [182°], a phenyl-hydrazide sulphonate [283°], a crystalline oxim, and an ethylo-iodide [192°]. - B'HgCl₂. B'C,H,N,O,

(B.3)-(a)-PYRIDYL-QUINOLINE $C_{14}H_{10}N_2$ i.e. CH.CH.C.CH:ÇH

CH. N .C.CH.C.C, H.N [104°]. Formed by heating the Ag salt of its carboxylic acid (O. Fischer a. H. van Loo, B. 19, 2475). Prisms.— ${
m B'_2H_2PtCl_6}.$ Carboxylic acid ${
m C_{15}H_{10}N_2O_2}$ i.e.

 $C_{\nu}H_{\nu}N.C \leqslant_{N-CH}^{CH:CH} \geqslant C.CO_{\nu}H.$ [273°]. Formed by oxidising (\$)-diquinolyl with CrO. Needles, v. sl. sol. water .- AgA': pale yellow pp.

PYRO. Use of this prefix applied to in-organic compounds; for pyro- compounds v. the compounds to the names of which pyro- is prefixed. Thus pyro-phosphoric acid will be found under Phosphoric Acid, and pyro-phos-

phates under Phosphates.

PYROCATECHIN C.H.O. i.e. C.H.(OH),[1:2]. Catechol. o-Di-oxy-benzene. Oxyphente acid. [104°] (F. a. M.); [111°] (Mortinon). (240°–245°). H.C.p. 685,200. H.C.v. 684,900. H.F. 85,800 (Stohmann, J. pr. [2] 45, 334). Occurs in urine, especially after administration of benzene or phenol (Baumann, H. 1, 244; 3, 157; Nencki a. Giacosa, H. 4, 335; Schmiedeberg, H. 6, 189). Occurs in the green leaves of the Virginia creeper (Ampelopsis hederacea) (Gorup-Besanez, B. 4, 905) and in the sap of the plants from which kino is prepared (Fluckiger, B. 5, 1). Occurs sometimes in raw beet sugar (Lippmann, B. 20, 3298). Occurs in wood-tar (Béhal a. Desvignes, Bl. [3] 9, 141).

Formation .- 1. By dry distillation of catechin. moritannic acid, and all varieties of tannin that turn green with FeCl₃ (Zwenger, A. 37, 327; Wagner, J. pr. 52, 450; 55, 65; Eissfeldt a. Uloth, 4. 92, 101; 111, 215).-2. By the dry distillation of wood (Buchner, A. 96, 188). -3. By heating cellulose, starch, or cane sugar with water at 200°-280° (Hoppe-Seyler, B. 4, 15).-4. By potash-fusion from o-iodo-phenol (Körner, Bull. Acad. Belg. [2] 24, 166; Lautemann, A. 120, 315).—5. By the action of HI on guaiacol (Gorup-Besanez, J. 1867, 688; Baeyer, B. 8, 155).—6. By the dry distillation of protocatechuic acid and of quinic acid (Strecker, A. 118, 285; Hlasiwetz a. Barth, J. 1864, 405; Tiemann a. Haarmann, B. 7, 617).—7. By potash-fusion from o-phenol sulphonic acid (Kekulé, Z. 1867, 643), benzoic acid, gum guaiacum (Hlasiwetz a. Barth, A. 130, 352; 134, 282), and, together with resorcin, from o- and m- bromo-phenol (Fittig, B. 8, 364).-8. By soda-fusion from phenol (Barth a. Schreder, B. 12, 419) .- 9. From phenol and H₂O₂ (Martinon, Bl. [2] 43, 157).— 10. By passing a rapidly alternating electric courrent through a solution of phenol.—11. A

product of the action of water at 200° on bens. ene hexachloride (Meunier, C. R. 100, 1591).

Preparation.—1. From HIAq and guaiacol at 200° or by heating guaiacol with conc. HClAq for 4 hours at 175° (Perkin, jun., C. J. 57, 587). 2. By fusing o-phenol sulphonic acid with potash at 350° (Degener, J. pr. [2] 20, 308).

Properties .- Large plates (from benzene) or needles (from water), v. sol. water, alcohol, and ether, m. sol. benzene and chloroform. insol. ligroin. Gives an acid reaction in presence of borax (Lambert, C. R. 108, 1017). FeSO, gives no colour. FeCl, colours the aqueous solution green, turned violet-red by alkalis (Ebstein a. Müller. Fr. 15. 465). The alkaline solution Müller, Fr. 15, 465). The alkaline solution absorbs oxygen, becoming brown. It reduces AgNO3, AuCl3, and platinic chloride. Ppts. a conc. solution of egg-albumen. Does not ppt. gelatin. Lead acetate gives a white pp. Quinone in ethereal solutions forms C.H.O.C.H.O.20 crystallising in deep-green needles with violet lustre [153°] (Clermont a. Chantard, C. R. 102, 1072). Ppts. a solution of quinine sulphate, forming C., H2, N.O. H2SO, C.HeO, aq, which separates from alcohol in yellow crystals [167°], v. sl. sol. cold water.

Reactions .- 1. Nitric acid acts violently, forming oxalic acid .- 2. Phthalic anhydride and ZnCl₂ at 150° form 'pyrocatechin phthalein'

C(C₆H₃(OH)₂)₂, a yellow mass forming

a blue solution in alkalis and yielding a tetrabenzoyl derivative [202°] (Baeyer a. Kochendörfer, B. 22, 2196). 3. Phenyl cyanate at 100° forms CaH4(O.CO.NHPh)2 [165°] crystallising in needles, v. sol. alcohol (Snape, C. J. 47, 772). 4. The disodium compound C₆H₄(ONa)₂ treated with CO₂ in the cold forms C₆H₄(O.CO₂Na)₂, which at 100° changes to the compound C, H, (O.CO, Na) (OH).CO, Na and at 210° to C_aH₂(OH)₂(CO₂Na)₂ (Schmitt a. Hähle, J. pr. [2] 44, 2).—5. Ammonium carbonate and water at 140° react forming protocatechuic acid and C_oH₄(OH)(CO₂H)₂[1:2:3].—6. K₂S₂O₇ acting on K salt forms crystalline C_oH₄(O.SO₂K)₂ and C₆H₄(OH)(O.SO₃K) (Baumann, B. 11, 1913).—7. Cl.CONH₂ forms C₆H₄(O.CONH₂)₂ [178°] crystallising from alcohol in needles. -8. Chlorine passed into its solution in acetic acid forms

CCl CCl₂CO crystallising (with 2aq)

from ether-ligroin, and from ligroin (with aq). melting at 94° (Zincke a. Klein, B. 21, 2719).-9. KOH and ClCO,Et form C₄H,CO₃ [118 [118°] (Bender, B. 13, 697), (225°-230°) (M. Wallach, A. 226, 84).

Estimation. - By extracting its acidified aqueous solution with ether, evaporating the ether, dissolving the residue in water, and precipitating with lead acetate. The pp. is dried at 100° and weighed (Degener, J. pr. [2] 20, 303).

Salt s.—C_oH₄O₂Pb. White pp.—C_oH₂O₃Sb or

 $C_eH_4 < O$ SbOH. Formed by adding SbCl₃ to a

solution of pyrocatechin saturated with NaCl (Causse, Bl. [3] 7, 245). Prisms, insol. water, alcohol, and ether, sol. alkalis and mineral acids. Ac2O at 125° forms C.H. (OAc), and Sb(OH) (OAc),. Di-acetyl derivative C.H. (OAc),

Di-acety lNeedles (Nachbauer, A. 107, 248).

Di-bensoyl derivative [84°]. Plates (Doebner, A. 210, 261; Hinsberg, 4. 254, 254).

Mono-methyl ether C₆H₁(OH)(OMe). Guaiacol. Mol. w. 124. [28·5°]. (205°) (Tiemann a. Koppe, B. 14, 2016; Béhal a. Choay, Bl. [3] 9, 142). S.G. 16 1·125 (V.); 21·153; 15 1·143 (B. a. C.). A product of distillation of gum guaiacum (Sobrero, A. 48, 19; Deville a. Pelletier, A. 52, 403; Völckel, A. 89, 349). Occurs among the products of the distillation of wood (Hlasiwetz, A. 106, 362; Gorup-Besanez, A. 143, 151). Prepared by heating calcium vanillate with slaked lime (Tiemann, B. 8, 1123) and by heating pyrocatechin with MeI and KMeSO, (Gorup-Besanez, A. 147, 248, or with NaOMe, McOH, and MeI). Liquid, with peculiar odour, sol. alcohol and ether, sl. sol. water, sol. dry glycerin and ligroïn. FeCl, gives a green colour in its alcoholic solution. Dissolves in alkalis. Yields C.H. OMe on heating with zinc-dust (Marasse, A. 152, 64). PCl, forms C,H,Cl.OMe (Fischli, B. 11, 1463). I and KOHAq give a coffee-brown pp. [125°-130°] (Messinger a. Vortmann, B. 22, 2320). The K salt is converted by acetochlorhydrose into $C_8H_4(OMe)(O.C_8H_{11}O_5)$ [157°] (Michael, Am. 6, 339). Phthalic anhydride and SnCl, at 115° form 'guaiacol-phthalein,' which yields a crystalline benzoyl derivative (Baeyer, B. 22, 2199). H₂SO₄ forms two sulphonic acids (Tikmann a. Koppe, B. 14, 2019).— C₀H₄(OK)(OMe) 2aq.—KHA'₂ aq: prisms (from alcohol), decomposed by water.—Pb(OH)A': flocculent pp. — C₂H₄(O.SO₃K)(OMe): white needles.—C₄H₄(OAc)(OMc). (235°-240°). V.D. 82·7 (obs.). Colourless liquid.

Di-methyl ether C_vH₄(OMe)₂. Veratrole. (205°). V.D. 68·6 (obs.; H=1). S.G. 15 1·086. Formed by heating veratric acid with baryta (Merk, A. 108, 60; Koelle, A. 159, 243; Tiemann, B. 14, 2016). It is obtained also from C, H, (OK) (OMe) and MeI (Marasse). Solidified

at 15°.

Methyl ethyl ether $C_0H_1(OMe)(OEt)$. (213°). V.D. (H=1) 75 6 (obs.). Liquid.

Methyl propyl ether C.H.(OMe)(OPr). (240°-245°). Liquid (Cahours, Bl. [2] ??, 270). Di-ethyl ether C.H.(OEt)... [44°]. Formed from pyrocatechin, Etl., and alcoholic potash

(Herzog a. Zeisel, M. 10, 152).

Di-benzyl derivative C6H4(OC,H4)2. [61°]. Yellowish needles (from alcohol). Forms a nitro-derivative crystallising in needles [98°].

The mono-benzyl derivative is liquid, but its nitro-derivative forms yellow needles (from alcohol) [129°] (Schiff a. Pellizzari, A. 221, 378; G. 13, 507).

Sulphonic acid $C_8H_3(OH)_2(SO_3H)[4:3:1]$. Formed by fusing phenol (a) disulphonic acid with KOH at 300° (Barth a. Schmidt, B. 12, 1260). Deliquescent needles, v. sol. water and alcohol, insol. ether. - KA'. - NaA'aq. - BaA'2.

References .- AMIDO-, BROMO-, CHLORO-, and NITRO- PYROGATECHIN, and TRI-BROMO-GUAIACOL.
PYROCINCHONIC ACID v. DI-METHYL-

MALEÏO ACID.

PYROCOLL C₁₀H₀N₂O₂ (Magnanini, B. 22, 2502). [269°]. A product of the distillation of gelatin when free from fat but containing albumen, casein, or gluten (Weidel a. Ciamician, M. 1, 279; 2, 29). Formed also, together with

C.H.(OBz)2. | HOAc, by heating the scetyl derivative of pyr-Tole (a)-carboxylic acid (Ciamician a. Silber, B. 17, 103; G. 14, 162, 563). Colourless plates, insol. water and cold alcohol, sl. sol. ether. Sublimes before fusion.

Reactions.-1. Boiling KOHAq converts it into pyrrole carboxylic acid .- 2. Alcoholic NH, forms the amide of pyrrole carboxylic acid. -3. PCl₃ forms C₁₀Cl₆N₂O₂ [above 320°] insol. ether and C₁₀Cl₁₀N₂O [197°] sol. ether (Ciamician a. Danesi, G. 13, 28). The perchloro-pyrocoll C10Cl6N2O2 is converted by boiling KOHAq into tri-chloro-pyrrole carboxylic acid, and by PCl. the C₁₀Cl₁N₂O₂ [1479]. 4. Bromine forms C₁₀H₃Br₁N₂O₂ [192°], C₁₀H₄Br₂N₂O₂ [290°], and C₁₀H₄Br₄N₂O₂, which is converted by KOHAq into di-bromo-pyrrole carboxylic acid (Ciamician, G. 11, 330; 12, 29; B. 16, 2388).

Reference.-CHLORO-, BROMO-, and NITRO-Pyrocoll.

PYROCRESOL. C₁₃H₁₁O? An inappropriate name given by Schwarz (B. 15, 2201; 16, 2141; M. 3, 726; cf. Armstrong, C. J. Proc. 3, 114) to some neutral substances found in coal-tar.

(a)-Pyrocresol [195°]. Thin silvery plates, yielding crystalline $C_{2n}H_{2\nu}Br_3O_2$? and oxidised by CrO_1 in HOAc to $C_{1\nu}H_{1\nu}O_2$ [168°] which yields $C_{1\nu}H_{1\nu}(NO_2)O_2$ [235°], $C_{1\nu}H_{1\nu}(NO_2)O_2$ and $C_{1\nu}H_{1\nu}(NO_2)O_2$ [235°], $C_{1\nu}H_{1\nu}(NO_2)O_2$ and $C_{1\nu}H_{1\nu}(NO_2)O_2$ [230°]? (Bott a. Miller, C.J. 55, 52). Chlorine acting on a solution of (a)-pyrocresol in chloroform gives C15H11Cl3O [225°]? HI reduces (a)-pyrocresol to a hydrocarbon C15 II 22? (Bott, C. J. Proc. 3, 114).

(a)-Pyrocresol [c. 124°]. Yields, on oxidation, '(B)-Pyrocresol oxide ' $C_{13}H_{12}O_{2}$ [95°]. (b)-Pyrocresol [165°]. Yields '(γ)-Pyrocresol oxide ' $C_{13}H_{12}O_{2}$ [95°]. oxide ' $C_{13}H_{12}O_{2}$ or oxidation. Bromine forms $C_{28}H_{12}Br_{2}O_{2}$? crystallising in trimetric plates.

PYROGALLIC ACID v. PYROGALLOL PYROGALLOL C.H., O. i.e. C. H., (OH), [1:2:3]. c-Tri-oxy-bensene. Pyrogallic acid. Mol. w. 126. [131°] (Etti, B. 11, 1882; cf. Stenhouse, A. 179, 236); [134°] (Stohmann). (210°). S. 40 at 12°. 40 at 12°. H.C.p. 633,300 (Berthelot a. Louguinine, A. Ch. [6] 13, 339; C. R. 104, 1577). H.F. (from diamond) 137,700 (B. a. L.); 132,000 (Stohmann, J. pr. [2] 45, 336). Occurs in woodtar as dimethyl ether.

Formation .- 1. By heating gallic acid (alone or mixed) with pumice stone (2 pts.) (Braconnot, A. 1, 26; Pelouze, A. 10, 159; Licbig, A. 101, 47).-2. By heating di-iodo-o-oxy-benzoic acid with KOHAq (Lautemann, A. 120, 299) .- 3. By heating (a)- or (β) - chloro-phenol sulphonic acid with KOH at 190° (Petersen a. Baehr, A. 157, 136).-4. By heating gallic acid (10 g.) with glycerin (30 c.c.) at 200° as long as CO₂ comes off (Thorpe, Ph. [3] 11, 990).-5. By heating gallic acid (1 pt.) with aniline (2 pts.) at 120° (Cazeneuve, Bl. [3] 7, 549). The product is aniline pyrogallate $C_6H_8O_32NPhH_2$ [56°], which gives off aniline when exposed to air, or when shaken with benzene.

Properties. - Prisms, v. sol. water, m. sol. alcohol and ether. Tastes bitter. Poisonous (Personne, Z. [2] 5, 728). Its alkaline solution rapidly absorbs oxygen, turning brown, and giving off a little CO in bulk about 30th of the oxygen absorbed (Calvert a. Cloez, A. 130, 248). Beduces KMnO, (Monier, C. R. 46, 577) and salts of mercury, Ag, Au, and Pt. FeSO, gives

a white milkiness, but if a ferric salt is present, or the pyrogallol solution has become slightly exidised by keeping, FeSO, gives an indigo-blue colour, changing to brownish red on standing and on adding HCl (Jacquemin, C. R. 77, 593; Cazeneuve, Bl. [2] 44, 114; C. R. 101, 56). FeCl., in absence of air, gives a transient blue colour, restored by cautious addition of alkali. A solution of pyrogallol renders borax slightly acid (Lambert, C. R. 108, 1017). Nitrous acid colours the aqueous solution brown (Schönbein, Fr. 1, 319). K₂CrO₄ and H₂SO₄ give a dark colour. Reduces CuSO₄ and, on addition of alkalis, gives a black colour changed by NH, to red. Cu(OAc)₂ gives at once a black colour. Pyrogallol fused with ammonium oxalate yields ammonium rufigallate, which dissolves in water with red colour and gives with K3FeCy, and K_Cr_O, a dark-brown pp. insol. alcohol (Kliebahn, Fr. 26, 641). A solution of iodine in presence of Na SO, gives a purple colour (Nasse, B. 17, 1186). A solution of HgCl, and pyrogallol in alcohol gives a black pp. with alkaloids but not with glucosides (Schlagdenhaufen, Ph. [3] 4, 772). An alkaline solution of pyrogallol absorbs about 50 vols. of NO in 12 hours, but no N₂O (Russell a. Lapraik, C. J. 32, 35). Pyrogallol does not react with hydroxylamine (Baeyer, B. 19, 163). A solution of potassium pyrogaliate which is absorbing oxygen in contact with alumina gives out a feeble light, especially in presence of Na.S (Lenard a. Wolf, P. [2] 34, 918).

Reactions .- 1. Fuming HNO, forms oxalic acid .- 2. Bromine forms tri-bromo-pyrogallol .-8. Chlorine in presence of HOAc forms mairogallol (vol. iii. p. 165) and crystalline leucogallol C18H8Cl12O12 2aq, which yields tri-chloro-pyrogallol when boiled with water and zinc-dust (Stenhouse a. Groves, C. J. 28, 706; Webster, (Stenhouse a. Groves, C. J. 28, 706; Webster, C. J. 45, 208; Hantzsch a. Schniter, B. 20, 2033).—4. Ozone passed through a solution of pyrogallol (1 mol.) and KOH (3 mols.) in water forms a syrupy acid C₄H₄O₇, which yields BaC₄H₄O, (Boeke, B. 6, 486).—5. Purpurogallin or pyrogalloquinone is formed by oxidation by alcoholic AgNO₃, by KMnO₄ and H₂SO₄, or by excess of FeCl₄ (Girard, C. R. 69, 865). It is also got from pyrogallel and quinone (Wichelbaus. got from pyrogallol and quinone (Wichelhaus, B. 5, 847; Nietzki, B. 20, 1278). It forms garnet-fed needles (by sublimation), sl. sol. water, m. sol. alcohol and ether, forming yellow solutions. Alkalis impart a transient blue colour. Purpurogallin dyes cotton mordanted with alumina violet-blue. When an aqueous solution of pyrogallol is mixed with gum arabic and exposed to the air, purpurogallin C20H18O. separates, the yield in the course of two months being 67 p.c. of the pyrogallol used (Struve, A. 163, 160; De Clermont a. Chautard, C. R. 94. 103, 104; De Ciermont a. Chautard, C. A. 94, 1189, 1254). A solution of pyrogallol and Na,HPO, also yields pyrogalloquinone on exposure to air (Loew, J. pr. [2] 15,322). Purpurogallin forms C₂₀H_{1,2}Ac₂O, and C₂₀H_{1,2}Br₂O₂.—6. An ammoniacal solution exposed to the air forms brown pyrogallein C₁₈H₂₀N₂O₁₆ (Rösing, J. 1868, 250). 7 Ammoniacal content of 1302 forms 259).-7. Ammonium carbonate at 130° forms pyrogallol carboxylic acid C,H,O, (v. Tri-oxy-benzoic acid) and pyrogallol dicarboxylic acid C,H,O, [270°] (Senhofer a. Brünner, M. 1, 468). 8. Distillation over zinc-dust yields benz-

ene.—9. CICO₂Et acting on the K salt forms C₂H₂O₄ [105°] converted by aniline into diphenyl-urea and the mono-ethyl ether of pyrogallol (Bender, B. 13, 698).—10. A few drops of POCl, added to a mixture of pyrogallol (2 pts.) and acetone (1 pt.) react violently, forming gallacetonin C₉H₁₀O₃, which crystallises from 15 p.c. alcohol in whetstone-shaped crystals, insol. water, decomposing about 250°, and yielding C₀H₀AcO₂ (Wittenberg, J. pr. [2] 26, 76). Its solutions are turned purple by FeCl, and reduce AgNO3.-11. A few drops of H2SO, added to a mixture of pyrogallol (12 g.) and acetoacetic ether (8 g.) form di-oxy-methyl-coumarin $C_{10}H_3O_4$, which crystallises from water in needles [235°] and yields O₁₈H_AC₁O₄ [176°] (Wittenberg, J. pr. [2] 26, 68; Pechmann, B. 16, 2127; 17, 2188).—12. Phthalic aphydride forms, on heat-163; —12. Interest of the state needles (Snape, C. J. 47, 774). -14. Cyanogen passed into an aqueous solution forms C.H.O.Cy, or a polymeride thereof, as an unstable crystalnne pp. (Loew, J. pr. [2] 15, 326).—15. Chloroacetic acid (2\frac{1}{2} pts.) followed by NaOHAq forms $C_8H_1(O.CH_2CO_2H)_3$ crystallising in needles [198°], S. 1·3 at 14·5° and yielding K_2A''' and KH_2A''' aq (Giacosa, J. pr. [2] 19, 398).—16. Benzotrichloride at 160° yields 'pyrogallobenzein' $C_{38}H_{21}O_{11}$, crystallising in minute red plates with green lustre forming a blue solution. line pp. (Loew, J. pr. [2] 15, 326).—15. Chloroplates with green lustre forming a blue solution in alkalis and a bluish-violet solution in alcohol. Zinc and HOAc reduce it to the anhydride of hexa-oxy-diphenyl-methane. Pyrogallol-benzein yields $C_{38}H_{20}Ac_4O_{11}$ [208°], $C_{38}H_{20}Bz_4O_{11}$ [251°], $C_{38}H_{20}O_{11}(C_5H_5O)_4$ [228°] (Döbner a. Förster, A. 257, 60).-17. Benzoic acid and ZnCl, at 145° form tri-oxy-benzophenone (Alizarin yellow A) C₆H₂(OH)₃.CO.C₆H₅[141°], which crystallises with aq. The same body is got by heating pyrogallol with benzotrichloride (G. P. 50,451 [1889] and 54,661 [1890]; Graebe a. Eichengrün, A. 269, 297).—18. On heating pyrogallol with salicylic acid and zinc chloride tetra-oxy-benzophenone 28. Solution of the chiral straints and the chiral straints are chiral straints. 20. Benzene sulphonic chloride added to a solution of pyrogallol kept slightly alkaline forms $C_eH_a(O.SO_aPh)_a$ [142°], sol. alcohol, sl. sol. ether (Georgesen, B. 24, 418).—21. Formic aldehyde and dilute HClAq form CH₂(C₆H₂(OH)₂)₂₀ a microcrystalline powder, insol. water, sol. alcohol (Caro, B. 25, 947).-22. Aldehyde and dilute H2SO, mixed with Na2SO, added slowly at 60° gives colourless crystals of C,H,O, 2aq, which when dried at 30° over H,SO, leaves violet C₃H₂O₃ aq (Causse, Bl. [3] 3, 865; cf. Michael a. Ryder, Am. 9, 133).—23. Benzoio aldelyde and a large quantity of HClAq form amorphous C₂₄H₂₂O, (Baeyer, B. 5, 280). Benzoic aldehyde, alcohol, and a little conc. HClAq form and enque, according and a fitther of the distribution app. of $C_{2n}H_{2n}O_9$, which yields $C_{2n}H_{n}Ao_0O_9$ (Michael a. Ryder, Am. 9, 130). On heating with benzoic acid alone pyrogallol forms resinous $C_{2n}H_{2n}O_7$ and red $C_{2n}H_{10}O_7$, which may be reduced to colourless $C_{2n}H_{2n}O_7$ (Baeyer, B. 5, 25). 24. KOH (83 pts.) and $K_{2n}S_{2n}O_7$ (70 pts.) heated

with water (33 pts.) and pyrogallol (25 pts.) at 70° form C₆H₃(OH)₂(O.SO₃K), crystallising in needles, v. e. sol. water (Baumann, B. 11, 1913).—25. CICONH₂ forms $C_4H_4(O.CO.NH_2)$. [1786], crystallising from alcohol in plates.

Salts. - CaH3(OH)2(ONH1). Crystals, got by passing NH, into an ethereal solution of pyrogallol (De Luynes, A. Suppl. 6, 252).— C.H.(OH)(O.Pb) aq. Crystalline pp. got by adding lead nitrate to ammonium pyrogallol.

Converted by conc. NH₃Aq into C₆H₈O₃3PbO.— (C.H.O.)Pb.OAc. Ppd. by adding lead acetate to a solution of pyrogallol (Deering, C. J. 26, 702). -C_gH₃(SbO)O₃. Plates, got by ppg. pyrogallol solution with tartar-emetic (Rösing). SbCl₃ (100 g.) dissolved in a saturated solution (250 c.c.) of NaCl, filtered, and slowly added to pyrogallol (50 g.) dissolved in saturated NaClAq (250 g.), forms a white pp. which changes to crystals of C₈H₃(OH) SbOH 2aq, insol.water and alcohol, sol. mineral acids (Causse a. Bayard, Bl. [3] 7, 794). At 100° the above liquids on mixing yield C₆H₃O₃Sb, which is also crystalline, whence Ac2O at 100° forms C6H3O3Ac3. AcCl in Ac₂O converts both antimonites into C₈H₃(OAc)₃.—C₆H₆O₃2NPhH₂. [56°] (Mylius, B.

19, 1003). Acetyl derivative C.H. (OAc), Got from pyrogallol and AcCl (Nachbauer, A. 107, 244).

Benzoyl derivative C.H. (OBz). [90°]. Got, together with a mono- or di- benzoyl derivative [131.5°], from pyrogallol and BzCl (Skraup, M. 10, 391).

Di-mcthyl ether C.H. (OH) (OMe) .. [52° (253°). Occurs in beech-wood creosote (Hofmann, B. 11, 333; 12, 1373). Formed from pyrogallol (1 mol.), KOH, and MeI (2 mols.) at 160°. Prisms (from water). Its alkaline solution does not turn brown in air. Oxidised by means of K₂Cr₂O, and HOAc to corulignone C₁₂H₄O₄(OMe)₄. Yields C₄H₃(OAc)(OMe)₂ as a sticky mass, and C₄H₃(OBz)(OMe)₂ [118°].

Tri-methyl ether C₄H₃(OMe)₄. [47°].

(235°). Formed by the action of Mel and KOH on pyrogallol dissolved in MeOH (Will, B. 21, 607). Needles, insol. water and alkalis, v. sol. alcohol and other. Yields C, Br, (OMe), [81°]. Conc. HNO₃ forms $C_8H_2(NO_2)(OMe)_3$ [100°] and the di-methyl derivative of dioxyquinone.

Mono-ethyl ether C,H3(OH)2(OEt). [95°] Formed, together with the di- and tri-ethyl ethers, by heating pyrogallol with KOH and KEtSO, at 100° (Benedikt, B. 9, 125; M. 2, 212; Hofmann, B. 11, 797). Needles, m. sol. water,

normann, B. 11, 797). Needles, m. sol. water, v. e. sol. alcohol and ether. FeSO, gives a bluish-violet colour. Volatile with steam.

Diethyl ether C,H_(OH)(OEt), [79°]. (262°). Crystals (from dilute alcohol). Oxidised by K,Or,O, and HOAo to ethyl-cerulignone. Nitrous acid passed into an ethereal solution. forms C20H21O6HNO3, which forms a brown solution in water.

Tri-ethyl ether C_cH_s(OEt), [89°]. Got from pyrogallol, alcoholic potash, and EtI (Herzig a. Zeisel, M. 10, 151). Needles, insol.

Ethylens ether C.H.(OH):O2:C2H4. (267°). Formed from pyrogallol, alcoholic potash, and ethylene bromide (Magatti, B. 12, 1860). Yields O.H.(OBz):O.C.H. [109°].

References .- AMIDO-, BROMO-, CHLORO-, and NITEO- PYROGALLOL.

CARBOXYLIC PYROGALLOL ACID GALLIC ACID.

Pyrogallol dicarboxylic acid

C₈H(OH)₃(CO₂H)₂[1:2:3:4:5]. Gallocarboxylic acid. [270°]. S. 05 at 0°. H.C. 633,700. H.F. Gallocarboxulic 231,300 (Stohmann, J. pr. [2] 40, 128). Formed by heating pyrogallol or gallic acid with ammonium carbonate at 130° (Schhofer a. Brunner, M. 1, 468). Needles (containing 3aq), sl. sol. cold water. • Gives a violet colour with FeCl,... K,A" 2aq: needles. -- BaA"aq. -- CaA" 6aq. -- Ag_2A''

PYROGALLOL SULPHONIC ACID C.H.SO. i.e. C₆H₂(OH)₃,SO₃H ½aq. Formed by dissolving pyrogallol in H₂SO₄ (Personne, Bl. [2] 12, 169; 20, 531; Schiff, A. 178, 179). Hygroscopic crystals.—KA' 2aq: prisms, v. sol. water. Converted by heating with POCl₃ into C₁₂H₁₀S₂O₁₁, a flocculent mass, v. sol. alcohol, which is converted by warming with HOAc and Ac.O into crystalline C₁₂H,Ac₃S,O₁₁ and C₁₂H,Ac₃S,O₁₁.
PYROGALLOQU.NONE v. PYROGALLOL. Re-

action 5, and PURPUROGALLIN.

PYROGENTISIC ACID is HYDROQUINONE. PYROGLUTAMIC ACID is OXY-TETRA-METHENYL DIHYDRIDE CARBOXYLIC ACID.

PYROGLYCERIN v. DIGLYCERIN.

PYROGUAIACIN C18H18O3 i.e. C18H18O(OH)2 [180.5°]. (258°) at 80 90 mm. V.D. 9.53 (calc. 9.76). A product of the distillation of gum guaiacum (Pelletier a. Deville, C. R. 17, 1143; Ebermaier, J. pr. 62, 291; Nachbauer, A. 106, 382; Hlasiwetz, A. 106, 381; 119, 277; Wieser, M. 1, 594). Plates, v. sl. sol. hot water, sl. sol. alcohol and other. Forms a blue solution in H2SO4. On distillation with zinc-dust it yields guaiene C₁₂H₁₂ [100°], which is converted by oxidation into a lemon-yellow quinone C₁₂H₁₀O₂ [121°]. Potash-fusion forms C₁₂H₁₂O₂ [202°], which is reduced by zinc-dust to guaiene. Pyroguaiacin yields C₁₈H₁₈Ac₂O₃ [122°], C₁₈H₁₈Bz₂O₃ [179°], C₁₈H₁₈Br₃O₃ [172°], and the salt C₁₈H₁₆K₂O₃.

PYROLIC ACID v. SEBACIC ACID.

PYRO-MECAZONIC ACID C,H,NO,. Formed by heating oxycomenic acid, with NH,Aq and also, in small quantity, along with the isomeric amido-pyro-meconic acid, by the reduction of nitro-pyromeconic acid. Prepared from oxypyro-mecazonic acid by reducing with HI (Ost, J. pr. [2] 19, 203; 23, 441; 27, 258).

Properties .- Streaked trimetric tablets. Combines with mineral acids, but not with acetic acid. Gives rise to a di-acetyl derivative [155°] and a bromo-derivative C.H.BrNO. Is stable in acid solutions, but soon turns brown in alkaline solution. Gives a blue colour with FeCl. BaCl₂ and NH₂ give a pp. which turns bright blue in air.

Reactions .- 1. Suspended in ether and mixed with HNO, forms 'pyromecazone' C.H.NO. Pyromecazone is a brick-red powder, insol. ether, v. sol. water, gives no colour with FeCl., and turns the skin violet. With BaCl, and NH, it gives, on exposure to air, a crimson pp. Crystal-lises from alcohol as C₁H₂NO₂,EtOH. Aqueous SO₂ converts pyromecazone back into pyrome-cazonic acid. These properties resemble those

of a quinone.—2. Suspended in HOAc and

treated with HNO, it forms yellowish prisms of nitro-pyromecazone C,H_(NO_)NO, aq. This body is decomposed by water at 30° into nitro-pyro-mecazonic acid C,H_(NO_)NO, CO, coming off through oxidation of some of the substance. SO, rapidly changes nitro-pyromecazone into nitro-pyromecazonic acid, so that the former resembles quinone in its ready reducibility. Nitro-pyromecazonic acid gives a blood-red colour with FeCl3, nitro-pyromecazone gives no colour with FeCl3, It yields the salt C,H_NaN_O,.

Salt .- HA'HClaq: needles.

Oxypyromecazonic acid C₃H₂NO₄. Formed by passing SO₂ into an ethercal solution of nitrosopyromeconic acid, and boiling the product (v. Nitroso-Pyromeconic acid) with CHCl₂ (Ost, J. pr. [2] 19, 177). Needles (containing aq or 2aq). Coloured dirty-violet by FeCl₂.—NaHA'₂.—KHA'₂.—TlHA'₂.—CaA'₂.—HA'HCl.

PYROMECONIC ACID C₅H²₄O₃. [117°]. (225° uncor.).

Preparation.—By distillation of meconic acid in a current of CO₂, some comenic acid being also formed (Ost, J. pr. [2] 19, 182; 23, 441; cf. Robiquet, A. 5, 90; A. Ch. [2] 5, 282; 51, 236; Stenhouse, P. M. [3] 24, 128; A. 49, 18; F. D. Brown, P. M. [4] 4, 161; 8, 201; A. 84, 32; 92, 321; Ihlée, A. 188, 31). The yield is 14 p.c.

Properties.—Glittering prisms from water or alcohol. V. sol. chloroform, much less sol. ether. Gives a blood-red colour with FcCl., Feeble acid. Does not react with hydroxylamine (Oderheimer, B. 17, 2081). Bromine forms C₃H₃BrO₃, crystallising in prisms and yielding PbA'₂ aq. Excess of Br yields C₃H₃BrO₃ aq [100°]. ICl forms C₃H₃IO₃ yielding BaA'₂ aq and PbA'₄.

Salts.—Forms two sories of unstable salts, alkaline to litmus: KA'.—HNaA',.—BaA', 3aq.—BaH,a',.—CaH,a',.—CaH,a',.—MgA',.—SrA',aq.—PoA',.—CaH,a',.—CaH,Q,.;HCl. Formed by passing HCl into ethereal solution of the acid. Decomposed into its constituents by water or alcohol. Sulphates C,H,Q,H,SQ, and (C,H,Q,),H,SQ. Got by adding H,SQ, to an ethereal solution (Ost, J. pr. [2] 19, 189).

Acetyl derivative C,H3AcO3. [91°]. Obtained by warming with AcCl.

Nitroso-pyro-meconic acid $C_5H_1(NO)O_3$. An unstable compound of this body with an equivalent of pyro-meconic acid is formed by passing N_2O_3 into an ethereal solution of that acid (Ost, J. pr. [2] 19, 195). An aqueous solution of SO_2 converts this compound by addition of H_2 into $C_3H_1(NO)O_3, C_3H_4O_3$, a compound which is split up by boiling chloroform, leaving so-called oxy-mecaronic acid, $C_3H_3NO_4$. This acid gives a violet colour with FeCl₃, and a blue pp. with BaCl₂ and NH_3 . By Sn and HCl it is reduced to pyro-mecaronic acid $C_3H_3NO_2$.

References.—Amido- and Nitro-Pyromeconic

PYROMELLIC ACID C, H, O, [238°]. Obtained in the electrolysis of aqueous KOH with earbon electrodes, and got also by oxidation of mellogen by KOCI (Bartoli a. Papasogli, G. 12, 113; 13, 51). Crystalline (containing 2aq), sol. water and alcohol. Yields the crystalline salt C, H, Na, O, and an ethyl ether crystallising in golourless needles [below 100°], insol. water.

PYROMELLITIC ACID C₁₀H₁₀C₆ 4.6. C₈H₂(CO₂H)₄[1:2:4:5]. Mol. w. 254. [264°]. S. 14·2 at 16°. H.C.p. 777,400 (Stolmann, J. pr. [2] 40, 140; 43, 540). H.C.v. 778,900. H.F. 689,600. Formed by gently distilling mellitic acid (Erdmann, A. 80, 281) and by oxidising s-durene (Jacobsen, B. 17, 2517). Crystallises from water in triclinic tables (containing 2aq), v. sol. hot water. Forms various compounds on heating with (a)-naphihol (Grabowski, B. 4, 726; 6, 1065).—Ca.A'* 6aq.—Pb,A'*aq.—Ag,A'*: pp.

Methyl ether Me, A'r. [138°]. Plates, sl. sol. hot alcohol (Baeyer, A. 166, 339).

Ethyl ether Et.A. [53°]. Formed from the Ag salt and EtI (Baeyer, A. Suppl. 7, 36). Needles (from alcohol).

Chloride C.H. (COCI). Got by heating the acid with PCI. Crystalline mass, v. sol. ether.

Anhydride C₆H₂(C₂O₃). [268°]. Got by distilling the acid. Needles (by sublimation), v. sol. hot water, being re-converted into the acid.

Tetrahydride C₈H₈(CO₂H)₄. Formed by the action of sodium-amalgam on the ammonium salt of pyromellitic acid (Baeyer). Amorphous hygroscopic mass, v. sol. water. When heated with Π₂SO₄ it yields pyromellitic, trimellitic, and isophthalic acids.

Iso-tetrahydride C₈H_a(CO₂H)₄. [above 200°]. Accompanies the preceding acid. Needles (containing 2aq). Behaves like the preceding hydride when heated with H₂SO₄. Yields a methyl ether [156°] which may be distilled.

References.—Amido- and Nitro- Pyromel-

PYROMUCIC ACID C.H.O. i.e.

CH.CH. C.CO₂H. Furfurans (a)-carboxylic acid. Mol. w. 112. [132°]. S. 3·6 at 15°; 25 at 100°. R_{∞} 40·18 (in a 2·19 p.c. aqueous solution).

Formation.—1. By the distillation of mucic acid (Houton-Labillardière, A. Ch. [2] 9, 365; Pelouze, A. 9, 273; Boussingault, A. 15, 184; Liès-Bodart, A. 100, 327).—2. By distilling dehydromucic acid (Heinzelmann, A. 193, 184).—3. By oxidation of furfuraldehyde by Ag₂O (Schwanert, A. 114, 63; 116, 257).—4. Together with furfuryl-carbinol by boiling furfuraldehyde with alcoholic potash (Ulrich, Z. 1861, 186; Schmelz a. Beilstein, A. Suppl. 3, 275; Limpricht, A. 165, 279).—5. By distilling isosaccharic acid in a current of CO₂ (Tiemann a. Haarmann, B. 19, 1271).—6. Occurs, together with pyromycuric acid C,H,NO, [165°] which yields BaA'₂1½aq, in the urine of dogs dosed with furfuraldehyde (Jaffé a. Cohn, B. 20, 2311).

Preparation.—By oxidising furfuraldehyde with alkaline KMnO₄ below 20° (Volhard, A. 261, 379).

Properties.—Long white needles (by sublimation), v. sol. alcohol and ether. FeCl₃ gives no colour.

Reactions.—1. Bromine in excess forms mucobromic acid. Dry Br gives C₂H,Br,O₃ [160°], oxidised by dilute CrO₂ to di-bromopyromucic acid (Tönnies, B. 11, 1086).—2. Distillation with soda-lime yields furfurane.—3. On heating with lime and ammonia-zine-chloride it yields pyrrole.

Salts.—KA': needles.— NaA'.—BaA',: orys-

tals, sol. water and alcohol.—CaA'2: crystalline

powder.—CuA'₂ 3aq.—PbA'₂ 2aq.—AgA': scales. Ethylether EtA'. [34°]. (209°). Laminæ, v. sol. alcohol and ether, insol. water (Malaguti, A. 25, 276). Combines with dry chlorine, forming C.H.Cl.O. S.G. 195 1-496. Dry Br forms C.H.Br.O. [48°] (Tönnies) and also the ethers of $(\beta\delta)$ -di-bromo-pyromucic acid [167°], of $(\beta\gamma)$ di-bromo-pyromucic acid [192°] and of (δ)-bromopyromucic acid [192°] and of (δ)-bromopyromucic acid [183°] (Hill a. Sanger, A. 232, 65).

Chloride C₅H₃O₂Cl. (170°).

[1430]. Amide C,H,O.CONH, Formed from the ether or chloride and NH, Aq (Wallach, B. 14, 751; 214, 227; Ciamician a. Dennstedt, B. 14, 1058; G. 11, 291). Large plates, sol. alcohol, sl. sol. ether. Converted by PCl, or P.O. into the nitrile.

Ethylamide C.H.O.CONHEt. [258° cor.). Formed from pyromucic other and ethylamine solution at 100°. Converted by PCl, into crystalline C₁H₂O.CCl_{...}NHEt. PCl_. in smaller quantity (¹/₃ pt.) forms the amidine C₁H₂O.C(NEt).NHEt, a liquid (240°) which gives B'_{...}H_{...}PtCl_{...}

Anilide C,H,O.CO.NHPh. [123.5°]. Long needles (Schiff, B. 19, 849).

Nitrile C,H,O.CN. Furfuryl cyanide. (148°). Liquid with sweet taste, sl. sol. water, smelling like benzoic aldehyde. On reduction it gives C.H.O.CH..NH.

(B)-Pyromucic acid, got by oxidation of fucusol, is a mixture of pyromucic acid with methyl-pyromucic acid [108°] (Bicler a. Tollens,

A. 258, 126).

Isopyromucic acid. [82°]. Formed, together with pyromucic acid, in the distillation of mucic acid. It decomposes BaCO₃ very slowly, and can be separated by shaking the product with BaCO, and extracting with ether (Limpricht, A. 165, 256). Plates (by sublimation), v. e. sol. water, alcohol, and ether. FeCl₃ gives a green colour. Br yields mucobromic acid.

References. — Bromo-, Bromo-sulpho-, Loro-, Nitro-, and Sulpho- pyromucic CHLORO-, ACIDS.

PYROMUCIC ALDEHYDE v. FURFURALDE-

PYROMYKURIC ACID C,H,NO, [165°]. Occurs in the urine of rabbits dosed with furfuraldehyde (Jaffé a. Cohn, B. 20, 2311). Prisms (from water). Split up by boiling baryta-water into glycocoll and pyromucic acid. -BaA', 1 aq: plates.—A urea compound (C,H,NO,)CO(NH,), [120°] occurs in the urine of dogs fed with meat. It crystallises from benzene in needles, v. sol. water and alcohol, sl. sol. ether, and is decomposed by heating with BaCO3 into urea and pyromykuric acid.

PYRONE. A name given to the ring co < CN:CH > 0.

PYROPHORUS. Any finely-divided substance which takes fire very easily when exposed to air is called a pyrophorus.

PYRORACEMIC ACID is PYRUVIC ACID. PYROTARTARIC ACID C.H.O. i.e. CO,H.CHMe.CH, CO,H.

Methyl-succinic acid. Mol. w. 182. [115°]. S. 66 at 20°. S.H. 3098 (from 0° to 50°) (Hess, A. Ch. [2] 85, 410). H.C.v. and p. 515,200

(Stohmann, J. pr. [2] 40, 209); 511,672 (Lou-guinine, C. R. 107, 597). H.F. 230,800 (S.).

Formation .- 1. By dry distillation of tartar (Valentin Rose, Gehlen's Journ. 3, 598) and of tartaric and racemic acids (Gruver, N. J. T. 24, 2, 55; Pelouze, A. Ch. [2] 56, 297; Weniselos, A. 15, 148; Fourcroy a. Vauquelin, A. Ch. 35, 161; 64, 42; Arppe, A. 66, 73).-2. By the reduction of ita-, citra-, and mesa- conic acids and of dibromopyrotartaric acid with sodiumamalgam (Kekulé, A. Suppl. 1, 342; 2, 95).-3. By saponifying its nitrile with HClAq (Maxwell Simpson, A. 121, 161). -4. By heating powdered tartaric acid with HClAq at 180° (Geuther a. Riemann, Z. [2] 5, 318).—5. By potash-fusion from gamboge (Hlasiwetz a. Barth, A. 138, 73).-6. By heating pyruvic acid alone at 170° or with HClAq at 100°, or by boiling it with baryta. 7. By boiling β-acetyl-α- or β- methyl-succinic ether with potash (Conrad, A. 188, 217; Kressner, A. 192, 135) .- 8. By heating allyl iodide (1 mol.) with KCy (2 mols.) and a little alcohol, and boiling the resulting nitrile with KOHAq (Claus, B. 5, 612; 8, 100; A. 491, 38). - 9. By heating propane tricarboxylic acid (Bischoff a. Guthzeit, B. 20, 614).-10. By oxidation of \$\beta\$. acetyl-n- and iso- butyric acid (Bischoff, A. 206,

Properties. - Trielinic prisms grouped like frog's feet (from ether), v. sol. water, alcohol, and ether. Begins to boil at 200°, yielding an anhydride together with some butyric acid (Claus, A. 191, 48). Its solution is not ppd. by lime-water or lead acetate, but gives a pp. with lead subacetate.

Reactions.-1. Bromine acts very slowly in the cold, but when the acid (10 pts.) is heated with Br (21 pts.) and water (10 pts.) at 120° for 6 hours bromocitraconic anhydride is formed (Lagermark, Z. 6, 299). When the acid (1 mol.) is heated with Br (4 mols.) at 132° acetylene tetrabromide is formed (Bourgoin, A. Ch. [5] 12, 419) .- 2. The K salt yields, on electrolysis, O, CO, and CO, at the positive pole (Reboul a. Bourgoin, C. R. 84, 1231).—3. Distillation with P₂S₄ yields methyl-thiophene.—4. On heating the acid (5 pts.) with resorcin (9 pts.) and ILSO, (18 pts.) at 150° there is formed pyrotartrylfluoresceïn C₁₇H₁₆O₈, a brownish-red powder, sl. sol. water, v. sol. dilute acids and alkalis. Its dilute alkaline solutions fluoresce yellowishgreen. It yields C17H12Br4O4 (Hjelt, B. 17, ĭ280).

Salts.—K₂A" aq: deliquescent.— KHA": monoclinic prisms.—Na₁A" 6aq: efflorescent lamina.—NaHA": small prisms.—(NH₄)₂A": deliquescent; gives off NH, on evaporation, leaving (NH,)HA", which crystallises from water in prisms, permanent in the air.—BeA".—BeH2A" -CaA" 2aq: powder. S. 1 at 100°. -CaH₁₀A", 2aq. -CaA"2aq: powder. S. 1 at 100°.—CaH₁₆A"₉2aq.
-SrA" aq. — SrA" 2aq. — SrH₄N"₂ 2aq.
-BaA" 2aq. — BaH₂A"₂ aq. — BaH₄A"₂ 2aq.
-BaH₄A"₂ 3aq. — BaH₄A"₂ 4aq. — MgA" 3aq. —
MgA" 6aq. — Al(OH)A". — Bi₄A"₄(HO)₄O. —
CdA" 3aq.—CdA" 2aq.—MnA" 3aq.—CuA" 2aq.
-Cu₂(OH)₂A". — Fe(OH)A" 2aq. — PbA" 2aq. —
Pb₂A"O₂.—NiA"2:q.—NiH₄A"₂2aq.—ZnA" 3aq.
-Ag₂A": white curdy pp., blackened by light.
Ethul ether EtA". (218° oor). 8.G.

Ethyl ether Et.A". (218° cor.). S.G. 15 10189; 25 10113. M.M. 9.347 at 17.4° (Perkin, C. J. 45, 516; cf. Malaguti, A. 25, 274).

Oktoride C.H.O.Ol. (190°-193°) (Hjelt, B. 16, 2624). Reduced in ethereal solution by sodium-amalgam and HOAc to liquid C, H,O,

(204°), S. 20, which is the anhydride of an acid $O_{\mu}H_{\nu}O_{\nu}$.

Anhydride $C_{\nu}H_{\nu}O_{\nu}$. (245° cor.) (Lebedeff, 4. 182, 327). Got by heating the acid at 200° alone or with $P_{\nu}O_{\nu}$. Heavy oil, slowly converted

by water into the acid.

CH_s.CH(CO.NH_s).CH_s.CONH_s. Amide [175°]. S. 7 at 10°. Large plates (Henry, C. R. 100, 943).

Imide CH, CH CO.NH. [66°]. Formed by heating acid ammonium pyrotartrate (Arppe, A. 87, 228). Six-sided trimetric plates, sol. water, alcohol, and ether.

Di-methylamide CaHa(CO.NHMe)2.

[115°] (Henry, Bl. [2] 43, 619).

Mono-anilide CO, H.CH., CHMe. CONHPh. [147°]. Formed from aniline and pyrotartaric anhydride in chloroform (Arppe, A. 90, 141; Anschütz, A. 246, 122). Got also by reducing the anilide of mesaconic acid with sodiumamalgam. Is identical with Reissert's 'pyranilpyroic lactone dihydride.' Bulky needles, m. sol. water.-PbA'2: white pp. -AgA'

Phenyl-imide CH₂.CH < CO .NPh. CH₂.CO (Arppe, A. 90, 139); [104°] (Biffi, A. 91, 105). Formed by heating the acid with aniline at 100° for ten minutes. Minute needles.

p-Nitro-anilide C₂H_e(CO₂H)(CO.NH.C₆H_eNO₂). [above 150°]. Formed by boiling the p-nitro-phenyl-imide with Na₂CO₂Aq. Minute tables, v. sl. sol. hot water. - AgA': white pp.

water.—AgA': white pp.
p-Nitro-phenyl-imide
C₂H₃:C₂O₂:NC₂H₃NO₂ [155°]. Formed by nicohol), almost insol. water.

p-Bromo-anilide C₂H₆(CO₂H).CO.NHC₆H₄Br. U₂H₄(CO₂H).CO.NHC₆H,Br. [158°]. Formed from the anhydride and p-bromo-aniline (Anschütz a. Hensel, A. 248, 269). Di-bromo-anilide

C₃H₆(CO₂H).CO.NHC₆H₃Br₂[1:2:4]. [139°]. Nitrile CH₃.CH(CN).CH₂CN. [c. [c. 12°]. (254°). Formed, amongst other products, by the action of KCN on allyl chloride (Pinner, B. 12, 2058). Prisms. Prepared from propylene bromide and alcoholic KCy at 100° (Maxwell Simpson, A. 121, 160). Liquid, sol. water, alcohol, and ether.

Ethyl ether of the seminitrile CO₂Et.CH₂.CHMe.CN. (198). S.G. 215 1.0275. V.D. 4.6. Formed from a-bromo-propionic ether and alcoholic KCy (Zelinsky, B. 21, 3162). Oil.

-NaA': very hygroscopic.

References.-Bromo-, Chloro-, Iodo-, Oxy-AMIDO-, and OXY- PYROTARTARIC ACID.

n-Pyrotartaric acid v. GLUTARIO ACID. Isopyrotartaric acid v. DI-METHYL-MALONIC

ACED. PYROTEREBIC ACID v. HEXENOIC ACID.

PYROTRITARIC ACID C,H,O, i.e. OCMe:CH Uvic acid. Di-methyl-furfurane carboxylic acid. Mol. w. 140. [135°]. S. 25 at 100°. A product of the distillation of tartaric acid (Wislicenus a. Stadnicki, A. 146,

806). Prepared by heating pyruvic acid with NaOAc and Ac₂O at 140°, the yield being 20 p.c. (Böttinger, B. 13, 1969; A. 172, 241; 208, 122; 247, 255), by heating pyruvic acid (30 g.) with dry sodium succinate (55 g.) at 110° (Fittig a. Parker, A. 267, 212), and by heating pyruvic acid (17.5 g.) with dry potassium propionate (20 g.) at 140° (Bischoff, B. 24, 2021). Formed also by heating methronic acid as long as CO, is given off (Fittig, A. 250, 190; cf. Harrow, C. J. 33, 425). Needles (from hot water), nearly insol. cold water, v. sol. alcohol and ether. affected by potash-fusion. PCl, gives a chloride, reconverted by water into the acid. Does not react with hydroxylamine or phenyl-hydrazine. Water at 160° forms acctonyl-acctone. By bromine it is converted into a tetra-bromoderivative and its tetra-bromide, which are both reduced back to pyrotritaric acid by sodiumamalgam. An excess of bromine at 100° forms penta-bromo-pyrotritario acid. By dry distillation it gives di-methyl-furfurane, a substance which is also obtained by distilling acetonylacetone with ZnCl₂ (Paal, B. 20, 1074; Dietrich a. Paal, B. 20, 1077).

Salts.—NaA' 2aq.—CaA', 2aq: prisms.— CaA', 4aq. — CaA', 6aq. — BaA', 4aq: plates.— BaA', 2aq. — BaA', 5aq. — ZnA, 8aq. – AgA'. Methyl ether MeA'. (192°). Got by dis-

tilling the Ag salt of carbopyrotritaric monomethyl ether (Knorr a. Cavallo, B. 22, 156).

Ethyl ether EtA'. (208° Pyrotritaric carboxylic acid v. METHRONIC ACID.

Carbopyrotritaric acid v. DI-METHYL-FUB-FURANC CARROXYLIC ACID.

PYROXANTHIN C15H12O2. [162°]. Extracted by NaOHAq from the product of the dry distillation of wood (Scanlan, J. pr. 7, 94; Gregory, A. 21, 143; Hill, Am. 3, 332; B. 11, 456). Orange needles (from alcohol), sol. benzene and HOAc. Forms a purple solution in H2SO4. Reduced by zinc-dust and HOAc to a colourless body. Bromine forms C15H10Br6O3 crystallising in small colourless triclinic needles, converted by alcohol and powdered Sb into C1.H10Br2O3, crystallising in yellow monoclinic needles, v. sol. hot alcohol.

PYROXYLIN v. CELLULOSE.

PYRRODIAZOLE C₂H₃N₂ i.e. N≪CH,NH [121°]. Formed by heating its carboxylic acid at 120° (Andreocci, B. 25, 229). Needles, v. e. sol. water and alcohol.

Pyrrodiazole carboxylic acid

CO₂H.C < N.NH. Formed by oxidising methylpyrrodiazole with alkaline KMnO4. White crystalline powder, v. sl. sol. water, alcohol, and ether.

PYRROLE C. H. N i.e. CH: CH NH. Pyrrhol. Pyrroline. Mol. w. 67. (130° i.V.). S.G. 1975 ·9752. S.V. 92·1 (Ramsay). H.F.p. 4,056 (Ramsay). Occurs among the products of distillation of coal (Runge, P. 31, 67) and of bones (Anderson, Tr. E. 20 [2] 247; 21 [4] 571; A. 80, 63; 105, 349).

Formation .- 1. By distilling ammonium mucate alone or with glycerin at 190° (Schwanert, A. 116, 279; Goldschmidt, Z. [2] 3, 280).—2. By heating its carboxylic scid.—8. By distilling succinimide with zinc-dust (Chichester Bell, B. 18, 877).-4. By distilling ammonium saccharate (Bell a. Lapper, B. 10, 1962).—5. By heating di-chloro-maleic imide with PCl, at 200°, and reducing the resulting perchloride C,Cl,N with zinc-dust and HOAc (Ciamician a. Silber, B. 17, 554; 19, 3027). The dichloro-maleïc imide may be got from succinimide and PCl. -6. By reducing tetra-iodo-pyrrole with zinc-dust and ROHAq (C. s. S.).—7. By heating albumen with Ba(OH)₂ at 150° (Schützenberger, Bl. [2] 25, 289).—8. By distilling pyromucic acid with ammonia-zinc chloride and CaO (Canzoneria. Oliveri, G. 16, 487).—9. By passing di-ethylamine through a red-hot tube (Bell, B. 10, 1868). 10. By passing ethyl-allyl-amine over PbO at 450° (Koenigs, B. 12, 2344).—11. By distilling glutamic acid (Haitinger, M. 3, 228).

Preparation.-Bone oil is shaken with acids and distilled. The fraction 98°-150° is heated with KOHAq and distilled, and the portion 125°-140° heated with solid KOH with inverted condenser. The solid C, H, NK thus obtained is washed with ether and decomposed by water, and the pyrrole distilled with steam (Ciamician, B. 13, 70; 19, 173; G. 16, 336).

Properties .- Oil with fragrant odour, resembling chloroform. Tastes hot and pungent. V. sol. alcohol and ether, insol. dilute alkalis. Turns brown in air. Turns pine-wood soaked in HClAq red. Dissolves in cold dilute acids, but on warming the solution pyrrole-red is formed as a bulky amorphous pp. FeCl, added to its solution in HClAq gives a green colour changing to black. Alcoholic HgCl₂ gives a white pp. Isatin and HOAc or dilute H₂SO₄ give a deep-blue pp. which forms a deep-blue solution in HOAc and H.SO, (V. Meyer, B. 16, 2974; Ciamician, B. 17, 142).

Reactions.—1. HNO, forms oxalic acid.—
2. Potassium acts very strongly, forming a colourless liquid, which solidifies on cooling to C.H.NK. Boiling with solid KOH gives the same body (Anderson, A. 105, 352). Sodium acts but slightly, forming C.H.NNa only at a very high temperature. NaOHAq has no action on pyrrole.—3. HCl passed into an ethereal solution ppts. crystalline (C,H,N),HCl, whence ammonia liberates an unstable base (Dennstedt a. Zimmermann, B. 21, 1478).-4. Hydroxylamine forms NH₃ and crystalline C₄H₈N₄O₂ [175°]. Converted by adding Na to its boiling alcoholic solution into tetramethylene-diamine (Ciamician, G. 14, 156; B. 22, 1968). The compound C,H,N2O2, when heated with phenyl-hydrazine, yields $C_{16}H_{18}N_{1}$, which crystallises from alcohol in plates [125°].—5. By a dilute solution of sodium hypochlorite (15 pts. of active chlorine in 1,000 pts. of water to 10 pts. of pyrrol) it is converted into di-chloro-maleic acid and chlorinated pyrroles. On the other hand, a concentrated solution of sodium hypochlorite (45 pts. of active chlorine in 500 pts. of water to 10 pts. of pyrrole) yields dichloro-acetic acid. An alkaline solution of bromine yields dibromomaleimide. Iodine in presence of alkalis yields tetra-iodo-pyrrol (Ciamician a. Silber, B. 17, 1743; 18, 1763).—6. Potassium pyrrole heated with ethyl iodide yields r-ethyl-pyrrole, di-ethyl-pyrrole C.H.Et:NEt, and probably also C.H.Et:NH. Potassium pyrrole and benzyl-chloride yield

v-benzyl-pyrrole (247°) (Ciamician, B. 22, 659; G. 17, 135).—7. Pyrrole (50 g.), boiled with par-G. 17, 135).—7. Pyrrole (50 g.), boiled with paraldehyde (50 g.) and ZnCl₂ (12 g.), forms oily ethyl-pyrrole C₂H₂N (164°) (Dennstedt a. Zimmermann, B. 19, 2189).—8. Pyrrole (1 pt.), acctone (10 pts.) and a drop of HCl give C₁₄H₁₈N₂ [291°), whence alcoholic AgNO₃ forms (C₁₄H₁₈N₂).AgNO₃, crystallising in needles (Baeyer, B. 19, 2184). The compound C₁H₁₂N₂ yields, on distillation, C₁₆H₁₂N (275°-285°), which is probably mesityl-pyrrole, and whence Ao₂O and NoOAc form resettly pyrrole. The compound NaOAc form v-acetyl-pyrrole. The compound C14H18N2, examined by Raoult's method, appears to have the formula C₂.H₁₀N₁. On heating pyrrole with acetone and ZnCl₂ isopropyl-pyrrole (174°) is formed. Among the products of the (174°) is formed. Among the products of the action of acctone on pyrrole there is also a yellow oil C₁₃H₁,N (?) (300°-305°), which soon blackens in air. This oil forms an acetyl derivative [above 360°], and is reduced by tin and alcoholic HCl to C₁₃H₁₁N (274°), which yields B'HCl [228°] and B'HSnCl, [170°] (Dennstedt a. Zimmermann, B. 20, 850, 2449; 23, 1870).— 9. Di-ethyl ketone, MeOH, and HCl give C₁₈H₂₆N₂ [210°], which yields B'_AgNO₃, crystallising in needles (Dennstedt a. Zimmermann, B. 20, 2455).-10. Chloroform converts potassium pyrrole into (β)-chloro-pyridine. Bromoform acts in like manner, giving bromo-pyridine. CH₂Cl₂ has no action, but CCl₄ forms chloropyridine, while benzylidene chloride yields (β)-phenyl-pyridine (Ciamician, B. 14, 1160; 15, 1172; 20, 191; G. 16, 140). - 11. Readily combines with diazo- compounds, forming azo- and disazo-Fischer a. Hepp, B. 19, 2251).—12. Pyrrole (5 g.) added to a lukewarm solution of alloxan (11 g.) in water (300 c.c.) forms colourless crystals of C₈H,N₂O₄ or NH₂.CO.NH.CO.CO.CO.O.Q.H₂NH, sl. sol. hot alcohol, nearly insol. water and ether, and yielding Ag₂A". Pyrrole-alloxan is converted by caustic potash solution into C,H_aN₂O₂ or NH₂CO.CO.CO.C₄H₃NH, which crystallises in white plates, v. sol. warm alcohol, and yields AgA' and crystalline MeA' (Ciamician, B. 17, 106, 1711; 19, 1708; G. 16, 198, 857).—

13. Pyrrole and MeOH distilled over zinc-dust yield (α)- and (β)- methyl-pyrrole, di-methyl-pyrrole, and di-methyl-dipyrrole (Dennstedt, B. 24, 2559).-14. Acetyl chloride, acting on potassium-pyrrole, forms v-acetyl-pyrrole and pyrryl methyl ketone (pseudo-acetyl-pyrrole), which may be separated by steam-distillation. Ac.O at 800° forms pyrrylene di-methyl diketone (Ciamician a. Silber, G. 15, 193). -15. Propionic anhydride and sodium propionate form, on boiling, v-propionylpyrrole, pyrryl ethyl ketone, and pyrrylene di-othyl diketone (Dennstedt a. Zimmermann, B. 20, 1760).—16. Bz₂O and NaOBz at 220° form pyrryl phenyl ketone (pseudo-benzoyl-pyrrole).

17. COCl, in benzene, added to C,H,NK in 17. COCl₂ in benzene, added to C₄H₄Na in ether, forms CO(NC, H₂), separating from ligroin in monoclinic crystals [63°] (238°) (Ciamician a. Magnaghi, B. 18, 415).—18. Phthalic anhydride and HOAc at 185° form C₁₂H₄NO, [241°], converted by Br into C₁₂H₃Pc,NO, [199°], and by boiling KOHAq into C₁₂H₃NO, [174°-184°], which yields McA' [105°] (Ciamician, B. 17, 2957;

The compound | Anderlini, B. 21, 2869). C12H, NO is reduced by water and Na to $C_4H_4N:C< \frac{O}{C_4H_4}>CH.OH$ [118°] (Ciamician, B.

19, 2206; 21, 1554).

Salts.-C.H.NK. Solid, absorbing CO, at 200°, forming pyrrole (β)-carboxylic acid.— B'2HgCl₂: crystalline powder, insol. water, sl. B'EHEOL; crystainne powder, mach mach sa sel. cold alcohol.—B',8CdCl,—B'ICl: black pp (Dittmar, B. 18, 1612).—Picrate: [c. 71°]; unstable (Hooker, B. 21, 3299).

Acctyl derivative C.H.NAc. (182° i.V.). Formed by the action of AcCl on potassiumpyrrole suspended in ether, and also as a byproduct in the preparation of pyrryl methyl ketone by heating pyrrole with Ac.N and NaOAc (Ciamician, B. 16, 2348; 18, 881). Oil, volatile with steam, saponified by hot KOHAq. Reddens acidified pine-wood. Gives a pp. with aqueous $\mathbf{HgCl}_{2}.$

C.H.N.COEt. Propionyl derivative (193°) (Dennstedt a. Zimmermann, B. 20, 1760).

Dihydride C.H.N. Pyrroline. (90° i.V.). Formed by reducing pyrrole with zinc-dust and HOAc (Ciamician a. Dennstedt, B. 16, 1536; 22, 2512; G. 15, 481). Hygroscopic liquid, v. sol. water. Yields a nitrosamine C,H,N(NO) sol. water. Yields a nitrosamine C,H,N(NO) [38°]. Absorbs CO₂ from the air.—B'HCl. [174°]. Flat prisms, v. sol. hot alcohol.—B',H,PtCl_a: triclinic crystals.—B'HAuCl, [152°].—B'C₆H₃N₃O₇. [156°]. Yellow crystals (from water). Benzoyl derivative C,H₈NBz. (160° at 2 mm.). Syrup, formed from the hydrochloride and BzCl at 110°. V. sol. alcohol.

Tetrahydride C,H₃N. Pyrrolidine. (38.5°). S.G. 225° -8520. Formed by reducing the dihydride by HIAq at P at 250° (Ciamician a. Macnaghi, G. 15. 483; B. 18, 2079). Formed

a. Magnaghi, G. 15, 483; B. 18, 2079). Formed also, together with tetra-methylene-diamine, by the action of Na on ethylene cyanide or succinimide in alcohol, and by distilling tetramethylenediamine hydrochloride (Ladenburg, B. 19, 782; 20,442,2215; Petersen, B. 21, 290). Formed from chlorobutylamine hydrochloride and KOHAq (Gabriel, B. 24, 3234). Liquid, with pungent ammoniacal odour. Yields a liquid nitrosamine (214°), v. sol. water.—B',H_l'rtCl_g. [200°]. Prisms.— B'HAuCl, [200°].—B'C₆H,N₄O, [112°].—B'₄H₂Bi,I₉.—B'H₂CdI, [219°]. Needles. **Pyrrole red** Cl₁₂H₄N₄O, Formed by boiling

pyrrole or its carboxylic acid with dilute H2SO4 or HCl (Anderson, A. 105, 357; Schwanert, A. 116, 280). Reddish-brown flakes, insol. water, ether, acids, and alkalis, sl. sol. alcohol. Yields

pyrrole on distillation.

Homopyrrole v. METHYL-PYRROLE.

References .- BROMO-, CHLORO-, IODO, NITRO-, and Oxy-AMIDO- PYRROLE.

PYRROLE - AZO- v. Azo- compounds and DISAZO- COMPOUNDS.

PYRROL-CARBO-KETONIC ACID v. PYRRYL-

GLYOXYLIC ACID. PYRROLE (a)-CARBOXYLIC ACID C.H.NO.

i.e. C.H. (CO.H.) NH. Carbopyrrolic acid. [1919].

Formation.—1. By the action of boiling baryta on its amide, which is got by distilling ammonium mucate (Malaguti, A. 15, 179; Schwanert, A.116, 270; Ciamician, B.17, 1, 1, 1).— 2. By boiling pyrocoll with KOHAq (Weidel a. Ciamician, M. 1, 285).—3. By fusing potassium (a)-methyl-pyrrole with potash (Ciamician, B.

14, 1054; G. 11, 228).-4. By heating pyrrole with ammonium carbonate and water at 140° (Ciamician a. Silber, B. 17, 1150; G. 14, 162).-5. By heating pyrrole with alcoholic potash and CCl. (Ciamician a. Silber, B. 17, 1437).—6. By the action of CO₂ on potassium pyrrole at a high temperature (C. a S.).

Properties.-Prisms (from water), sol. water and alcohol. Decomposed by heat into CO, and pyrrole. HClAq forms, on warming, CO2, pyrrole

red, and NH₂Aq.
Salts.—NH₁A': m. sol. water.—CaA'₂: scales.—BaA'₂ (dried at 100°): 'plates, sol. water and alcohol.—PbA'₂: nacreous scales, v. sol. water.—AgA': small needles, sl. sol. water.

Methyl ether Med. [173°]. Prisms. Ethyl ether Eth. [39] (231°). Amide C.H. (CONH.)N. [173°]. Lamins. v. sol. alcohol and ether, m. sol. water.

Acetyl derivative C,H,N.CO.OAc. [75°]. Formed from the Ag salt and AcCl. Scales, readily decomposed by water into acetic acid and pyrrole carboxylic acid. At 75° it decom-

poses into HOAc and pyrocoll.

Pyrrole (β)-carboxylic acid C,H,(CO,H):NH. • [162°]. Formed by fusing potassium (β)-methylpyrrole with potash (Ciamician, B. 14, 1054). Needles, partially decomposed by boiling water into CO, and pyrrole. The lead salt is sl. sol. water.—BaA'2: needles. A pyrrole carboxylic acid [166°], got by potash-fusion from isopropylpyrrole, and yielding a methyl ether [129°] (Dennstedt a. Zimmermann, B. 20, 855), is probably identical with the (B)- acid.

Pyrrole v-carboxylic acid

Ethyl ether C,H,N.CO.Et. Tetrol-thane. (180°). Formed from potassiumurethane. (180°). pyrrole and ClCO_Et in ether (Ciamician a. Dennstedt, G. 12, 84). Oil.

Amide C.H.N.CONH2. [167°].

from the ether and NH₃.

Nitrile C₄H₄N.CN. Tetrol cyanuramide. [210]. Got by passing CyCl into potassium-pyrrole in ether (Ciamician a. Dennstedt, G. 13, 102). Needles, insol. water, sol. hot alcohol. Boiling alcoholic potash forms pyrrole, CO, and

Pyrrole dicarboxylic acid C.H.NO. i.e. C4H2(CO2H)2NH. Formed by oxidising pyrrylene dimethyl diketone, and fusing the product with potash (Ciamician a. Silber, G. 16, 377; B. 19, 1958; 20, 2601). Needles (from dilute alcohol), sol. ether and hot water. Blackens at 260°, giving pyrrole and CO₂. FeCl₃ gives a brown pp. The Ba salt crystallises in needles. The Ag salt is a curdy pp.

Mono-methyl ether MeHA". [243°].

Di-methyl ether Me₂A". [132°]. Di-ethyl ether Et₂A". [82°].

References .- Bromo-, Chloro, and Nitro-PYRROLE CARBOXYLIC ACIDS.

PYRROLINE. A name used both for Pyrrole and Pyrrole DIHYDRIDE.

PYRROLYLENE v. BUTINENE.

PYRROLYLENE TETRABROMIDE v. Tetra-BROMO-BUTANE

PYRRONE v. DI-PYRRYL-KETONE.

PYRROYL-FORMIC ACID v. PYRBYL-GLY-

PYRROYL - PYRROL C4H4N.CO.C1H3NH [63°]. Formed, together with di-pyrryl-ketone

CO(C.H.NH), by intramolecular transformation of carbonyl-pyrrole by heating it to 250° for a few hours (Ciamician a. Magnaghi B. 18, 1829). White silky plates. Not volatile with steam. By heating with aqueous KOH it is split up into pyrrole and pyrrole-(a)-carboxylic acid.
PYRROYL-PYRUVIC ACID. Ethyl ether

C.H.,NH.CO.CH.,CO.CO.Et. [128°]. Formed by the action of NaOEt and oxalic ether on pyrryl methyl ketone (Angeli, B. 23, 1794, 2155). Yellowish plates, v. sol. alcohol, sl. sol. water. Decomposed by alkalis, even in the cold, into oxalic acid and pyrryl methyl ketone. Hydroxylamine forms $C_{10}H_{10}N_2O_3$ [124°], which on saponification yields the acid CH CH.N.N:C.CO.CH. [179°], crystallising in white needles. Aniline (2 pts.) caystantising in whice needles. Annihe (2 pts.) in HOAc forms $C_4H_3NH.CO.CH_2.C(NPh).CO.Et$ [115°]. Phenyl-hydrazine forms $C_1_6H_{15}N_3O_2$ [168°] which is the ether of an acid [215°].

Anhydride CH CH.C.CO.CH₂ [250°]: Formed by adding HCl to the mother-liquor from which the ether has separated (Angeli, B. 23, •1795). Yellow needles (from benzene), v. sol. alcohol. o-Phenylene-diamine forms C.H.N.O. a reddish-yellow crystalline powder forming a bluish-green solution in H₂SO₄ and yielding a benzoyl derivative [c. 166°]. Aniline forms C4H4N CO.CNPh [218°], whence cold KOHAq forms an acid C₁₄H₁₂N₂O₃ [179°].

PYRRYLENE DIETHYL DIKETONE C.H.NH(COEt)2. [117°]. Formed by heating pyrrole with propionic anhydride at 260° (Dennstedt a. Zimmermann, B. 20, 1761). Plates.

PYRRYLENE DI-METHYL DIKETONE

C,H,NO, i.e. NH CAc:CH. [162°]. by heating pyrrole, pyrryl methyl ketone, or acetyl-pyrrole with Ac2O at 250° (Ciamician, B. 17, 432, 2953; 18, 881, 1466; 19, 1957; 20, 2595). Needles, sol. hot water and hot KOHAq. May be sublimed. Yields a nitro-derivative [149°] and a di-bromo-derivative [172°].- AgA'.

PYRRYLENE DISTYRYL DIKETONE (C₆H₃.CH:CH.CO)₂C₄H₂NH. [240°]. Formed by heating pyrrylene dimethyl diketone with benzoic aldehyde and KOHAq (Ciamician a. Denn-Stedt, B. 17, 2953). Crystals (from HOAc), sl. sol. alcohol. Forms a violet solution in H₂SO₄.

PYRRYL ETHYL KETONE C, H, NO i.e. C2H3.CO.C4H3NH. [52°]. (224°). Formed by boiling pyrrole with propionic anhydride and sodium propionate (Dennstedt a. Zimmermann, B. 20, 1761). Colourless needles.—AgA': pp.

PYRRYL-GLYOXYLIC ACID C.H., NO, aq i.e. C,H,NH.CO.CO,H aq or C,H,NH.C(OH),CO,H. Formed by oxidation of pyrryl methyl ketone by KMnO, (Ciamician a. Dennstedt, B. 16, 2350; 17, 2949). Crystallises from benzene in yellow needles (of C,H,NO4) melting at 76°, v. sol. hot water. After drying over sulphuric acid the acid (C,H,NO) decomposes at 114°. The aqueous solution gives a red colour with FeCl. On heating with HClAq it gives a crimson colour turned yellowish-green by alkalis .-- AgA': colourless needles, sol. hot water.

Methyl ether MeA'. [72°]. (285°). Monoclinic crystals, sl. sol. water.

Carboxy-pyrryl-glyoxylic acid CO₂H.C, H₂NH.CO.CO₂H. Formed by oxidation of pyrrylene dimethyl diketone (Ciamician a. Silber, B. 19, 1412, 1961). Crystalline, v. sol. Methyl ether Me₂A". [145°].

DI-PYRRYL KETONE CO(C₁H₃NH)₂. [160°].

Formed, together with (C,H,N)₂CO, by the action of COCl₂ on C,H,NK. Formed also, together with pyrroyl-pyrrole, by heating (C,H,N)₂CO at 250° for a few hours (Ciamician a. Magnaghi, B. 18, 414, 1829). Trimetric crystals; a:b:c=2.531:1:2.901. V.sol.alcohol, ether, and benzene, nearly insol. water. Ag,A": yellow pp.

PYRRYL METHYL KETONE C,H,NO i.e.

CH₃.CO.C₄H₃NH or NH < CAc:CH CH:CH acetyl-pyrrole. [90°]. (220° uncor.). V.D. 3.8 (calc. 3.8). Formed by boiling pyrrole with Ac.O and NaOAc (R. Schiff, B. 10, 1501; Ciamician a. Dennstedt, B. 16, 2348; 17, 432, 2944; 18, 1456; 20, 2605; G. 15, 175). Formed also by heating pyrrole with Ac₂O and ZnCl₂ (Dennstedt a. Zimmermann, B. 19, 2204), and by heating CH₃.CO.C₄H₃N.CO₂K with K₂CO₃ at 290° (Ciamician a. Silber, B. 19, 1963). Long monoclinic needles, sol. hot water, v. sol. aqueous alkalis, sparingly volatile with steam. Not converted into pyrrole and KOAc by potash.

Reactions.—1. Yields pyrryl-glyoxylic acid when oxidised by KMnO,—2. Benzoic aldehyde and dilute KOH form pyrryl styryl ketone. - 3. Water and sodium-amalgam reduce it to crystalline pyrryl methyl pinacone $C_{12}H_{16}N_2O_2[120^\circ]$ and pyrryl-methyl-carbinol CH_3 , CH(OH), C_4H_3NH Pyrryl-methyl-pinacone an oil (290°-300°). C,H,N.CMe(OH).CMe(OH).C,H,N crystallises in prisms (containing 2aq) melting at 98° when hydrated .- 4. Oxalic ether and NaOEt form pyrroyl-pyruvic ether (Angel, B. 23, 1357, 1794). 5. Cold furning H.SO, yields an unstable sulphonic acid, which forms a crystalline K salt.

Salt.—C₁H₃AcNAg. Crystalline pp.

OximCH₃.C(NOH).C₁H₃NH. [146°]. Needles. Phenyl-hydrazide

CII, C(N.HPh). Q.H, NH. [147°]. White powder. References.—Amido., Bromo., Bromo.nitro., and NITRO- PYRRYL METHYL KETONE.

PYRRYL METHYL KETONE CARBOXYLIC ACID C,H,NO, i.e. CH, CO.C,H,N.CO,H. [186°]. Formed by saponification of its methyl ether, obtained by heating methyl pyrrole (a)-carboxylate with Ac.O at 260° (Ciamician a. Silber, G. 14, 169; B. 17, 1155). Leaflets, sol. water, alcohol, and ether. FeCl, gives a brown pp .-CaA'₂7aq: triclinic prisms.—*PbA'₂: needles.—AgA': powder, sl. sol. water.

AgA': powder, st. sol. water.

Methyl ether MeA'. [113°]. Gives with
ammoniacal AgNO, a pp. C.H.,AgNO.

PYRRYL PHENYL KETONE C.,H.,NO i.s.

C.H.,CO.C.H.,NH. [78°]. Formed by heating pyrrole with benzoic anhydride and dry NaOBz at 200°-240° (Ciamician a. Dennstedt, B. 17,

at 200°–220° (Ciamician a. Dennstedt, B. 17, 432, 2955). Needles, v. sol. alcohol, sl. sol. hot water.—C₁₁H₂AgNO.

FYRRYL STYRYL KETONE C₁₂H₁₁NO i.e.
C₃H₂,CH:CH.CO.C,H₂NH. [142°]. Formed by obling pyrryl methyl ketone with C₂H₃CHO and KOHAq (Ciamician a. Dennstedt, B. 17, 2947). Yellow needles, sl. sol. alcohol, insol. water .-C₁₈H₁₀ONAg: yellow needles, insol. NH₂Aq.

PYRUVIC ACID C.H.O. i.s. CH., CO.CO.H. Pyroracemic acid. Di-oxy-propionic acid. Mol. w. 88. [9°]. (c. 165°). S.G. 18 1-2752; 28 1-2700. M.M. 3-557 (Perkin, C. J. 61, 836).

Formation.—1. By distilling racemic or tartaric acid (Berzelius, A. 13, 61; Völckel, A. 89, 65; Wislicenus, A. 126, 225).—2. By gradually heating tartaric acid with HClAq in sealed tubes to 180° (Geuther a. Riemann, Z. [2] 5, 318).—3. By heating tartaric acid with conc. H₂SO₄ at 40°–50° (Bouchardat, C. R. 89, 99).—4. By heating silver di-a-chloro-propionate with water (Beckurts a. Otto, B. 10, 265; 18, 227).—5. By distilling glyceric acid (Moldenhauer, A. 131, 338; Böttinger, A. 196, 92).—6. By boiling acetyl cyanide with dilute HCl (Claisen a. Shadwell, B. 11, 1563).—7. By oxidation of a cold aqueous solution of calcium lactate by KMnO₄ (Beilstein a. Wiegand, B. 17, 840).

Preparation.—1. Tartaric acid (3 lbs.) is distilled from a glass retort (30 lbs. capacity). The distillation takes three hours. A fresh quantity of tartaric acid is then added and the operation repeated. The distillate is fractionally distilled (Clewing, J. pr. [2] 17, 243).—2. Dried, and finely powdered, tartaric acid is mixed with an equal weight of sand and distilled (Seissl, A. 249, 297).

8. Tartaric acid is distilled with KHSO₄, the yield being 50 to 60 p.c. (Erlenmeyer, B. 14,

321).

Properties.—Liquid, smelling like acetic acid, v. e. sol. water, alcohol, and ether. Colourless crystals below 9° (Simon, Bl. [3] 9, 111). Partially decomposed on distillation. Reduces ammoniacal AgNO₂, forming a mirror, and yielding CO₂ and acetic acid. Coloured cherry-red by alkaline sodium-nitroprusside, the colour being discharged by HOAc (Von Bitto, A. 267, 377). Readily ppd. by phenyl-hydrazine. Forms an

Reactions.—1. Dilute H.SO, at 150° splits it up into aldehyde and CO₂ (B. a. W.).—2. By long heating at 170° it is converted into CO₂ and acetic, pyrotartaric, uvic, and citraconic acids (Böttinger, B. 9, 670, 837, 1823).—3. HClAq at 100° forms CO, and pyrotartaric acids (De Clermont, B. 6, 72).—4. Boiling with Ag₂O yields CO₂ and acetic acid.—5. Reduced to lactic acid by sodium-amalgam, and by Zn and H.SO,.— 6. HI reduces it to propionic acid.—7. Zinc when added to its alcoholic solution forms CO2H.CMc(OH).CMc(OH).CO2H (Böttinger, B. 9, 1064) .- 8. PCl, forms di-a-chloro-propionic acid (Klimenko, B. 3, 465; Beckurts a. Otto, B. 11, 386) .- 9. Dry bromine at 0° forms crystalline di-bromo-lactic acid (?). Br and water give di-bromo-pyruvic acid (Wislicenus, A. 148, 208; Wichelhaus, A. 152, 265).—10. Oxidised by chromic acid mixture to CO₂ and acetic acid.—11. HNO forms oxalic acid and CO₂.—12. Boiling baryta-water forms uvitic, uvic, pyrotartaric, oxalic, and acetic acids and CO, (Fincht, A. 122, 182; Böttinger, B. 8, 957; A. 172, 241, 253; 188, 313; 208, 129). Baryta-water added to a cold solution of pyruvic acid ppts. barium hydruvate BaC.H.O., or the basic salt Ba.H.(C.H.O.). Hydruvic acid is a syrup.— 18. On heating with excess of quickline it yields a little aldehyde (Hanriot, C. R. 101, 1156; Bl. [2] 45, 81).—14. HCN followed by HCl forms lactic soid. KCN followed by HCl yields

ACID. On warming pyruvic acid with HON under pressure the product is CMe(NH,)(CO,H), crystallising in unstable prisms (Körner a. Menozzi, G. 17, 104).—15. Alcoholic ammonia forms methyl - pyridine dicarboxylic acid.-16. Aniline added to an ethereal solution forms C₉H₉NO₂, i.e. CH₃.C(NPh).CO₂H [122°] (Böttinger, B. 10, 818). Aniline alone forms, on heating, C.,H.,N.20, crystallising from dilute alcohol in needles [195°], while p-toluidine gives C., H.,N.20 [238°] (Lazarus, B. 17, 998). Antline and furfuraldehyde form C.,H.,C.H. C.C.,H.)C, crystallising in greenish-yellow needles [210°-215°] (Doebner, A. 242, 285). Tetra-amido-anisole forms the quinoxaline C₈H(OMe)(N₂C₃H₄O)₂ as orange-vellow flakes, v. sol. alkalis (Nietzki a. Kurtenacker, B. 25, 284).—17. H,S passed into water containing the Agsalt forms thiolactic acid (Böttinger, B. 9, 404; Loven, J. pr. [2] 29, 376).—18. PH₂ and HCl passed into an ethereal solution form 'phosphortrianhydropyruvic' acid C.H.PO., crystallising in needles, insol. alcohol and ether, and forming with phenyl-hydrazine the compounds forming with pnenyl-nydrazine the compounds $C_bH_1PO_3PhN_1H_1$ [132°] and $C_bH_bN_1O_4$ (7) [162°]. The acid $C_bH_bPO_g$ is converted by aniline into $C_aH_aN_1PO_4$ [158°], whence phenyl-hydrazine forms $C_aH_aN_2O_4$ [169°]. Tolylene-diamine converts $C_bH_aPO_g$ into $C_bH_aPO_g$ (7), [178°] (Messinger a. Engels, B. 21, 334, 2919).—19. Pyruvio acid (50 g.) heated with dry sodium succinate (92 g.) and Ac.O (58g.) at 110° forms di-methyl-maleïc anhydride (pyrocinchonic anhydride) (Fittig a. Parker, A. 267, 204). Pyruvic acid (30g.) heated with dry sodium succinate (55 g.) at 110° forms uvic (pyrotritaric) acid.—20. Pyruvic acid (30g.) heated with sodium pyrotartrate (60 g.) and AcO (36g.) at 140° forms methyl-ethyl-maleic anhydride (F. a. P.) .- 21. Benzonitrile and cold anhydride [F. a. F.].—21. Benzontrite and courty-SO₄ form an acid C_{1,1}H_{1,6}N₂O₄ crystallising in tables [172°], insol. water, v. sol. acetone (Böttinger, B. 14, 1599).—22. Phenyl-acetonitrile and H₂SO₄ form, in like manner, C₁₀H₂₀N₂O₄ [145°] (B.).—23. By heating with aldehydes R.CHO and baryta-water it is considered in the solution of the form verted into s-alkyl-isophthalic acids of the form C₂H₂R(CO₂H)₂(Doebner, B. 23, 2378).—24. Benzoic aldehyde and aniline in ether form, in the cold, C22H18N2O or CHPh:CH.C(NPh).CONHPh [225°], insol. water, acids, and alkalis, sl. sol alcohol and ether. Cuminic aldehyde and aniline give C_uH_{z1}N₂O [216°] (Doebner a. Giesoke, A. 242, 290; 249, 102). Benzoic aldehyde and p-toluidine form, in like manner, C2.H2N2O [205°].-25. Isobutyric aldehyde and aniline in alcoholic solution react forming CHPr.CH.C(NPh).CONHPh (?) [222°] crystallising from HOAc in needles, while isovaleric aldehyde and aniline in ether give C20H21N2O [160] (Doebner, A. 242, 275). Isovaleric aldehyde in warm alcoholic solution forms the acid C.H.NO. —26. Thioglycollic acid gives rise to CO.H.CMe(OH).S.CH.CO.H [110°] with evolution of heat; while HCl passed through a mixture of pyruvic and thioglycollic acids produces CO₂H.CMe(S.CH₂CO₂H)₂ [162°] crystallising from ether (Bongartz, B. 19, 1933; 21, 484).—27. Phenyl mercaptan forms the compound CH₂C(SPh)(OH).CO₂H, while p-bromo-phenyl mercaptan forms CH₂C(SO₂H₄Br)(OH).CO₂H

CH, C(OH)(CN).CO,H v. GYANO-OXY-PROPIONIC

[114.5°] (Baumann, B. 18, 263).-28. Ethylene mercaptan forms a substance [96°] which crystallises from benzene as a fine powder, and may be

condensed to CH₂.S CMe.CO₂H [102°], which

on oxidation gives ethylene ethylidene disulphone [198°] (Fasbender, B. 21, 1473).—29. Benzene and H.SO, form CH, CPh, CO, H, while phenol and H.SO, yield C₁₈H₁₁O₄ (Böttinger, B. 14, 1595; 16, 2071).—30. Distillation of the K salt with KOAc forms acetone and pyrotartaric acid (Wichelhaus, Z.[2] 5, 254).—31. Pyruvic acid (1 pt.) heated with urca (2 pts.) at 100° forms pyvuril or 'pyruvic diureide 'C₃H₈N₄O₃, which crystallises in tables, S. 10 at 100°, insol. alcohol and ether in tables, S. 10 at 100°, insol. atcord and eater (Grimaux, C. R. 79, 526, 1304, 1478; 80, 53; A. Ch. [5] 11, 373). Pyvuril is decomposed by long heating at 160°, forming amorphous 'tetrapyruvic tetraureido' C₁₈H₁₈N₈O₈, insol. water. Boiling dilute HClAq converts pyvuril into urea and 'dipyruvic triureido' C₂H₁₂N₈O₃, which crystallises from hot water in needles, S. 4 at \$\frac{1}{2}\text{Coll}_{2}\text{Lownward}\$ by beiling allelis into urea 100°, decomposed by boiling alkalis into urea, pyruvic acid, and pyvuril. Boiling conc. HClAq converts pyvuril into urea and 'pyruvic ureido

 $C_{_4}\mathrm{H}_{_4}\mathrm{N}_{_2}O_{_2}$ or $CO{<}^\mathrm{N}_\mathrm{NH,CO}^\mathrm{M=CMe}$,

powder, m. sol. hot water, insol. alcohol. Nitric acid converts pyvuril into nitro-pyruvic ureide C,H3(NO2)N2O2 [above 200°], which is decomposed by boiling bromine-water into parabanic acid and CBr. NO2. Pyruvic acid heated with an equal weight of urea at 100° forms amorphous insoluble 'tripyruvic tetraureide' C13H16N8O, and dipyruvic triureide .- 32. Sodium hippurate and Acoo at 100° form the dibasic acid C12H2NO4 [157°] (A. Hoffmann, B. 19, 2555).-33. solution of indoxyl forms on adding conc. HCl

the indogenide $C_9H_4 < \stackrel{CO}{\sim} > C:CMe.CO_2H$ [197°],

crystallising in red needles forming a blue solution in H.SO, (Baeyer, B. 16, 2199).-34. Glycerin and KHSO, form 'glycuvic acid,' or 'pyruvin,' which is also got by heating glycerin with glyceric acid at 120°, and by distilling glycerin with citric acid. Glycuvic acid is probably

 CH_3 .CO.CO.O.CH₂.CH< $\stackrel{C}{O}$. It is crystalline [82°] (241°), and yields pyruvic acid when boiled with baryta (Böttinger, B. 10, 286; 14, 316; A. 263, 246; Jowanovitch, M. 6, 467; Erhardt, M. 6, 511; Schlagdenhauffen, C. R. 74, 672; De

Clermont, C. R. 105, 520).

Salts.-The salts crystallise well, provided heat is avoided in their preparation; otherwise they become amorphous. The acid also is changed by evaporation of its aqueous solution into a non-volatile syrupy mass.—NaA': large prisms.—BaA', aq: scales.—BaA', 2aq: amorphous.-PbA'2 aq: crystalline pp.-ZnA'2 3aq: white microcrystalline powder, sl. sol. water (Beckurts a. Otto, B. 18, 227).—CuA'₂ aq.—AgA': scales, sl. sol. water.

Combinations with bisulphites (Clewing, J. pr. [2] 17, 241).—HA'NaHSO, aq: orystals. NaA'NaHSO, aq. — NaA'NaHSO, 1 2 aq. HA'KHSO₂; aq. — MAN MARSO₃ 1₃84. — HA'KHSO₃ cotahedra. — KA'KHSO₃ aq. — CaA'₂0a(HSO₃)₂ 3aq. — (CaA'₂)₄(Ca(HSO₃)₂)₂ 24aq. — (CaA'₂)₄(Ca(HSO₃)₂)₂ 3aq. — SrA'₂Sr(HSO₃)₂ 5aq. — BaA'₂Ba(HSO₃)₂.

Vol. IV.

Methyl ether MeA'. (c. 136°). S.G. 9 1.154. Got from AgA' and MeI.

Ethyl ether EtA'. Oil. Converted by aniline into two crystalline bodies [144°] and [c. 250°]. The compound O(CMe(OH).CO,Et)2, formed by the action of nitrous acid on amidopropionic ether, is an oil (80°-86° at 120 mm.) (Curtius, J. pr. [2] 38, 472).

Isoamyl ether C,H,A'. Got by distilling the acid with isoamyl alcohol (Simon, Bl. [3] 9,

Amide CH₃.CO.CO.NH₂. [125°]. Got from acetyl cyanide and HCl (Claisen a. Shadwell, B. 11, 1566). Prisms or tables (from alcohol).

Nitrile v. ACETYL CYANIDE.

Phenyl hydrazide CH3.C(N2HPh).CO2H. [192°] (F.); [185°] (Japp a. Klingemann, B. 20, 3284; A. 247, 208; C. J. 53, 519). Ppd. when a solution of phenyl-hydrazine hydrochloride is added to a dilute seven 1 in 1000) solution of pyruvic acid (Fischer, B. 16, 2241; 17, 578). Prisms, sol. hot water and hot alcohol. Reduced by sodium-amalgam to phenyl-hydrazido-propionic acid [172°]. At 190° it gives off CO, and H., and forms the phenyl-hydrazide of di-methyl diketone [242°] and the oily phenyl-hydrazide of aldehyde. The ether CH3.C(N2HPh).CO.Et[117°], crystallises in yellow needles (from ligroin).

o-Chloro-phenyl-hydrazide C₆H₄Cl.NH.N:CMc.CO₂H. [178°]. Lemon-yellow needles, forming a crystalline ethyl ether [168°] (Hewett, C. J. 59, 211).

p-Nitro-phenyl-hydrazide C,H,(NO2).NH.N:CMe.CO2H. Yel Yellow (Fischer a. Ach, A. 253, 64). V. sol. hot alcohol.

p-Sulpho-phenyl-hydrazide SO₃H.C_cH₁.NH.N:CMe.CO₂H. Solid, insol. ether, v. sol. water and alcohol (Pfülf, A. 239, 217). -NaA' aq: nodules.

Phenyl-methyl-hydrazide C₁₀H₁₂N₂O₂ NPhMe.N:CMe.CO₂H. [78°]. Yellowish NPhMe.N:CMe.CO₂H. [78°]. needles (Fischer, B. 16, 2245; 17, 559). Converted by heating with HClAq into methyl-indole carboxylic acid and NH3. The phenyl-ethylhydrazide is converted in like manner into ethyl-indole carboxylic acid.

Di-phenyl-hydrazide
NPh₂.N.CMe.CO₂H. [145°]. White needles
(Fischer a. Hess, B. 17, 567). Sol. hot benzene and CHCl, forming deep-yellow solutions. Converted into phenyl-indole carboxylic acid by heating with HClAq.

o-Tolyl-hydraside C_sH₁MeN₂H:CMe.CO₂H. [156°] (J.); [159°] (R.) Formed by saponifying the product of the action of o-diazotoluene chloride on sodium methylacctoacetic ether (Japp, A. 217, 213), and from o-tolyl-hydrazine hydrochloride and pyruvic acid (Raschen, A. 239, 228). Small yellow plates (from benzene). Yields o-tolyl-hydrazido-propionio acid [148°] on reduction. At about 160° it forms the di-o-tolyl-di-hydrazine of dimethyl-di-ketone, a yellow crystalline powder

o-Tolyl-hydrazide C,H,N,H:CMe.CO,H. [162°]. Formed in the same way as the o-isomeride. Yellow plates (from benzene). At 165° it is converted into the di-p-tolyl-hydrazide of di-methyl-di-ketone [230°]. Gives an ethyl ether $C_{12}H_{16}N_2O_2$ [106°], crystallising from ligroin in yellowish plates.

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Methyl-p-tolyl-hydraside C,H, N,O, [83°]. Yellow prisms (Hegel, A. 232, 215). Ethyl-p-tolyl-hydraside C12H16N2O2.

Needles, v. sol. alcohol and ether (H.).

Ψ-Cumyl-hydrazide C_sH₂Me₃NH.N:CMe.CO₂H. r148°7. Vellow needles (Ruhemann, C. J. 57, 55).

p-Benzoylphenyl-hydrazide C.H.Bz.N.H:CMe.CO.H. [200°]. Lemon-coloured crystals (Ruhemann a. Blackman, C. J. 55, 616).

(a)-Naphthyl-hydrazide C₁₀H.,N₂H:CMe.CO₂H. [159°] (Fischer, A. 232, 236). Yields EtA [100°] (Schlieper, A. 239, 229).

(β) - Naphthyl-hydrazide [166°]. Yields
 EtA' [181°] (Schlieper, A. 236, 176).
 (B. 4)-Quinolyl-hydrazide

C.H.,N.NH.N:CMe.CO.H. [174°]. Formed from pyruvic acid and (B. 4)-hydrazido-quinoline acetate (Dufton, C. J. 59, 758). Light-yellow pp., insol. water, sol. acids and alkalis.

Oxim CH3.C(NOH).CO2H. a-Nitroso-propionic acid. Formed by the action of cold KOHAq on its ether, which is got by adding a dilute solution of KNO2 (10 pts.) to methylacetoacetic ether dissolved in water (3 pts.), KOH (2 pts.), and some alcohol, the yield being 16 p.c. of the methyl-acetoacetic ether used (V. Meyer a. Züblin, B. 11, 692; Gutknecht, B. 13, 1116). Got also from pyruvic acid and hydroxylamine (V. Meyer a. Janny, B. 15, 1527 : Schäfer, A. 264, 153; Hantzsch, B. 24, 50). Crystalline powder, sl. sol. ether, v. sol. water and alcohol. Decomposes suddenly at about 177°. Oxidised by potassium permanganate to ethyl-nitrolic acid CH₃.CH(NO)(NO₂). Yields acetonitrile on heating with hydroxylamine hydrochloride. Reduced by tin and HClAq to alanine. Salts .-KA' aq: pearly plates, sol. water.—BaA'2: soluble prisms.—Cu₂OA'₂ aq.—AgA': white insoluble powder. Ethyl ether EtA'. [94°]. (233° cor.). Formed as above, and also by the action of HNO2 on methyl-malonic ether and on propionyl-propionic ether (Bergreen, B. 20, 533). Needles or prisms, with weak acid properties.

References .- Bromo-, Chloro-, and Oxy-

PURTIFIC ACID.

PYRUVIC ALDEHYDE CH3.CO.CHO. Methyl-glyoxal. Got by the action of dilute acids upon CH₄.C(OH)(SO₃Na).CH(SO₃Na).NHSO₃Na, which is got from nitroso-acetone and NaHSO. (Pechmann, B. 20, 2543).

Mono-oxim v. NITROSO-ACETANE.

Di-oxim CH₂C(NOH).CH:NOH. Methylglyoxim. [153°]. Formed by the action of hydroxylamine on CH₂CO.CH.NOH or upon CH₂CO.CHCl₂ (V. Meyer a. Janny, B. 15, 1165; Treadwell, B. 15, 2787). Small prisms (from alcohol) or needles (by sublimation). Salt.— AgC₅H₂N₂O₂ pp.—Diacetyl derivative

[519]. C₂H₄(NOAc)₂. [51°]. (Schramm, B. 16, 2187). Prisms (from ligroin)

Phenyl-hydraside of the oxim CH,.C(N,HPh).CH:NOH. [184°]. Formed from nitroso-acetone and phenyl-hydrazine (Pechmann a. Wehsarg, B. 21, 2994; A. 262, 278). Prisms or needles (from alcohol). H.SO, forms a reddish-yellow solution, coloured deep blue by FeCl₃. Ac₂O yields CH₃.C(N₂HPh).ĈH:NOAc [163°], crystallising in colourless needles.

Phenyl-methyl-hydrazide of the oxim CH₃.C(N₂PhMe).CH:NOH. [118°]. Orange

yellow prisms (from alcohol).

Phenyl-hydrasids CH, CO.CH:N2HPh.

[150°]. Formed from sodium acetoacetic ether and diazobenzene chloride (Japp, A. 247, 198, 218; C. J. 53, 519). Plates (from benzene or MeOH). Yields CH₂-CO.CH:N₂AoPh [93°], orystallising from ligroin in needles. NaOEt and chloro-acetic ether yield, on saponification of the product, CH₃.CO.CH:N.NPh.CO.H [162°], which crystallises from hot water in needles, and is reduced by tin and HClAq to phenyl-amido-acetic acid [127°].

Di-phenyl-di-hydrazide CH₃.C(N₂HPh).CH:N₂HPh. [145°]. Formed by heating the phenyl-hydrazide of acetyl-carbinol with phenyl-hydrazine hydrochloride and NaOAc in alcohol at 100° (Laubmann, A. 243, 248). Formed also by warming pyruvic aldehyde or its mono-oxim, phenyl-hydrazide, or phenyl-hydrazide of the oxim with phenyl-hydrazine acetate (Pechmann, B. 20, 2543; 21, 2755; Japp, A. 247, 207). Yellow plates or needles (from dilute alcohol), sl. sol. alcohol. Conc. H, SO, forms an olive-green solution, changing through slaty-blue to violet. Yields a crystalline hydrochloride [197°]. Oxidised by K,Cr,O, and HOAC to CH N.NPh crystallising in needles [107°]. ČMe:N.NPh

whence boiling HClAq produces CH:N>NPh a colourless oil (150° at 60 mm.), oxidised by alkaline KMnO, to the acid C₀H₂N₃O₂ [192°].

Acetyl derivative of the di-phenyl-di-hydraside CH3.C(N2HPh).CH:N.NPhAc. [229°]. Formed from the acetyl derivative of the phenyl-hydrazide and phenyl-hydrazine (Japp, C. J. 53, 519). Yellowish needles.

Phenyl-methyl-hydrazide

CH. CO.CH:N.NPhMe. [64°]. Formed from the phenyl-hydrazide, NaOMe, MeOH, and MeI (Japp). Flat needles (from MeOH), v. e. sol. alcohol. Converted by phenyl-hydrazine into CH, C(N, HPh). CH: N. NPhMe [152°], crystallising in pale-yellow needles.

Phenyl-ethyl-hydrazide CH₃.CO.CH:N.NPhEt. [55°]. Prepared in like manner. Prisms (from ligroïn).

PYRUVYL ALCOHOL v. ACETYL CARBINOL.

QUARTENYLIC ACID v. ISOGROTONIC ACID. CHCl₃. Occurs in quassia-wood (Winckler, Rep. QUASSIN $C_{2:}H_{4:}O_{10}$ or $C_{2:}$

(10 pts.) with boiling water (45 pts.), evaporating (to 10 pts.) at a gentle heat, ppg. by tannin, mixing the pp. with lead carbonate, and extracting with boiling alcohol. The product is recrystallised from water and alcohol (yield 01 pt.) (Oliveri a. Denaro, G. 15, 6).

Properties.-Slender monoclinic needles, v. sol, alcohol and chloroform, sl. sol, ether. Sol, conc. HClAq and KOHAq, insol. Na₂CO₃Aq., Reduces Fehling's solution (Oliveri), or, according to Allen (An. 12, 107), has no reducing power. Not coloured by FeCl₂. Ppd. by tannin. Quassin appears to be the dimethyl ether of quassic acid, and probably contains two hydroxyls, two CO, Me, and two CO groups, and is perhaps a derivative of anthraquinone (Oliveri). Phenyl-hydrazine forms $C_{32}H_{40}O_8(N_2HPh)_2$ (?), a yellow amorphous powder, decomposing at about 230° without fusion (Oliveri, G. 18, 169).

Reactions.-1. Boiling dilute (4 p.c.) H2SO forms 'quasside' C₂₂H₂₂O₃, a white amorphous very bitter substance [194°], which reduces Fehling's solution, and is reconverted by boiling dilute alcohol into quassin. - 2. Ac O and NaOAc form, on boiling, the amorphous anhydride $C_{22}H_{40}O_8$ [150°-158°], sol. alcohol and ether.—3. Bromine forms $C_{22}H_{41}Br_3O_9$, a very bitter yellow powder [155°].—4. Fuming HClAq in a scaled tube at 100° forms MeCl and quassic acid.—5. PCl, gives C₃₂H₃₉Cl₃O₈, a yellow powder [120°] decomposed on fusion.—6. HIAq and P at 150°— 280° form durene (188°-195°) C₁₁H₁₆ (220°-240°) and anthracene (Oliveri, G. 17, 575).

Quassic acid $C_{30}H_{38}O_{10}$ or $C_{30}H_{40}O_{10}$. [245°]. S. 0043 at 23°. Formed, together with McCl (2 mols.), by heating quassin with HClAq. Monoclinic prisms (containing aq), sol. hot alcohol, sl. sol ether. Alkalis give a reddish-yellow colour. FeCl, gives a greenish-yellow colour. Reduces Fehling's solution and ammoniacal AgNO₂. Hydroxylamine forms C₁₀H₁₆(NOH)₂O₂ (?), crystallising in rectangular prisms [230°].—BaA"7aq: reddish-yellow crystals.—PbA"6aq: white amorphous pp.—Fe,A"₃: brownish-green pp.

QUEBRACHAMINE. [142°]. Occurs in white

quebracho bark (Hesse, A. 211, 269). Plates, v. sol. alcohol, benzene, CHCl, and ether. alcoholic solution is alkaline and tastes bitter. H₂SO₄ and K₂Cr₂O, give a dark-violet colour.

QUEBRACHINE $C_{21}H_{26}N_2O_3$. [216°]. [a]_D = 62·5 in a 2 p.c. alcoholic solution at 15°; = 18.6 in chloroform. Occurs in white quebracho bark (Hesse, B. 13, 2308; A. 211, 254). Colour-less needles, sol. alcohol, ether, benzene, and CHCl, v. sl. sol. cold water, NaOHAq, and Dextrorotatory. Its solutions are al-NH,Aq. kaline, bitter, and poisonous. Its solution in H,SO, is turned blue by PbO, or K,Cr,O,, and finally brown. FeCl, gives no colour. Salts.—B'HCl.—B'₂H₂PtCl₂ 5aq: crystals.-

B'2H,SO, 8aq: cubes or short prisms, v. sol. hot B₂H₂S₃O₄O₈H₂C₂O₄.—Tartrate B'₂H₆C₄O₆ faq.—Citrate B'₂C₄H₂O₇: nodular groups of needles.

Hypoquebrachine C₁₂H₂₈N₂O₂. [80°]. Strong base with bitter taste, v. sol. alcohol and ether,

forming yellow amorphous salts. Platino-chloride.—B'₂H₂PtOl₄4aq (Hesse, A. 211, 264). QUEBRACHITE C₆H₁₁MeO₆. [187°]. S.G. 2 1.54. (c. 210° in vacuo). [a]₀ = -80°. Occurs

in the seeds of Aspidosperma quebracho, from which it can be extracted with alcohol (Tanret,

C. R. 109, 908). Trimetric prisms with sweet taste, v. sol, water and alcohol, insol, ether. Does not ferment with yeast or reduce Fehling's solution. Reduces ammoniacal AgNOs. Not affected by dilute acids or alkalis at 100°. Ppd. by ammoniacal lead acetate, but not by lead subacetate. Heated with HI it gives off MeI and a little benzene. Ac.O and ZnCl₂ form an acetyl derivative [89°]. Gives on heating with HNO₂ the same reactions as inosite.

QUEBRACHO BARK. Quebracho blanco, or white quebracho bark, used as a febrifuge, contains about 8 p.c. of alkaloids, consisting of Aspr-DOSPERMINE, ASPIDOSPERMATINE, ASPIDOSAMINE, QUEBRACHINE, HYPOQUEBRACHINE, QUEBRACHAMINE,

and QUEBRACHOL (Hesse, A. 211, 251).
QUEBRACHO GUM. Occurs in quebracho colorado, the bark of Loxopterygium Lorentii (Jean, Bl. 28, 6; Arata, Anales de la Sociedad cientifica Argentina, July 1878; Feb. 1879; C. J. 34, 986). Brittle red concretions, with astringent taste, sol. boiling water and alcohol, insol. ether. Quebracho gum contains quebrachitannic acid, a pale-red amorphous mass, m. sol. hot water. giving a green colour with FeCl, turned dark red by NaOAc. Quebrachitannic acid ppts. Pb(OAc)2, gelatin, albumen, and alkaloids. yields pyrocatechin and a liquid (100°-120°) on distillation. Potash-fusion gives protocatechuic acid and phloroglucin; nitric acid yields oxalic and pieric acids.

QUEBRACHOL C₂₀H₃₄O. [125°]. [a]_D -29·3°. Occurs in white quebracho bark (Hesse, A. 211, 272; 228, 288). Plates, v. e. sol. alcohol and ether, insol. water and alkalis. When the solution in chloroform is shaken with H.SO. the chloroform is coloured red (cf. Cholesterin). .

A cetyl derivative $C_{20}H_{33}$. OAc. [115°]. QUERCETAGETIN $C_{27}H_{22}O_{13}$ 4aq. Yello Yellow crystals, extracted by alcohol from the blossoms of the common marigold, Tagetes patula (Latour

a. Magnier, Bl. [2] 28, 337). QUERCETIN $C_{21}H_{10}O_{11}$ 3aq (Liebermann a. Hamburger, B. 12, 1178) or C15H10O, (Herzig, M. 12, 172). (6)-Rhannetin (Herzig, M. 10, 561). [above 250°]. S. (alcohol) 5·5 at 78°; 4 in the cold (Stein, J. 1862, 499). Mol. w. (by Raoult's method) 258 (calc. 302). Formed, together with isodulcite, by the action of dilute H.SO, on quercitron, a yellow dye-stuff consisting of the shavings of the bark of Quercus tinctoria, growing in the United States (Rigaud, A. 90, 289). Rutin and robinin also yield quercetin when treated with dilute H.SO. (Zwenger a. Dronke, A. 123, 153; Suppl. 1, 261; Schunck, C. J. 53, 262; Hlasiwetz, A. 112, 96; J. pr. 94, 65). Occurs in Persian berries (Kane, A. Ch. [3] 8, 380; Bolley, C. J. 13, 327), in the ripe fruit, flowers, and leaves of the horse-chestnut (Rochleder, A. 112, 112), in the berries of the seabuckthorn (Hippophae rhamnoides), in appletree bark, in tea-leaves, and in catechu (Loewy. Fr. 12, 127).

Properties. — Lemon - yellow crystalline powder, sl. sol. water, v. sl. sol. ether. Gives off water of crystallisation at 130°. May be sublimed as yellow needles. Dissolves in alkalis, forming yellow solutions. Dyes fabrics mordanted with alumina yellow; with iron, grey or black. Its alcoholic solution is coloured dark green by FeCl, the colour becoming dark red on warming.

Pb(OAc)₂ gives a brick-red pp. Reduces AgNO₃ in the cold, and Fehling's solution on heating.

Reactions.—1. On fusion with potash it yields phloroglucin and quercetic acid, and by prolonged fusion, paradatiscetin C_{1.}H₁₀O₂, quercimeric and protocatechuic acid.—2. Boiling dilute alcoholic potash gives phloroglucin and protocatechuicacid (Herzig, M. 6, 863).—3. KClO₃ and HCl yield protocatechuic acid.—4. Sodium-amalgam forms phloroglucin, a compound C_{1.}H_{1.}O₃ crystallising in needles, sl. sol. water, and a compound C,H₂O₃, which forms granular crystals [130°], v. sol. water.—5. Bromine in HOAc forms C_{2.}H_{1.}Br_{2.}O_{1.} vystallising in lemon-yellow needles [237°] and yielding C_{2.}H₃Ac₃Br₃O₁₁. Excess of Brin HOAc forms C_{2.}H_{1.}Br_{2.}O_{1.}, vystallising from HOAc in needles [253°]. Licebermann obtained the compounds C_{2.}H_{1.}Br_{2.}O₁₁, C_{2.}H_{1.}Br_{2.}O₁₁, public the compounds C_{2.}H_{1.}Br_{2.}O₁₁, C_{2.}H_{1.}Pa_{2.}C_{2.}Br_{2.}O₁₁ [218°], C_{2.}H_{2.}Br_{2.}O₁₁, nad C_{2.}H₃c₃Br₃O₁₁ [228°], all crystallising in needles.—6. Phenyl cyanate at 160° forms C_{2.}H_{1.}Br_{3.}O_{1.} (Co.NHPh)₃, a white amorphous powyler [200°–205°] (Tesiner, B. 18, 2609).—7. Ammonia at 150° forms amorphous 'quercetamide' (Schützenberger a. Paraf, Z. 1862, 41).

 $\begin{array}{l} {\rm Salts.-C_{27}H_{20}K_{2}O_{13}\,(?).-C_{27}H_{20}Na_{2}O_{13}\,(?).-}\\ {\rm C_{27}H_{20}ZnO_{14}\,(II.\ a.\ F.).} \end{array}$

Acetyl derivative C., H., Ac., O., or C., H., Ac., O., (Herzig, M. 5, 72; 6, 890; 9, 557; 10, 561; 12, 174; cf. Liebermann, B. 12, 1178; A. 196, 319). [191°]. Formed by boiling quercetin or rhamnetin with Ac., O., and NaOAc. Needles (from alcohol). Liebermann obtained C., H., Ac., O., [198°], crystallising in needles.

Methyl ether C., H., O., (OMe). Rhamnetin.

Methyl ether C₁₃H₂O₄(OMe). Rhamnetin. Formed, together with isodulcite, by heating xanthorhamnin with dilute H₂SO₄ (Gellatly, N. E. P. J. 7, 256; Liebermann a. Hörmann, B. 11, 1618; Herzig, M. 6, 889; 9, 560; 12, 175. Lemon-yellow powder, nearly insol. water, alcohol, and ether, v. sol. hot phenol. Forms a yellow solution in KOHAq. Reduces ammoniacal AgNO₄ and hot Fehling's solution. Yields protocatechuic acid and phloroglucin on fusion with potash or on treatment with sodium-amalgam (Smorawski, B. 12, 1595). Converted by H1 into quercetin and MeI. Dyos iron mordants black and alumina yellow. Yields C₁₃H₃Ac₄O₄(OMe) [185°]. KOH and EtI give ethyl-rhamnetin [108°], whence Ac₅O and NaOAc form an acetyl-ethyl-rhamnetin [157°]. Rhamnetin yields also (tetra-?) propionyl [158°–162°] and (tetra-?) benzoyl [212°] derivatives, and an acetyl-dibromo-derivative [212°].

Methyl derivative C₂₁H₁₀Me₄O₁₁ or C₃₁H_Me₄O₄. [157°]. Formed from quereetin, KÖMe, and MeI (Herzig, M. 5, 83) and got also by heating xanthorhamnin with KMeSO, and MeOH at 120°, and from rhamnetin, KOH, and MeI (Liebermann a. Hörmann, A. 196, 317; Herzig, M. 6, 889; 9, 552). Golden needles, sl. sol. alcohol, converted by alcoholic potash at 140° into the di-methyl derivative of protocatechuic acid. Boiling AcO and NaOAc give C₂₁H₄Ac₂Me₄O₁ or C₁₅H₄AcMe₄O, crystallising in needles [167°].

Ethyl derivative C₃H₁₆Et₆O₁₁ or C₁H₄Et₆O₁ (122°]. Got by boiling quercetin with alcoholic potash and EtI (Herzig, M. 9, 587). Yellow needles, m. sol. alcohol. Yields

C₂H₃(OEt)₂CO₂H when heated with potash at 140°. Ac₂O and sodium acetate give the colourless acetyl derivative C₂₁H₈Ac₂Et₄O₁ or C₁₅H₁₅AcEt₄O, crystallising in needles [153°]. Mol. w. (by Raoult's method) c. 426 (Herzig, M. 12, 172).

A compound of quercetin and rhamnetin which sometimes occurs in Persian berries (Herzig, M. 10, 561) yields an acetyl derivative [171°], an acetyl-ethyl derivative [142°], and an ethyl derivative [102°].

[142°], and an ethyl derivative [102°].

Faradatiscetin C_{1.}H₁₀O₂. Formed from quercetin by potash-fusion (Hlasiwetz a. Pfaundler, J. pr. 94, 65). Yellowish needles (from dilute alcohol), nearly insol. water, m. sol. ether. Acid in reaction. FeCl₃ colours its alcoholic solution violet. Potash forms a yellow solution, turning green in air. Reduces AgNO₃ and Fehling's solution on heating. Potash-fusion yields phloroglucin but not protocatechuic acid. Boiled with water and BaCO₃ it yields BaA'₂ 2aq.—SrA'₂2aq.

Quercetic acid C₁₃H₁₀O₇ 3aq (?). Formed,

Quereetic acid C₁₃H₁₀O, 3aq (?). Formed, together with phloroglucin, by heating quereetin (1 pt.) with moist KOH (3 pts.) till a sample no longer gives a flocculent pp. with HCl and the residue quickly turns dark red at the edges (Hlasiwetz, A. 112, 96; 119, 213; J. pr. 94, 65). Slender silky efflorescent needles, si. sol. cold water, v. sol. alcohol and ether. Its aqueous solution turns yellow, and finally crimson, in air. H₂SO₄ forms a brown solution, whence water gives a red pp. forming a purple solution in NH₃Aq. FeCl₄ gives a blue-black colour. Reduces AgNO₃ Potash-fusion gives protocate-chuic acid. AcCl forms C₁₅H₈Ac₂O₇, crystallising from alcohol in prismatic needles.

from alcohol in prismatic necures.

Quercimeric acid C_AΠ_AO₃ aq (?). Formed from quercetin by potash-fusion. Colourless prisms, v. sol. water, alcohol, and other. Tastes bitter. Alkalis colour its solutions purple-red. FeCl₂ gives a dark-blue colour. Reduces AgNO₃ and Fehling's solution. Potash-fusion gives protocatechuic acid.

QUERCIN C₁H₀(OH)_g. [340°]. Occurs in oak bark, being obtained from the mother-liquors in the preparation of quereite (Gerber, A. 48, 348; Vincent a. Delachanal, C. R. 104, 1855; Friedel, 105, 95; Bl. [2] 48, 113). Efflorescent monoclinic prisms (containing xaq), sl. sol. water, insol. boiling alcohol. Inactive to light. Does not ferment with yeast, nor reduce Fehling's solution. Does not react with phenyl-hydrazine. Reduces ammoniacal AgNO₃ after addition of NaOH. Gives a gelatinous pp. with lead subacetate. After evaporation with IINO₃ it gives a rose-red colour with NH₃Aq and CaCl₂. Not coloured by boiling NaOHAq.

Acetyl derivative.—C_uH_u(OAc)_e. [301°].

QUERCITANNIC ACID C₁₇H₁₆O₉ or

C₁₈H₁₆O₁₉. S. ·6. S. (ether) ·035. Occurs in
oak bark, from which it is got by powdering,
sifting from bast fibres, extracting with dilute
alcohol, and shaking the filtrate with ether and
EtOAc. The acetic ether when evaporated deposits ellagic acid. The filtrate is evaporated
to dryness, and the residue washed with ether
and then extracted with Et₂O and EtOAc (Etti,
Sitz. W. [2] 81, 495; M. 1, 264; 4, 514; cf.
Stenhouse, A. 45, 16; Böttinger, A. 202, 270;
240, 331; 263, 112; Lowe, Fr. 20, 210). Occurs

also in tea (Rochleder, A. 63, 205). Reddishwhite powder. FeCl, colours the alcoholic solution dark blue. Pb(OAc)₂ ppts. the alcoholic solution. Quercitannic acid is not a glucoside (Etti). At 130° to 140° it forms an anhydride which gives C₃₄H₂₈BaO₁₇ (Etti). On evaporating with NaCl it is converted into a mixture of anhydrides which give with bromine-water an amorphous pp. $C_{10}H_{14}Br_{2}O_{10}$, m. sol. alcohol and EtOAc, v. e. sol. a mixture of these solvents, reacts with hydroxylamine, and is converted by Br into C19H10Br4O10, whence Ac2O forms C₁₉H,Ac,Br,G₁₀. QUERCITE

C₅H₁₂O₅. Penta-oxy-benzene Mol w. 164. [234°] Böttinger, hexahydride? B. 14, 1598). S.G. 131.585. S. 9 at 12°; 11 at 20°. $[a]_D = 24.17$. H.C. v. 710,100 (Berthelot a. Recoura, A. Ch. [6] 13, 341). H.F. 268,200. R_{∞} 58.95 in a 7.7 p.c. aqueous solution (Kanonnikoff). Occurs in acorns (Braconnot, A. Ch. [3] 27, 392; Dessaignes, A. 81, 103, 251; Prunier, A. Ch. [5] 15, 5; U. R. 84, 1318; 85, 808; 86, 338, 1460; Hofmann, A. 190, 282).

Preparation. - Acorns are extracted with cold water, the extract concentrated at 40°, ppd. by lead subacetate, filtered, mixed with yeast to remove sugar, and, after fermentation, freed from lead by H₂S, and evaporated to crystallisa-

Properties. — Monoclinic prisms, a:b:c = *800:1: 766, $\beta = 68$ °57', insol. other, benzene, and chloroform, v. sl. sol. hot alcohol. Does not undergo alcoholic fermentation. Dextrorotatory. Does not render borax solution acid.

Reactions .- 1. At 100° it slowly loses water, forming $C_{21}\Pi_{10}O_{19}(?)$. At 240° in vacuo it gives $C_{12}H_{22}O_{9}$ [230°], v. sl. sol. water. Rapidly heated to 290° it swells up and gives off quinhydrone and hydroquinone.—2. Potash-fusion gives quinone, hydroquinone, CO₂, formic acid, and oxalic acid.—3. H₂SO₄ and MnO₂ give quinone. 4. Conc. HClAq forms, at 100°, C₂H,Cl(OH)₄ [200°], sol. ether, and viscid C₂H₂ClO₃, which is converted by baryta-water into amorphous quereitan $C_cH_{10}O_1$, sol. water and alcohol, insol. ether. HClAq at 120° – 140° gives $C_cH_1Cl_4(OII)_2$ [155°], converted by further treatment with HCI into C.H.Cl. [102]. - 5. Distillation with HIAq forms benzene, phenol, iodo-phenol, quinone, hydroquinone, and hexane. - 6. Nitric acid forms mucic and tri-oxy-glutaric acids (Kiliani a. Scheibler, B. 22, 517).-7. Phenyl cyanate at 165° forms C₈H,(O.CO.NHPh), [120°-140°], a white amorphous powder (Tesmer, B. 18, 2606).

8. Benzoic acid at 200° forms solid 'benzoquercite ' CaH10Bz2O3 (?) insol. water, sol. alcohol and ether. Stearic acid forms a similar body, while tartaric acid gives 'quercitartaric acid C₂₂H₃₂O₂₇ (Berthelot, C. R. 44, 452; A. Ch. [3] 54, 82).

Salts. - (C.H.,O.) Ba 3aq: amorphous, sol.

water and alcohol.—(C₆H₁,O₃)₂CaSO, 2aq.

Acetyl derivatives. The compounds

C₆H₁,AcO₃, C₆H₁,AcO₃, C₈H₈AcO₃, C₈H₈AcO₅,
and C₆H₄AcO₃ have been prepared.

Butyryl derivatives. Heating with butyric acid gives rise to C_sH₁₁(C_tH₂O)O_s, C₆H₉(C₄H₇O)₂O₃, and C₆H₇(C₄H₇O)₅O₅, all being amorphous with bitter taste.

Pentanitrate C₄H₁(NO₃)₃. Formed from queroite (1 pt.), H₂SO₄ (10 pts.) and HNO₃

(4 pts.) (Hofmann, A. 190, 288). Resin, insol. water, sol. alcohol and ether. Explodes when heated. Zinc-dust and alcoholic soda give off

heated. Zinc-auss and action the N as NH₃.

QUERCITRIN C₃₆H₃₈O₂₆ or, more probably,
C₃₁H₂₀O₁₂ (Herzig, M. 14, 53). [168°]. S. 04 in
the cold; 7 at 100°. S. (alcohol) 4 in the cold
29 at 78° (Stein). S. (ether) 8 (Schunck, C. J 53, 201). Geenam question and the state of the control of the cont J. pr. 85, 351; Hlasiwetz, A. 112, 109). Occurs also in fully-developed horse-chestnut leaves (Rochleder a. Kawalier, Sitz. W. 55 [2] 46), in leaves of the ash (Gintl, Z. [2] 4, 732), and in leaves of Andromeda japonica (Eykman, R. T. C. 2, 200).

Preparation .- Quercitron bark is exhausted with alcohol, and the evaporated extract dissolved in water and shaken with ether. The ethereal solution is evaporated, the residue dissolved in alcohol, and the quercitrin ppd. by water and crystallised from boiling water (Löwe,

Fr. 14, 233; cf. Herzig, M. 6, 877).

Properties.—Yellow needles or plates (containing 3aq). Neutral and tasteless. Nearly insol. cold water, sol. alkalis and HOAc. FeCl. colours its solution dark green. FeSO, gives no colour. Ppd. by I'b(OAc). Reduces aqueous AgNO₃ in the cold, and Fehling's solution after long boiling. Boiling dilute acids split it up into quercetin (q.v.) and isodulcite (Liebermann a. Hamburger, B. 12, 1178). Bromine forms $C_{30}\Pi_{41}Br_{1}O_{20}$, which is crystalline and is decomposed by acids into isodulcite and tetra-bromoquercetin.

Salt.-C36H36K2O20: yellow pp. Violaquerotrin C_EH₄₀O₂₁. Occurs in Viola tricolor (Mandelin, J. 1883, 1369). Yellow needles (from water). Split up by dilute acids

into glucose and quercetin.

QUILLAJIC ACID C₁₁₁II₂₀O₁₀. Extracted by water from the bark of Quillaja Saponaria (Kobert, C. C. 1888, 972). White flakes, sol. water and alcohol, insol. ether. Coloured dark red by H2SO4. Boiling dilute acids split it up into sapoginin and an unfermentable glucose. The Na salt violently attacks the mucous membrane, and is very poisonous when injected into the blood.

QUINACETOPHENONE is DI-OXY-ACETO-PHENONE.

QUINALDINE v. METHYL-QUINOLINE. QUINALDINIC ACID v. QUINOLINE CARB-

OXYLIC ACID. QUINAMINE v. vol. ii. p. 179.

QUINAMICINE v. vol. ii. p. 180.

QUINAMIDINE v. CINCHONA BASES. QUINANISOLE v. Methyl derivative of Oxy-

QUINOLINE. QUINAZOLE v. METHYL-INDAZINE.

QUINAZOLINE. This name is given to the ring C.H. CH:N v. Oxy-QUINAZOLINE.

QUINAZOLINE DIHYDRIDE C,H,N, i.e. $C_sH_s < \stackrel{CH_s,NH}{N=CH}$. [127°]. Formed by reducing o-nitro-benzyl-formamide by Zn and HClAq (Gabriel a. Jansen, B. 23, 2814; 24, 3097). Yellowish crystals, sol. warm water, forming an alkaline solution.—B'HCl.—B'C₈H₈N₂O₇. [215°]. Small crystals, sl. sol. water.—B'₂H₂PtCl₈.

QUINENE v. vol. ii. p. 181. QUINETHONIC ACID C₁₄H₁₈O₈ i.e. C.H.(OEi).C.H.O., [146°]. Occurs in urine after a dose of C.H., OEt (Kossel, H. 4, 296; 7, 292; Lehmann, H. 13, 181). Crystalline. Lesvorotatory. Does not reduce Fehling's solution. Converted by dilute H2SO4 into crystalline The double salt Pho.So. BaA'aq (dried at 110°) and with cresol and indoxyl the corresponding C,H,O.SO,BaA'aq and C,H,NSO,BaA', all three

QUINHYDRONE C₁₂H₁₀O₄. Formed by mixing aqueous solutions of quinone and hydroquinone; by oxidising hydroquinone; and by reducing quinone (Wöhler, A. 51, 153; Liebermann, B. 10, 1614, 2000; Hesse, A. 200, 248; Nietzki, A. 215, 130; Wichelhaus, B. 5, 840; 12, 1500; Stenhouse a. Groves, B. 13, 1305). Brownishred prisms, with green metallic lustre. May be sublimed. Sl. sol. cold water, v. sol. alcohol and ether, forming yellow solutions. Decomposed by boiling water, giving off quinone and leaving a solution of hydroquinone. Its ammoniacal

QUINIC ACID C,H₁₂O₆ i.e. C₆H₁(OH), CO₂H.

Mol. w. 192. [162° cor.]. S.G. *5 1-637 (Henry a. Plisson, B. J. 10, 186). S. 40 at 9°. $[a]_D = -44^\circ$ at 20° in a 20 p.c. solution (Thomsen, J. pr. [2] 35, 156). H.C. 833,700. H.F. 238,300 (Berthelot a. Recoura, C. R. 105, 144; Bl. [2] 48, 703; A. Ch. [6] 13, 342). R_{∞} 66.52 in an 18 p.c. aqueous solution (Kanonnikoff, J. pr. [2] 31, 348). Occurs as calcium salt in cinchona bark (Hoffmann, Crell's Ann. 2, 314; Vauquelin, A. Ch. 59, 162; Pelletier a. Caventou, A. Ch. [2] 15, 340; Liebig, P. 21, 1; 29, 70; Baup, A. Ch. [2] 51, 5; A. 6, 7; Woskrosensky, A. 27, 200; Hesse, A. 110, 194; 112, 52; 114, 292; 176, 124; Clemm a. Will, A. 110, 345). Occurs also in the bilberry plant (Vaccinium Myrtillus) (Zwenger, A. 115, 108; 129, 203; Suppl. 1, 77), in the leaves and beans of the coffee-plant (Z.), and in hay

(O. Loew, J. pr. [2] 19, 310; 20, 476).

Preparation.—Cinchona bank is extracted with dilute H₂SO₄, the extract ppd. by milk of lime, filtered, and evaporated. The residue is boiled with alcohol and the calcium quinate left undissolved is crystallised from water and de-

composed by oxalic acid.

Properties.-Monoclinic prisms. V. e. sol. water, m. sol. alcohol, nearly insol. ether.

Levorotatory.

Reactions .- 1. Heated to 200°-225° it gives off aq, forming quinide C,H₁₀O₅, a crystalline anhydride, v. sol. water, sl. sol. dilute alcohol. Quinide is acid in reaction, and is reconverted by bases into quinic acid. On dry distillation quinic acid gives hydroquinone, phenol, benzoic acid, and pyrocatechin.—2. Ac₂O at 170° forms tri-acetyl-quinide C₆H,(OAc)₃<0

and tetra-acetyl-quinic acid (Erwig a. Königs, B. 22, 1458; cf. Hesse, A. 200, 233). By further heating with Ac.O at 240°-250° monoclinic crystals of iso-tri-acetyl-quinide [189°] are obtained.—8. Bromine added to an aqueous

solution forms protocatechuic acid (Hesse).--4. Hot H₂SO₄ forms CO and hydroquinone disulphonic acid.—5. Hydroquinone is formed by boiling the aqueous solution with PbO₂. Distillation with MnO₂ and dilute H₂SO₄ yields quinone (detection of quinic acid in bark: Stenhouse, A. 59, 100).—6. HNO, gives oxalic acid. 7. KClO, and HCl give chlorinated quinones and chlorinated acetones (Städeler, A. 69, 300; 111, 293).—8. Conc. HIAq at 120° reduces it to benzoic acid (Lautemann, A. 125, 9).—9. Conc. HClAq at 150° gives p-oxy-benzoic acid and hydroquinone (Hesse, A. 200, 232). Dilute (3 p.c.) HClAq at 100°-120° forms phenol, hydroquinone, and p-oxy-benzoic acid (Chadounski, C. C. 1888, 1029). — 10. Fuming HBrAq at 130° gives protocatechuic and benzoic acids (Fittig, A. 193, 197).-11. PCls forms m-chloro-benzoyl chloride (Graebe, A. 138, 197). 12. Gives protocatechuic acid on fusion with KOH or NaOH .- 13. Boiling with iodine and KOHAq yields iodoform.—14. Calcium quinate fermented by schizomycetes in presence of air yields protocatechuic acid, in absence of air it gives propionic, acetic, and formic acids (Löw, B. 14, 450).

Salts .- NaA' 2aq .- NaA' 5aq. BaA', 6aq: dodecahedra, very soluble in water.-CaA' 10aq. S. 17 at 16°. Plates, insol. alcohol. -CaA'Ac aq (Gundelach, B. 9, 852).—SrA'₂10aq.
-SrA'₂15aq.—MgA'₂6aq.—CdA'₂. S. '4 in the cold.—ZnA'₂.—CoA'₂5aq.—NiA'₂5aq: crystals.
CuA'₂5aq: blue needles.—CuC,II₁₀O₄2aq. S. '09 at 18°.—PbA'₂2aq: needles, sol. alcohol, v. e. sol. water.—Pb₂C₇H₈O₆. Amorphous, insol. water.—MnA'₂. S. 5 in the cold.—FeC₁₄H₂₁O₁₅. -AgA': mammellated groups of crystals.

Ethyl ether EtA'. Viscid mass, with

bitter taste, v. sol. water and alcohol. Converted by boiling Ac₂O into C₈H₇(OAc), CO₂Et crystallising from water in plates [135°], sl. sol. boiling water.

Tetra-acetyl derivative

C₆H₂(OAc)₁.CO₂H. [130°-136°]. Formed by heating quinic acid with Ac₂O and ZnCl₂ (Erwig a. Koenigs, B. 22, 1461). Crystalline crusts, sl. sol. cold water, insol. ligroin.—AgA': needles.

Anilide C₁₃H₁₇NO₃. [174°]. Formed by heating quinic acid with aniline at 180°. Small silky needles (containing aq), v. sol. water and alcohol, sl. sol. ether.

QUINICINE v. CINCHONA BASES. QUINIDE v. QUINIC ACID.

QUINIDINE v. vol. ii. p. 180. QUINIENE v. vol. ii. p. 181.

QUININE C₂₉H_{2l}N₂O₂ [173° cor.] (Lenz, Fr. 27, 559; Hesse, A. 258, 133). The trihydrate melts at 57° (H.). S. 05 at 15° (Regnauld, J. Pharm. Chim. [4] 21, 8). S. (of the trihydrate) 06 at 15° (Hesse, B. 10, 2152); 06 at 100 (15 to 100); 15 to 100 (15 to 100); 16 to 100 (15 to 100); 16 to 100 (15 to 100); 17 to 100 (15 to 100); 18 to 100); 18 to 100 (15 to 100); 18 to 100); 18 to 100 (15 to 100); 18 to 100); 18 to 100 (15 to 1 drate) '06 at 15' (Hesse, B. 10, 2152); '06 at 20°, '11 at 100° (Sestini, Fr. 6, 359). S. (of the anhydrous base) '051 at 15' (H.); '07 at 20°, '13 at 100° (S.). S. (ether) 100 at 10° (Hesse, A. 135, 327); 4.4 at 18° (van der Burg, J. 1865, 438). A conc. ethereal solution often gelatinises, The quinine thus separated being less sol. ether (S. about 5 at 15°). S. (chloroform) 57.5 (Pettenkofer, J. 1858, 363). S. (benzene) -5 at 15° ; 3.8 at 80° (Oudemans, J. 1874, 867). S. (xylene) -11 at 15° ; -645 at 138° (Swaving, R. T. C. 4, 186). $[a]_{\rm B} = -166^{\circ}$ at 18° ; -163°

at 25° in alcoholic solution (Hesse, A. 166, 217) -145.2 + .657p in a solution of p grammes in 100 c.c. of 97p.c. alcohol at 15° (Hesse, A. 176, 206; 182, 131). [α]_D = -158.7 + 1.911p in an ethereal solution containing from 1.5 to 6 p.c. base. In solutions containing not note than 1.6 p.c. quinine, Oudmans, jun. (Ar. N. 10, 193), found $[a]_b = -167.5^\circ$ (in alcohol); -136° in benzene; -127° in toluene; -117° in chloroform. Dispersive power: Grimbert, J. Ph. [5] 16, 295,

Occurrence.—In cinchona bark, v. vol. ii. p. 175. According to Grimaux (Bl. [3] 7, 304), cupreine heated with NaOMe, MeOH, and MeCl or MeNO, yields 10 to 15 p.c. of quinine, while MeI gives chiefly quinine di-methylo-di-iodide.

Preparation .- The bark is extracted with dilute H2SO,, and the solution ppd. by NaOHAq. The pp. is dissolved in ether, the ether shaken with dilute H₂SO₄, and the boiling solution neutralised by ammonia. Quinine sulphate separates on cooling. The sulphate is decomposed by ammonia.

References. — Vide references in articles Cinchona Bark and Cinchonidine, and also Pasteur, C. R. 36, 26; 37, 110, 162; Schützenrasteur, U. M. 30, 26; 37, 110, 162; Schützenberger, A. 108, 347, 350; Robiquet, A. Ch. [2] 17, 316; Stratingh, R. P. 15, 139; Pelletier, J. Ph. 11, 249; Duflos, B. J. 27, 1, 110; Strecker, A. 91, 155; Thiboumery, J. Ph. [3] 16, 369; Alluard, J. Ph. [3] 46, 192; Körner, Z. [2] 1, 150; Bouchardat, A. Ch. [3] 9, 213; De Vrij, N. J. P. 14, 268; Laudrin, C. R. 108, 750.

Properties.—Phd. by ammonic from solvers.

Properties .- Ppd. by ammonia from solutions of its salts in an amorphous anhydrous form, which quickly changes, especially in presence of free ammonia, into the crystalline hydrate (containing 3aq), consisting of minute four-sided prisms terminated by pyramids. The hydrate gives off its water of crystallisation over H₂SO₂. Quinine is v. e. sol. ether and alcohol, v. sol. CS₂, m. sol. benzene, v. sl. sol. ligroïn, sol. volatile and fixed oils. It is alkaline in reaction. Its solutions are levorotatory. A 5 p.c. solution of the sulphate gives $\alpha = -22^{\circ}$ in a depth of 200 mm. (Rozsnyay, Fr. 23, 589). Its solutions in dilute H2SO, HNO3, H3PO4, and HOAc exhibit blue fluorescence, destroyed by HCl, HBr, HI, or H₄FeCy₈. Fluorescence of the sulphate is prevented by a large excess of sulphate of cupreïne (Grimaux a. Arnaud, Bl. [3] 7, 304). Chlorine-water and ammonia give a green pp. dissolving in excess of ammonia to an emerald green liquid. On addition of an acid the colour changes through blue (when neutral) to red, the green colour returning on adding ammonia (Brandes, Ar. Ph. 13, 65; André, J. Ph. 22, 132). Excess of chlorine-water and of ammonia should be avoided. Chlorine does not render a solution of quinine sulphate turbid (Lepage, J. Ph. 26, 140). Bromine-water and ammonia give the green colour even in exceedingly dilute solutions (Flückiger, Fr. 11, 318). The green colour may be also got by mixing 01 g. of the salt to be tested with an equal bulk of KClO₃ and a drop of conc. H.SO, followed by excess of ammonia (Mylius, C. C. 1886, 602). Chlorine-water followed by K,FeOy, gives a red colour in a alcohol, insol. ether and NaOHAq. Alcoholic solution of quinine sulphate (Vogel, A. 73, 221; NH, converts this salt into C₂₀H₂₁N,O₂HI? which 86, 122). Quinine gives the usual alkaloidal is white, v. sol. alcohol, al. sol. ether [155°-

reactions. It is coloured green by potash-fusion (Lenz, Fr. 25, 81). Potassium sulphocyanide gives a white pp., sol. excess (Schrage, Ar. Ph. [3] 13, 25). Boiled with dilute H₂SO₄ and PbO, quinine forms quinetin, a red substance (Marchand). Dilute HNO, gives no colour. Sunlight acting on an aqueous solution, even in an atmosphere of H, ppts. brown flocculent quiniretin, insol. water, alcohol, and ether (Flückiger, Ph. [3] 8, 885). ICl gives a light-brown crystal-line pp., sl. sol. HClAq. Quinine is antiseptic, hindering putrefaction and the alcoholic, lactic, and butyric fermentation. Quinine is a febri-

fuge. Its salts taste bitter. Reactions .- 1. The sulphate is oxidised by

KMnO, to pyridine tricarboxylic acid, oxalic acid, and NH, (Hoogewerff a. van Dorp, B. 12, 158). At 0° the first product is chitenine (n.H₂₂N₂O₄, which crystallises in colourless prisms [240°–286°], insol. ether and alcohol, prisms [240°-286°], insol. etner and alcoho, sol. dilute acids and alkalis (Skraup, B. 12, 1104; M. 10, 39). Quinine (5 g.) is apparently oxidised by KMnO₄ (50 g.) to pyridine dicarboxylic acid (Ramsay a. Dobbie, C. J. 33, 102). Boiling nitric acid also forms pyridine dicarboxylic acid. oxylio (cinchomeronic) acid. Aqueous CrO, oxidises quinine to quininic or methoxy-quinoline carboxylic acid.—2. A mixture of HNO, and H2SO, reacts, and on diluting an amorphous pp., apparently $C_{20}H_{22}(NO_2)_2N_2O_2H_2O$ is got (Rennie, C. J. 39, 469).—3. PCl₃ converts is got (hennie, C. J. 31, 403).—5. FO, converts it into colourless quinine-chloride $C_{20}H_{22}N$,OCI [151°] which by boiling with alcoholic KOH gives chinen $C_{20}H_{22}N_2O$ (Comstock a. Königs, B. 17, 1988).—4. Reduced by zinc and dilute H_2SO_4 to hydroquinine $C_{20}H_{20}N_2O_{20}$ an amorphous bitter resin (containing aq), sol. alcohol and ether, giving a green colour with chlorine-water and aminonia (Schützenberger, A. 108, 347).-5. Heated with water at 250° it yields quinoline (Reynoso, C. R. 24, 795). The same body is formed by heating with conc. KOHAq at 190° (Gerhardt a. Wertheim, J. 1840, 370).—6. Fuming H2SO4 forms a sulphonic acid. Conc. Husto, dissolves quinine, forming isocinchonine. Dilute H₂SO₄ at 125° converts quinine into quinicine.—7. *Iodic acid* gives off much gas on warming (Brett, J. Ph. [3] 27, 116).—8. Conc. HClAq at 150° forms McCl and apoquinine. (Hesse, A. 205, 317). Concentrated HClAq at -17° slowly forms hydrochloroquinine C₁₀H₂ClN₂O₁[87°], while hydrogen bromidegives C₂₉H₂BrN₂O₂, which forms B'H₂Br₂ (Comstock a. Königs, B. 20, 2510).—9. Heated for a long time with 12 pts. of HIAq. S.G. 1-96 for 3 hours at 100° it gives methyl iodide and a yellow salt C₁₉H_{2,N}N₂O₂3HI [238°] sol. alkalis. Alcoholic NH₂Aq converts it into C₁₉H_{2,N}N₂O₂2HI mixed with a little C₁₉H_{2,N}N₂O₂HI, which yields an oxalate [187°] (C₁₉H_{2,N}N₂O₂HI)H₂C₂O₄ mixed with (C₁₉H_{2,N}N₂O₂H₂H₂D₁H₂CO₄ (Schubert a. Skraup, M. 12, 684). HBrAq acting on quinine at 100° forms C₁₉H₂BrN₂O₃HBr aq, crystallising in needles, from which sodium carbonate sets free C₁₉H₂N₂N₂O₂, a powder [210] (Julius, M. 6, 751). at -17° slowly forms hydrochloroquinine needies, from which solution carbonate sets free C₁₉H₂₂BrN₂O₂, a powder [210] [Julius, M. 6, 751). 10. Quinine dried at 120°, heated with HIAq (S.G. 1.7) at 100°, forms C₂₉H₂₂N₂O₂3HI [280°], a yellow crystalline mass, v. sl. sol. water, sl. sol.

160°]. Its solution in dilute H₂SO, shows blue fluorescence, and gives a brownish-yellow pp. with chlorine-water and ammonia. It gives rise to the salts ((C₂₀H₂₁N₂O₂),H₃I₃)₂8H₂C₂O₄? and C₂₀H₂₁N₂O₂H₂HNO₃? [217°] (Schubert a. Skraup, M. 12, 678; cf. Lippmann a. Fleissner, M. 12, 329).—11. Bromine added to a solution of quinine in dilute H2SO4 ppts. B'Br2 2aq, B'2Br6, and B'Br, as bitter yellow curdy pps., melting at 160°-180° (Colson, C. R. 108, 678).

Estimation.—V. Cinchona Bark. V. also Lenz, Fr. 27, 549-631. Quinine may be ppd. as chromate (De Vrij, C. C. 1889, 708; Ar. Ph. [3] 24, 1073; Vulpius, Ar. Ph. [3] 24, 1022; Schlikum, Ar. Ph. [3] 25, 128; Hesse, Ph. [3] 17. 585). A solution of quinine sulphate requires more ammonia to redissolve the pp. first formed than solutions of the sulphates of the alkaloids usually present with it (Kerner a. Weller, Ar. Ph. [3] 25, 712,749; Fr. 1, 159; 27, 115; cf. Schäfer, Ar. Ph. [3] 25, 1033; Ruddiman, C. N. 58, 202, 216, 226; Jungfleisch, J. Ph. [5] 15, 5). Use may also be made of the sparing Bolubility of quinine oxalate in presence of K₂C₂O₄ (Schäfer, Ar. Ph. [3] 25, 64, 1041).

Constitution.—Chitenine C₁₀H_{2,}N₂O₄ may be

got by oxidation of both quinine and cinchonine. On further oxidation chitenine yields quinic, pyridine tricarboxylic, and cincholeuponic acids. From this it may be surmised that one half of the quinine molecule has the same composition as one half of the cinchonine molecule (Skraup, M. 10, 39, 220). Quinine, quinidine, and quinicine are probably stereo-isomeric, since they give the same products of oxidation; they are derivatives of (B. 2)-methoxy-quinoline while cinchonine is a derivative of quinoline. Cincholeuponic acid C_sH₁₃NO₄ [225°] yields C_sH₁₃NO₄ĤCl [194°] and C_sH₁₂AcNO₄, and is converted by nitrous acid into the dibasic nitroso derivative C₂H₁₂(NO)NO. Oxidation of quinine also yields a base, cincholeupone C₂H₁NO₂ oxidised by CrO₂ to cincholeuponic acid and other products. Cincholeupone when heated with zinc-dust yields (B)-ethyl-pyridine. By nitrous acid cincholeupone is converted into C_bH_{1s}(NO)NO₂, which is an acid. Ac₂O forms acid C_bH_{1s}AoNO₂. Oxy-quinoline (cynurine) is also a product of oxidation of quinine. From these experiments Skraup concludes that quinine and cinchonine contain a quinoline nucleus united to an ethyl-pyridine nucleus; quinine being methoxy-cinchonine. Cupreïne heated with NaOMe (1 mol.), McI (6 mols!), and McOH forms quinine di-methylo-di-iodide (Hesse, A. 266, 244; cf. Grimaux a. Arnaud, C. R. 112, 774; A. 267, 379). The chief product is, however, cupreïne mono-methylo-iodide.
only 1 mol. MeI is used, no quinine is got.

Salts.—C₂₀H₂₂AgN₂O₂ Gelatinous pp. got by adding AgNO₃ to a solution of quinine in alcoholic NH₃ (Skraup, M. 2, 613).—B'HCl 2aq: groups of white needles (Hesse, A. 176, 210; 267, 142). Melts (when anhydrous) at 160° without undergoing any change. S. 2.5 at 10°. V. e. sol. alcohol and ether. $[a]_0 = -134^{\circ}$ in a 2 p.c. solution at 17° (Oudemans). Its solution is not ppd. by silver nitrate (1 mol.) until added in excess (Vulpius, Ar. Ph. [3] 20, 361) .-

or gelatinous mass. S. 100 in the cold. Melts at 15° (A. Clermont, J. Ph. [5] 15, 15). B'H,PtCl, aq: yellowish flocculent pp., soon becoming orange and crystalline (Gerhardt, B. J. coming orange and crystalline (Gernardt, B. J. 23, 354). S. 07 in the cold; 8 at 100° (Duflos). —B'_H_PtCl_3aq: orange amorphous pp. (Hesse, A. 207, 308).—B'H_HgCl_1. Ppd. by mixing alcoholic solutions of quinine, HCl, and HgCl_2 (Hinterberger, A. 77, 201).—B'_H_ZnCl_2aq: prisms (from alcohol) (Gräfinghoff, Bl. [2] 4, 391).

B' H ZnCl_2ac_arrestalline — B'H Br_3ac_arrestalline — - B'2H, ZnCl, 3aq: crystalline. - B'H, Br, 3aq: crystals, v. e. sol. water.—B'HI: lemon-yellow prisms (Herapath), or heavy white powder. Sl. sol. water, v. e. sol. alcohol (Winckler, Jahrb. pr. Pharm. 20, 321). Melts at 150°-155°, but softens at about 100° and then blackens (Lippmann a. Fleissner, M. 13, 436).—B'HIEt20 (from ether). Crystals.—B'H_IL_5aq (Regnault). Crystals. V. Reaction 9, supra.—B'H_IL,: [230°]. Converted by NH_Aq into B'HI.—B'_2H_SO, 8aq (Hesse, A. 119, 361; 225, 97; Carles, BL. [3] 7, 108; cf. Cownley, Ph. [3] 7, 189). Commercial specimens are somewhat effloresced. Monoclinic efflorescent prisms. Loses 6aq over H,SO. S. chloreform and fatty oils. [\alpha]_D = 163° in a 2 p.c. solution in 80 p.c. alcohol.—B'H_SO, 7aq. [100°]. Rectangular prisms (from hot solutions) or small needles. S. 9 at 13°; 12.5 at 22°. or small nections. B. 3 at 15, 125 at 25. Loses 6aq over H_2SO_4 . $[a]_b = -164.9 + 31p$ in a solution of p g. in 100 c.c. water, where p is between 1 and 6 (Hesse, A. 176, 215; 182, 134).—B'(H₂SO₄)₂ 7aq: prisms, v. e. sol. water, m. sol. alcohol. Its hot alcoholic solution deposits gelatinous B'(H_2SO_4)₂5aq. [α]_D = -170 + 94p.— B'₂ $H_2Cl_2H_2SO_4$ 3aq. Mass of small needles, \mathbf{v}_{\bullet} sol. water. S. (of anhydrous salt) 86. [120°] (hydrated); [165°-170°] (anhydrous) (Grimaux, Bl. [3] 7, 819).—B'₂H₂Br₂H₂SO₄ 3aq. S. 26 at 21°.-B'2H,L,H,SO, 2aq: yellow crystals, form-21°.—B₂H₂H₂B₂O₂ 2aq: yeilow crystalis, norming a colourless solution. Crystallises also with 4aq.—B'₂H₂Cl₂H₃PO₁9aq: small needles, solwater. - B'₂H₂B₇H₁PO₁7aq. - B'₂H₃I₄H₂PO₆6aq. - B'₂H₃S₀O₂2aq. S. 3 (Wetherill, A. 66, 150; How, N. Ed. P. J. [2] 1, 47).—B'HNO₂ aq: prisms (Strecker, A. 91, 159).—B'AgNO₃ aq: crystalline pp. Chlorate.—B'HClO, 2aq (Tichborne, Z. 1866, 665; cf. Serullas, A. Ch. [2] 45, 279).—B'(HClO₄), 7aq: trimetric octahedra.—B'(HClO₄) 2aq. [210°] (Boedeker, A. 71, 61).—B'(HO₄) 3aq: needles (Langlois, A. Ch. [3] 31, 274).—B'₄(HCl)₅(HI)₄II; small brown crystals.—B'₄(HCl)₅(HI)₄II; blackish-groen flat needles Herapathite. Formed by adding an alcoholic solution of iodine to a solution of quinine sulphate in HOAc (Herapath, P. M. [4] 3, 161; 4, 186; 6, 171, 346; 7, 352; 9, 366; 14, 224; C. J. 11, 130; Haidinger a. Stokes, Sitz. W. 10, 106; Jörgensen, J. pr. [2] 14, 230). Large colourless plates with metallic green lustre. Polarises light, so that two plates at right angles are opaque. S. (90 p.c. alcohol) 125 at 16°. Decomposed by cold water. Dried over H.SO, they become B',(H,SO), I, 3aq (Hauer, Z. [2] 1, 481).

—B',(H,SO),(HI),I, 2aq. Crystals, resembling B'HOl 1 saq. Large monoclinic octahedra, deposited at 0°.—B'2HCl. Groups of white needles, herapathite, decomposed by hot alcohol into

iodine and herapathite. -B's(H2SO4)s(HI)4I144aq: | iodine and herapathite.—B'₁(H,SO₁)₆(H1),I₁, 4aq: brownish needles.—B'₂H₂SO₄(H1),I₂; red needles.—B'₂H₂SO₄(H1)₂I₄: brown rectangular plates with olive-green reflex.—B'₂H₂SO₄(H1)₂I₈: black crystals with green reflex.—B'₂(H,SO₁)₂(H1)₂I₈.—B'₃(H,SO₁)₂(H1)₂I₄.—B'₄(H,SO₁)₂(H1)₂I₅.—B'₄(H,SO₁)₂(H1)₂I₄.—B'₄(H,SO₂)₂(H1)₄I₅I₈.
B'H,SO₄ 7aq: trimetric tables, insol. alcohol (Hjortdahl, J. 1879, 794).—B'₄(H,SO₂)₃(H1)₄I₁, I₈.
Isomorphous with herapathite, which it greathly resembles. Almost insol. cold alcohol (Jürgen, resembles. Almost insol. cold alcohol (Jörgenresembles. Almost insol. cold alcohol (Jörgensen, J. pr. [2] 15, 65, 418). B'_H_CO_0. S. ·042 at 15° (André); ·037 at 14°; ·05 at 16° (De Vrij, Ar. Ph. [3] 24, 1073; ·625 at 100° (A.). Ppd. by adding K₂CrO₄ to a solution of the neutral or acid sulphate. Tufts of golden needles.—B'₂H₂CrO₄ 2aq (Hesse, Ph. [3] 17, 585, 665). Becomes aphydrous et 80° but we cheath 665). Becomes anhydrous at 80°, but re-absorbs 2aq on exposure to moist air.—B'H.CrO, 7aq. Ppd. by adding K, Cr.O, to a solution of quinine in excess of dilute H.SO₄ (André, J. Ph. [3] 41, 341). Orange pp., decomposed by light, and turned brown when heated to 60°-65° or when boiled with water. More soluble than B'2H2CrO4. B'H2CO3 aq. Efflorescent needles, with alkaline reaction, deposited from a solution of quinine in aqueous CO... Sol. alcohol, insol. ether (Langlois, A. Ch. [3] 41, 89).—B'_.II,PO, 8aq. S. 127 at 10° (Hesse). Tufts of long needles.— [6] 13, 236).—B'H₂SiF₆. Got by passing SiF into a solution of quinine in absolute alcohol (Cavazzi, G. 17, 563). Minute crystals, insol. ther and CS₂, sl. sol. hot alcohol. Its aqueous solution is fluorescent.—B'₂H₃AsO₄8aq. Prisms, v. sol. hot water (Hesse).—B'₄H₃AsO₄6aq (Sestini).—B'H₃AsO₂2aq.—B'H₁FeCy₂3aq (Dollfus, Herrory 1997). A. 65, 227). -B'H_aFeCy_a 1 aq: golden plates.— B'H_aPtCy_a aq (Wertheim, A. 73, 210). Crystals.— Directory,—Billoys. Lennon-yellow monoclinic crystals (W.).—B'HCyS aq. S. 18 at 20° (Hesse, A. 181, 48).—B'₃(HCyS)₂HgCl₂.—B'₄(HCyS)₂HgCy₂.—B'(HCr(CyS),(NH₃)₂)₂2aq. Formed by ppg. a solution of the acid sulphate with Reinenbelle acid (Cheiriceae). with Reinccke's salt (Christensen, J. pr. [2] 45, 366). Red crystals, v. sl. sol. hot water.—Nitro-prusside. S. 04 (Davy, Ph. [3] 11, 756).—Cyanurates B'H₂C₁N₂O₃ 9aq. [237]. Sl. sol. hot water (Claus, J. pr. [2] 38, 227).—B'(H₂C₁N₂O₃)₂ 7aq. [213°]. — Oxalates. —B',H₂C₂O₄ 6aq. S. 1 at 10°. Prisms (Hesse, A. 176, 218; cf. Regnault, A. 26, 37).—B'H₂C₂O₄ 3aq. [a] = -131°.—B'HOAc. [140°]. Long needles, v. sol. hot water (R.).—B'Cu(OAc)₂. Green crystals (Skraup, M. 2, 611).—Chloro-acetate B'C₂H₄CiO₂ 2½aq. S. 1·6 at 21° (Mazzara, G. 13, with Reinccke's salt (Christensen, J. pr. [2] B'C₂H₃ClO₂ 23aq. S. 1.6 at 21° (Mazzara, G.13, 525).—Di-chloro-acetate B'C₂H₂Cl₂O₂ 2aq. S. 24 at 22°.-Formate: colourless needles (Bonaparte, J. Chim. Med. 18, 680). - Valerate B'C,H₁₀O, 1½aq (Bonaparte, J. Chim. Med. 18, 680; 19, 330; Chatin, J. Ph. [4] 1, 268).—B'C,H₁₀O, (Stalmann, A. 147, 132; Schmidt a. Sachtleben, A. 193, 100). S. 9 in the cold; 2.5 at 100° (Wittstein, Repert. 87, 295; Landerer, 118°]. Yellow powder (Mazzara, G. 18, 868).-

N. Br. Arch. 119, 240). — Succinate B'C,H,O, 8aq. S. 1 at 10°. Prisms, v. sol. hot water.—Tartrate B'2C,H,O,2aq. Crystalline powder (Hesse, A. 243, 134; cf. Arppo, J. pr. 53, 2014). Bid NO. 2. (Posture J. 1853, 421). 334).—B'C₄H₄O₈aq (Pasteur, J. 1853, 421). The levo tartrate is more soluble than the dextro-tartrate, and has a different crystalline dextro- tartrate, and has a different crystalline form.—BC,H,(SbOH)O_a2aq. Resin (Clarke, B. 15, 1540).—Citrate B'₂C₆H₆O, 7aq. S. 11 at 12° (Hesse); 44 at 100³ (Mandelin, J. 1879, 796; Scribani, G. 9, 284).—B'₂C₂H₆O₄: minute prisms. S. 11 in the cold; 2·4 at 100°.—Bmall prisms. S. 16 in the cold, 2·6 at 100°.—Chloro-crotonate B'C,H,ClO₂[201°]. Sl. sol. ether (Daccomo, J. 1884, 1385).—Trich lograpsubants B'C, H Cl. O... [140°]. Trichlorocrotonate B'C,H,Cl₂O₂ [140°]. Trichlorocrotonate B'C₃H₃Cl₃O₃. Sl. sol.

Tri-chloro-lactate B'C₃H₃Cl₃O₃. Sl. sol.

B'C₃H<sub>Br₂O₃.

Noodles</sub> ether.—Di-bromo-pyruvate $B'C_sH_sB_TQ_s$. [93°] (D.). — Mucate $B'_2C_sH_{10}O_s$. Needles (Ruhemanna. Dufton, C.J.59,754).—Ben zoate B'HOBz. S. 27 at 10°. Small prisms. -Sali-B'HOBZ. S. 27 at 10°. Small prisms. - Sall-cylate B'C,H_O₂. S. 44 at 16°. S. (ether) 83 at 16°. Prisms (from alcohol). — Melitate B'C,H_O₁₂. Crystalline powder, v. sl. sol. cold water (Karmrodt, A. 81, 170). — Tannates B'(C₁₁H₁₀O₃), 4aq and B'(O₁₁H₁₀O₃), 8aq (Jobst, Ar. Ph. [3] 12, 331; Neumann, Fr. 28, 664).—
Macongate B'CH O. Crystala (Austen. Ph. Meconato B'C,H,O,. Crystals (Austen, Ph. [3] 3,1016).—Urate B'C,H,N.O,. Minute prisms. S. 117 in the cold, 2.7 at 100°. S. (alcohol of S.G. 823) 063 in the cold, 2.2 on boiling (Elderhorst, A. 74, 77; Andrew, Pharm. Viertelj. 10, horst, A. 74, 77; Andrew, Pharm. Viertelj. 10, 382). Doxtro-tropate. [187°]. — Lawotropate. [187°]. — Lawotropate. [188°] (Ladenburg, B. 22, 2590). Dextro-iso-propyl-phenyl-glycollate [193°]. S. 18 at 19°; S. (alcohol) 1·44 at 20°. [a]_b = -79° . — Lawo-iso-propyl-phenyl-glycollate [205°]. S. 09 at 15°; S. (alcohol) 54. [a]_b = -118° (Fileti, J. pr. [2] 46, 560). Compound with benzene B'C₄H_a. Needles (from benzene) (Oudemans, J. 1874, 867).—Compound with toluene B'C,H_a. Needles. — Compounds with phenol

Needles. — Compounds with phenol B'PhOH. Crystals (from alcohol). S. 25 at 16° (Romai Z 1917 200). (Romei, Z. [2] 5, 383; Jobst, N. R. P. 24, 193). — B'_H_Cl_PhOH 2aq: prisms. S.1 at 15° (Jobst a. Hesse, A. 180, 248).—B'H_SO_PhOH 2aq (Hesse, Hesse, A. 180, 248).—B'H.SO, PhOH 2aq (Hesse, Pharm. Zeit. 34, 191).—B'H.SO, PhOH aq. S. 147at15°. Prisms.—B'₂H.SO, PhOH 6aq (Cotton, Bl. [2] 24, 535).—Compound with tribromo-phenol B'C, H.Br.O. Silky needles (from alcohol) (Purgotti, G. 16, 528).—Compound with anethole B'₂C, H.O. 2aq. Monoglinic crystals (from ether). sl. sol. cold alcohol clinic crystals (from ether), sl. sol. cold alcohol (Hesse, A. 123, 382). Compound with (Hesse, A. 123, 382). Compound with eugenol B'C₁₀H₁₂O₂. [110°]. S. (ether) 8.5 at 10°. Long silky prisms (Hesse, A. 185, 329). — Compound with pyrocatechin B',C, H, O, H, SO, aq: colourless needles (Hesse, C. C. 1889, 519).—Compounds with resorcin C. 1857, 319).—Compounds with resortin B'C_uH_uO₂H_sO₄ aq: needles (Malin, A. 138, 77).

—B'₂C_uH_uO₂H_sSO₄ aq (Hesse).—Compound with phloroglucin B'C_uH_uO₂H_sSO₂aq: stellate groups of needles (Hlasiwetz, Z. [2] 1,613).

—Compound with oroin B'C_uH_uO₄H_sSO₄aq. Needles (Hlasiwetz a. Barth, A. 134, 290; 138, 77).-Compound with chloral B'C.HCl.O. [149°]. Amorphous, sl. sol. cold alcohol (Mazzara, G. 13, 270).—Compound with m-nitrobenzoic aldehyde B'C, H, (NO.). CHO. [118°].

nitro - camphor Needles. [c. 131°]. with Compound $B'(C_{16}H_{16}(NO_2)O)_2$ aq. Needles. [c. 131°]. [a]_D = +46° in a 2.7 p.c. alcoholic solution Cazeneuve, Bl. [2] 49, 97).—Compound with urea B'CON,H,H,Cl, 5aq. S. 6. Small prisms (Drygin, C. C. 1878, 622; 1881, 245).—Com-(Drygn, C. C. 18/8, 622; 1861, 245).—Compounds with quinidine B'C₂₀H₂₁N₂O₂2\$aq.—B'C₂₀H₂₁N₁O₂O₄H₃2aq (Wood a. Barret, C. N. 45, 6; 48, 4; Hesse, A. 243, 146).—Compound with hydroquinidine B'C20H26N2O2 2 aq: slender white needles, v. sl. sol. water, m. sol. ether.—Compounds with cinchonidine B'2C₁₉H_{2N}O. Rhombohedra, very slightly sol. ether (Hesse, A. 243, 131).

—B'7C₁₉H₂₂N₂O. Crystals (from alcohol).—
B'₁(C₁₉H₂₂N₂O)₄(H₂SO)₃ 20aq. S. 597 at 15°. Needles.—B'₂(C₁₉H₂₂N₂O)₄(C₁H₂O)₃ 6aq.—
B'₂(C₁₉H₂₂N₂O)₄(C₁O)₃ 18aq: crystals.—
B'₂(C₁₉H₂₂N₂O)(H₂CO)₃ 6aq (?). Long colourless needles.—Compounds with cupreine B'C₁₉H₂₂N₂O 4aq. [177°]. [a¹_D = -236°. Trimetric prisms (Howard a. Hodgkin, C. J. 41, 66; Hesse, A. 225, 98; 226, 242; 230, 72). Its solution in diluth H₂SO₄ shows blue fluorescence.—B'C.H.—N.OH. PtCl. 2aq: orange-red prisms. sol. water, m. sol. ether.-Compounds with Boltubal Hi unit; 11,354, shows the hadrened reserved.

B'C₁₉H₂₂N₂OH₄PtCl₃ 2aq: orange-red prisms.

B'C₁₉H₂₂N₂OH₃SO₄6aq: six-sided prisms. S. 3

at 100°.—B'C₁₉H₂₂N₂OC₄H₄O₄ 2aq: needles.

Acetyl derivative C₂₀H₂₁AcN₂O₂. [108°].

Formed by heating quinine with Ac₂O (Hesse,

A. 205, 317). Prisms, sol. alcohol and chloroform, sl. sol. ether. $[a]_{\rm p}=-54^{\circ}$ in a 2 p.c. solution in alcohol (of 97 p.c.) at 15°. $[a]_{\rm p}=-115^{\circ}$ in presence of 3HCl. Decomposed by alcoholic potash into quinine and HOAc.—B'H, PtCl, 2aq.

Potasi mod difficult 1103.0. $= 11_{2} \text{Tr} C_{9} \text{ 2ad}$. $-B'(\text{HaCl}_{4})_{2}$ aq: yellow flocculent pp. Propionyl derivative $C_{20}H_{22}(C_{3}H_{2})\text{N}_{2}O_{2}$. $[129^{\circ}]$. Six-sided prisms, sol. ether and alcohol. $[a]_{0} = -100^{\circ}$ in a 2 p.c. solution at 15° (Hesse). $-B'H_{2}\text{PtCl}_{6}$ 2aq. -

B'(HAuCl₄), 2aq: yellow amorphous pp.

Benzoyl derivative C₁₀H₂₃BzN₂O₂. Amorphous (Schützenberger, C. R. 47, 334).—
B'H.PtCl₆.

Methylo-iodide B'MeIaq or C₁₀H₁(OMe)N.C₂H₁,NMeIO (Grimaux, Bl. [3] 7, 573). [233°-236°]. Formed by boiling quinine (1 mol.) with MeI (6 mols.) in MeOH (Streeker, 4. 91, 164; Claus a. Mallmann, B. 14, 76). Formed also from cupreïne, NaOEt and MeI (Hesse, A. 266, 240). Colourless needles (from water), v. sol. hot water and alcohol. Not attacked by alkalis in the cold. Boiling KOHAq or moist Ag₂O converts it into methyl-quinine C₂₂H₂₂MeN₂O₂, an oil which yields an amorphous hydroiodide, crystalline B'H₂PtCl₈ aq (Hesse) or B'H₂PtCl₈ 2aq (Lippmann, M. 12, 512), and C₂₂H₂₂MeN₂O₂MeI aq crystallising in needles, decomposed at 218°.

B'MeI_s. Methylo-periodides methyto-personates B'Mel₃. Black needles (Jörgensen, J. pr. [2] 3, 145; 14, 261).—
B'2Me_I_4L_5O_4. Reddish-brown needles (from alcohol).—B'2Me_I_4H_5O_4. Brown plates.—
B'4Me_I_1_52H_5O_4. Almost black laminæ.—
B'4Me_I_22H_5O_4. Almost black needles with green lights.

green lustre.

Methylo-chloride B'MeCl aq. [182°]. Needles. B'2MeHPtCl, : orange prisms. [126°].

Methylo-bromide B'MeBr aq. Siender needles, sl. sol. cold water.

 $B'Me_2I_2$ 3aq. Di-methylo-di-iodide [158°-162°]. Formed by heating B'Mel with

MeI and MeOH in sealed tubes at 100°. Got also. together with B'MeI from cupreïne by the action of NaOMe followed by MeI (Hesse, A. 266, 240). Yellow tables (from water). Converted by cold NaOHAq, or better NaOH in MeOH, into a resin and a smaller quantity of a yellow crystalline body. S. (boiling MeOH) 1, melting about 280°, sol. acids and reppd. by alkalis as a jelly. Its solutions are yellow with green fluorescence. A similar body is got by the action of alkalis on the methylo-iodide of methoxy-quinoline (obtained from quinine). - B'Me2PtCla 2aq. -B'2MeAuCl.

Ethylo-iodide B'Etlaq (Howard, C. J. 26, 1180). [211°]. Trimetric needles (from ether), with very bitter taste. Lævorotatory.

—B'EtI,: black needles.

Ethylo-chloride B'EtCl 3aq. needles.—B'EtHPtCl_s: yellow pp. Ethylo-bromide B'EtBr 2aq.

Ethylo-sulphates B'2Et2SO4 8aq.-B'EtHSO, 2aq: needles, v. e. sol. water.

Ethylo-cyanide B'EtCN. [90°]. White necdles (Claus a. Merck, B. 16, 2746).

Di-ethylo-di-iodide B'Et₂I₂3aq. [115°]. Prepared by heating quinine with EtI and alcoholic potash (Skraup, M. 2, 610). Monoclinic tables, sol. alcohol, insol. ether.

Methylo-ethylo-di-iodide B'MeEtI, aq. [208°]. Formed by boiling B'MeI with EtI and alcohol (Claus, B. 14, 76). An isomeride [157°-160°] is got from B'EtI and MeI.

Benzylo-chloride B'C,H,Cl. Amorphous. B'(C,H,)HPtCl_a 2aq: crystalline (Mazzara, G. 13, 530).—B'(C,H,),PtCl_a: yellow powder.

Tolyl-quinine C₂₉H₂₂(C,H,)N₂O₂. Two modi-

fications are formed by heating quinine with otoluidine, and two from p-toluidine. The o and p (a) modifications form oils soluble in ether; the o and p (β) modifications form amorphous yellow powders insoluble in ether, soluble in chloroform and alcohol. B'aH,Cl,PtCl,aq: ycllow crystalline powders (Claus a. Bottler, B.

Quinopropyline C₂₄H₂₈N₂O₂. [164°]. Got by heating sodium-cuproïne with PrNO₄ and PrOH at 110° (Grimaux a. Arnaud, Bl. [3] 7, 310). White powder.—B'_H,SO, 1 aq. Silky needles. [224°]. $[a]_D = 229$ at 22° .

Quinoisopropyline [154°]. Formed in like manner from PrNO₃.—B'₂H₂SO₄aq. S. 3 at 10°.

 $[a]_D = 229^{\circ}$.

Quinoamyline C₂,H₃₂N₂O₂. [167°]. Formed from sodium-cupreïne and amyl chloride in amyl alcohol at 105°. Amorphous.—B'.H.SO, 2aq. Needles. S. 025 at 11°. Its solution in dilute H2SO, fluoresces.

Quinine sulphonic acid C20H23(SO3H)N2O2 [209°]. Formed by moistening quinine tetrasulphate with Ac2O, and treating the product with hot water (Hesse, A. 267, 141). Small white prisms (containing aq when air-dried).

[a]_D = -182° in a 2 p.c. solution containing HGl
(3 mols.).—H₂A'₂H₂PtCl₂ 8aq.

Quinine (Iso)-sulphonic acid

C20H23N2O2(SO3H). Formed from quinine and furning H2SO, (Hesse, A. 267, 138). V. sol. water, forming a slightly acid lavorotatory solution with blue fluorescence. Gives a dark-green colour with chlorine-water and NH,Aq.-HA'HAuCl,: yellow flocculent pp.

Apoquinine $C_{10}H_{22}N_2O_2$. [160°]. [α]_D = -178° in a 2 p.c. solution of alcohol (of 97 p.c.) at 15°. $[a]_p = -247^\circ$ in water containing 3HCl. Formed by heating quinine or cupreïne with HClAq at 140° (Hesse, A. 205, 323, 341; 230, 65). Amorphous powder (containing 2aq), sol. alcohol, ether, CHCl,, and hot water. A solution of its sulphate shows no fluorescence. Chlorine-water and ammonia give a dark-green colour in the cold. The sicoholic solution gives a dark brownish-red colour with FeCl₃. Fuming HClAq at 150° forms C, H, ClN, O, 2aq [160°], which gives the salts B'H,Cl, 3aq, B'H,PtCl, 2aq, and C₁₀H₂₁Ac₂ClN₂O₂ [184°]. Salts. — B'H₂PtCl₈ 3aq. — B'HI.

Small crystals (Lippmann a. Fleissner, M. 12, 331).

Acetyl derivative C10H20Ac2N2O2: amorphous powder, sol. ether and alcohol.

Isoapoquinine C₁₉H₂₂N₂O₂. [176°]. Formed by the action of boiling alcoholic potash on C, H22N2O23HI [238°] (v. QUININE, Reaction 8): Crystalline (Lippmann a. Fleissner, M. 12, 331). -B'H2PtCls aq: granules, sl. sol. water.

Isoquinine $C_{\infty}H_{24}N_2O_2$. [186°]. $[a]_D = -181^\circ$ in a 4 p.c. solution. Formed from the compound C₂₀H₂₄N₂O₂3HI [230°] (v. QUININE, Reaction 9) with alcoholic potash (Lippmann a. Fleissner, M. 12, 332). Needles (containing aq), v. e. sol. benzene, sl. sol. ether, v. sl. sol. boiling water. Coloured green by chlorine-water and ammonia. -B'HCl 2aq: needles, v. sol. water. -B'2HCl, m. sol. water.—B'II,PtCl_e: yellow crystalline pp.— B'2H2SO 10aq : needles, v. e. sol. water.— B'AgNO,: needles.

#-Quinine C₁₂H₂₄N₂O₂. [191°]. Formed, together with nichine C₁₂H₂₄N₂O₂ (?), by heating quinine hydroiddie with alcoholic potash B. 25, 2911). Lævorotatory. (Skraup, B'HCl, B'HNO, and B', HNO, all sl. sol. water and readily crystallised.

Chinene or Quinene v. QUINIENE, vol. ii. p. 181.

Homoquinine v. Cinchona Bases.

QUININIC ACID v. Methyl derivative of (B, 3)-OXY-QUINOLINE CARBOXYLIC ACID.

QUINISATIC ACID C.H. (NH.). CO. CO. CO. H. o-Amido-benzoyl-glyoxylic acid. Formed by oxidation of (Py. 1,2,3)-tri-oxy-quinoline with FeCl. (Bacyer a. Homolka, B. 16, 2219). Yellow prisms, v. sol. water. On reduction with zincdust and HOAc and exposure of the filtrate to the air it forms a dark-blue colouring matter.

Anhydride C,H, CO.CO. [255°-260°].

Formed by heating the acid at 120°. Red crystals, forming a red solution in alcohol. Readily combines with water, with re-formation of the acid. Dilute NaOHAq forms a yellow solution, very quickly becoming colourless.

NaOEt gives a body crystallising in indigo-blue needles. Gives an oxim $C_6H_4 < CO.C(NOH)$ erystallising in orange prisms [208°].

QUINITANNIC ACID. An acid occurring in cinchona bark (Schwarz, J. pr. 56, 76; cf. Pelletier a. Caventou, A. Ch. [3] 15, 837). Hygroscopic yellow mass. Its alkaline solutions absorb oxygen. Converted by boiling dilute acids into glucose and a brownish-red powder C28H22O14, which gives acetic and protocatechnic acid when fused with potash (Rembold, A. 143, 270).

QUINITE C.H.,O. i.e.

 $CH(OH) < CH_2 \cdot CH_2 \cdot CH(OH)$. Hudroguinons hexahydride. Formed, by reduction with sodium. amalgam in a current of CO, from the product of the action of dilute H.SO, on the dihydride of di-oxy-terephthalic ether (succinyl-succinic ether) (Bacyer, B. 25, 1037, 1840). V. sol. water and alcohol. Occurs in two modifications, trans [144°] and cis [90°], which yield acetyl derivatives melting at 106° (trans) and 32° (cis). Both acetyl derivatives boil at 244°. Quinite is converted by HBr into di-bromo-benzene hexahydride (trans [114°], cis an oil), which on heating with quinoline give oily benzene dihydride (81°), which forms a tetrabromide [182'].

QUINIZARIN v. DI-OXY-ANTHRAQUINONE.

Substances supposed to be QUINIZINE. derived from the hypothetical quinizine were subsequently found to be derivatives of phenyl-pyrazole. Thus oxy-methyl-quinizine is oxyphenyl-methyl-pyrazole (q. v.).
QUINOL v. Hydroquinone.

QUINOLIC ACID Coll, N.O. . Got by oxidation of cinchonine with HNO, (Weidel, A. 178, 91; B. 12, 1152). Woolly crystals, almost insol. water, v. sl. sol. alcohol, sol. HClAq. Alkalis give a transient crimson colour. Br and water at 180° give hexa-bromo-quinoline. HNO, at 170° forms cinchomeronic acid.—AgA'.—
11A'HCl.—H₂A'_H_PtCl_u: orange needles.

QUINOLINE C_yH₁N i.e.

CH:CH.C.CH:CH. Chinoline. Leucoline. Mol. CH:CH.C.N :CH. w. 129. (237.5°) (Young, C. J. 55, 485); (234°) (Schiff, B. 19, 566); (241° cor.) (Kretschy, M. 2, 80). S.G. 2 1.106 (O. de Coninck, Bl. [2] 37, 208); 2 1·108 (Skraup). S.V. 139·8 (Schiff). Vapour-pressure: Young. Heat of neutralisation: Colson, A. Ch. [6] 19, 409. Absorption of ultra-violet spectrum: Hartley, C. J. 41, 47. Occurs in coal-tar (Runge, P. 31, 68; Hofmann, A. 47, 76; 53, 427; 74, 15; Greville Williams, Tr. E. 21 [2]; [3] 377; O. Fischer, B. 16, 720; Jacobsen a. Reimer, B. 16, 1084).

Formation.-1. By distilling quinine, cinchonine, or strychnine with potash (Gerhardt, A. 42, 310; 44, 279; O. de Coninck, A. 42, 310; 44, 279; O. de Coninck, C. R. 94, 87; Bl. [2] 35, 296). Quinoline free from homologues is got from cinchonine by treatment with potash and CuO (Wyschnegradsky, B. 13, 2318). -2. By passing allyl-aniline over heated PbO (Königs, B. 12, 453).—3. From hydrocarbostyril (vol. i. p. 180) by treatment with PCl, and reduction of the product with HI and HOAc (Baeyer, B, 12, 1320) .- 4. By distillation of acrolein-aniline (Königs, B. 13, 911) .-5. By distilling anil-uvitonic acid with sodalime (Böttinger, B. 13, 2165).-6. By heating a mixture of nitro-benzene, aniline, glycerin, and H.SO, for three hours with inverted condenser (Skraup, M. 1, 316; 2, 139, 535).—7. By heating its carboxylic acids with lime. -8. By adding a few drops of NaOHAq to a cold dilute solution of equimolecular quantities of o-amido-benzoic aldehyde and acetic aldehyde (Friedländer a. Gohring, B. 16, 1833).—9. By heatingthe hydrochloride of quinoline tetrahydride with water and Hg(OAc), at 150° (Tafel, B. 25, 1623).—10. By fusing methyl-acetanilide with ZnCl, at 290° (Pictet, B. 23, 1903).

Preparation.—A mixture of aniline (38 pts.), glycerin (120 pts.), nitro-benzene (24 pts.) and H₂SO₄ (100 pts.) is heated with inverted condenser. Potash is then added, and the base distilled over with steam and fractionally distilled. It may be further purified by means of the acid sulphate and freed from aniline by oxidation or by treatment in acid solution with NaNO₂. The

yield is 60 p.c. (Skraup).

Properties.—Colourless liquid with peculiar odour, slowly becoming yellow. V. sl. sol. water, miscible with alcohol, ether, and GS₂. Quinoline is very hygroscopic, forming the hydrate (C,H,N),3aq, which becomes turbid on warming (Hoogewerff a. Van Dorp, R. T. C. 1, 1, 107). It is antiseptic, antipyretic, and antizymotic (Donath, B. 14, 178). Quinoline separated from solutions of its salts dissolves in excess of NH. or ammonium carbonate, but not in NaOH or Na CO. Iodine in KI gives a brown pp., insol. HClAq. Phosphomolybdic acid a yellowish-white pp., sol. NH,Aq. Picric acid a yellow amorphous pp. HgCl. a white pp., sol. HClAq. K2HgI, a yellow amorphous pp., changed to yellow needles on adding HCl. K.Cr.O, gives crystals, sol. excess. Potassium ferrocyanide an amorphous orange pp. (Donath, B. 14, 1769). On shaking with cone. CuSO, Aq a green pp. (CuSO, 4(CuO, H,), 4aq is got (Borsbach, B. 23, 924; cf. Lachovitch, M. 10, 884). NaOBr gives no reaction (Deniges, C. R. 107, 662). Quinoline forms very soluble crystalline compounds with NaHSO₃ (Brunck a. Graebe, B. 15, 1785). It combines with iodoform (Rhoussopoulos, B. 16.

Reactions.—1. On passing through a red-hot tube it yields (β)-diquinolyl (Zimmermann a. Müller, B. 17, 1965).—2. On boiling with sodium or sodium-amalgam it is converted into 'diquinoline,' which forms a scarlet hydrochloride which dyes silk a transient orange (Greville Williams, Pr. 31, 536; C. N. 37, 85).—3. Reduced by tin and HClAq to quinoline tetrahydride (244°) (Wyschnegradsky, Bl. [2] 34, 339).—4. Zincdust and NH, Aq or alcohol and sodium-amalgam give the tetrahydrides of quinoline and of diquinoline (Königs, B. 14, 99) .- 5. Oxidised by bleaching-powder or other hypochlorites to oxyquinoline (carbostyril) and chloro-oxy-quinoline (Erlenmeyer, B. 19, 489; Einhorn a. Lauch, A. 243, 342). Chlorine passed into its solution in HOAc forms tri-chloro-oxy-carbostyril.—6. On heating with SbCl, at 170°-400° and passing in chlorine, the products are C₂Cl₆ and C₆Cl₆ (Smith a. Davis, C. J. 41, 413).—7. Bromine (2 pts.) added to a mixture of quinoline (1 pt.) and water (3 pts.) forms the tetrabromide C.H.NBr., which crystallises from chloroform in very unstable red needles, and is converted, by heating with alcohol, into C_bH.NBr₂HBr [86°] crystal-lising in red prisms, insol. chloroform, v. sol. alcohol and ether, decomposed at 180° into HBr and bromo-quinoline-hydrobromide (Grimaux, Bl. [2] 38, 125; C. R. 95, 85). Bromine added to an ethereal solution of quinoline forms the dibromide C₀H₇NBr₂, yielding B'HCl [100°-105°] and B'HBr [88° cor.], which form red crystals (Claus a. Collischonn, B. 19, 2765).—8. KMnO. in alkaline solution forms pyridine dicarboxylic acid (Hoogewerff a. Van Dorp, R. T. C. 1, 1, 107; cf. Dewar, Pr. 26, 65). KMnO, and conc. H₂SO.

also give quinolinic acid. KMnO, and dilute H₂SO, form quinoline (B. 3)-carboxylic acid, diquinolyl being an intermediate product (Georgievitch, M. 12, 312).-9. H2SO, at 220° forms the (B. 4)-sulphonic acid; at 250° the (B. 2)-sulphonic acid is produced (Georgievitch, M. 8, 578, 641).-10. Oxygen passed through platinised asbestos containing quinoline and quinoline hydrochloride at 190 forms (a)-diquinolyl. Oxygen acting on a mixture of aniline and quinoline hydrochloride forms (Py. 3; B. 2)-diquinolyl and p-amido-(Py. 3)-phenyl-quinoline, while quinoline and o-toluidine hydrochloride are converted by oxygen into amido-phenyl-methyl-quinoline (Weidel, M. 8, 120; 9, 99).—11. p-Amido-phenyl-quinoline is also formed by heating quinoline hydrochloride with aniline.—
12. BzCl at 240° gives (β)-diquinolyl.—13.

Alloxan added to a solution of quinoline saturated with SO₂ forms B'C₂H₁N₂O₃SO₃H₂ orystallising in yellowish prisms (Pellizzari, A. 248, 150).—
14. SiCl, forms (C₉H₂N)₂SiCl, (Harden, C. J. 51, 40). SiF₄ forms (O₉H₂N)₂SiF₄, crystallising in Arguer Arguer (176).—15 needles (Comey a. Jackson, Am. 10, 176).—15. Nitroso-di-methyl-aniline and hydrogen cyanide form B'(C₆H₄(NO).NMo₂)₂HCy, crystallising in golden plates (Lippmann a. Fleissner, M. 6, 543). — 16. Glycerin dichlorhydrin forms (C₆H₄N)C₂H₄Cl, which is deliquescent and forms (B'C₈H₃Cl)₂PtCl, and B'C₈H₃AuCl, —17. Ethylene chloride at 100° forms B', C, H, Cl., orystallising in needles, yielding B', C, H, PtCl, (Rhoussopoulos, B. 16, 879).—18. Ethylene bromide (1 mel.) heated with quinoline (1 mol.) at 80° forms the brome-ethyle-bromide B'BrC₂H₄Br, crystallising from alcohol in needles and yielding B'ClC2H1Br and (B'ClC2H,Br)2PtCl, (Berend, B. 14, 1349). Ethylene bromide (1 mol.) with quinoline (2 mols.) at 40° forms B'C₂H₄Br₂ aq crystallising from alcohol in needles.—19. By heating quinoline (16 g.) with glycolic chlorhydrin (10 g.) and water (10 c.c.) for 3 days at 100° there is formed B'Cl.C.H.OH, crystallising from alcohol-ether in splendid prisms (Wurtz, Pr. 33, 452; C. R. 95, 263; 96, 1269). It is hygroscopic, v. sol. water and alcohol, insol. ether. On boiling with moist Ag.O it forms a caustic liquid that soon turns crimson. It yields B'(C.H.OH)AuCl,, crystallising in minute pointed hexagons, and also B'(C,H,OH)Cl6HgCl,, and (B'(C,H,OH)Cl),PtCl,. 20. Iodoform (1 mol.) heated with quinoline (2 mols.) for 8 days at 100° forms B', CH, I, crystallising in long needles [132°] (Rhoussoby AgCl into B'₂CH₂Cl₂ [168°], which gives B'₂CH₂PtCl₆. Iodoform (1 mol.) added to quinoline (3 mols.) in ethereal solution forms B'₃CH₄. crystallising in needles [65°], not affected by AgCl.—21. Chloro-acetic acid forms quinolinebetaine C₁₁H₃NO₂ [171°], which separates from alcohol in thick crystals (containing aq) and forms (C₁₁H₃NO₂).H.PtCl₄2aq (Gerichten, B. 15, 1254; Rhoussopoulos, B. 15, 2006).—22. Chloroacetic ether forms CuH, NCl. CH2. CO2Et crystallising in needles, v. e. sol. water, converted by lising in needles, v. e. sol. water, converted by moist Ag.O into quinoline. It yields the salt (C₁₃H₁₄NO₂)₂H₂PtCl_{e*} — 23. Chloral in ether forms C₂H₃NC₄HCl₄O aq [66°], crystallising from benzene (Rhoussopoulos, B. 16, 881). It is insol. water and decomposed by alcohol. It yields (C₂H₃NC₄HCl₄O aq).3PtCl₂ — 24. Reservin at 100° forms (C,H,N),C,H,O,, [102°], S. 25 in the cold (Hock, B. 16, 886). It crystallises from dilute alcohol in silvery plates, decomposed by HClAq.-25. Phthalic anhydride at 150° forms 'quino-phthalone' C17H2NO2 [235°] (Traub, B. 16, 297).

10, 297).

Salts. — B'HCl. [94°]. Deliquescent nodules, v. e. sol. alcohol, chloroform, and hot ether (O. de Coninck, Bl. [2] 37, 208).—

B'₂H₂PtCl₄ 2aq [225°] (Skraup); [218°] (Lellmann, A. 237, 323).—B'₂H₂PtCl₄ aq. S. 07 at 11°.—B'₂PtCl₄; insoluble powder.—B'₂H, PtCl₄. B'HAuCl, Canary-yellow needles.—B'HCdCl₃aq. —B'CdCl₂: white pp.—B'HgCl₂. Pearly plates (Bromeis, 4, 52, 136).—B'₂H₂H₂Cl₁2aq. [91°]. (Bromeis, A. 52, 136).—B.,H.,HgCl, 2aq. [91].
Monoclinic crystals.—B',H.,PdCl,. Crystals.—
B'H,SnCl, 2aq: needles.—B'HSnCl,. [127].
Thin needles.—B',H.,SnCl,. [above 240].—
B',H.,UrO,Cl,: yellow prisms.—B'SbCl,.—
B',HB,BiCl,.—B',H,ZnCl,.—B',ZnCl,.—
B'HSlCl,.—B',H,ZnCl,.—B',ZnCl,.—
B'HCHCl. [118] (Östermayer). Yellow pp., converted by ammonia into explosive B'NH2I (Dittmar, B. 18, 1613).—B'ICl. [160°]. Small white needles (Pictet a. Krafft, Bl. [3] 7, 73).— B'Br.HCl. [100°-105°]. Orange crystals (Claus, B. 19, 2766). - B'HMnCl3: rose-red needles (Borsebach, B. 23, 433).—B'HFeCl₄. [150°]. Formed by adding HCl to a solution containing quinoline and FeCl₃ (B.). Small needles, decomposed by boiling water.—B'₂CoCl₂: blue triclinic crystals.—B'_Cu(OAc), nearly black crystals.—B'Cu(OAc), nearly black crystals.—B'Cu(OAc), nearly black crystalline powder.—B'_ZnI_z: white powder, sl. sol. cold water.—B'₂ZnBr₂.—B'CdBr₂.—B'CdI₃..—B'₂CaI₃. —B'HgBr₂. [201²].—B'HgI₂. [168²].—B'Br₃. [92°-100°]. Red crystals (Lubavin, *J. R.* 18, 434).—B'Br., Red needles.—B'Hbr., [86°].—B'Br., HCl. [100° 105°].—B'I₂. [90°]. Formed by adding I to a solution of quinoline in CS. (Claus a. Istel, B. 15, 824). Dark-green lustrous needles.—B'HI₄. [67°]. Ppd. by adding I in KI to a solution of quinoline sulphate (Dafert, M. 4, 509). Green crystalline pp., sol. alcohole and benzene.—B'H.SO. [164°]. S. (alcohol) 2 at 18°; 11 at 78° (Krakau, J. R. 17, 364). Deliquescent crystals.—B'.H.Cr.O., [c. 167°]. Yellow needles (from hot water). S. 36 at 10°. -B'HNO3. Needles (from alcohol), v. sol. water, insol. ether. - B'2AgNO3: needles. -Whete, 1000, 100, Silky needles (from alcohol). Decomposes at Shky heedes (from account). Decomposes at 100° (Williams).—B'₂HgCy₂: long needles (from water) (H. Schiff, A. 131, 112).—Tartrate B'₃4C₄H_aO₃. [125°] (Friese, B. 14, 2805).—Cyanurate B'₃H₃C₃N₃O₃. Crystals (Claus, J. pr. [2] 38, 226).—B'HSCy(Cr(SCy)₃NH₃). Red lamelle, sl. sol. hot water (Christensen, J. pr. [2] 45, 365). - Picrate: [203]. - o-Oxybenzoate B'C,H,O,. Crystalline powder.

Alkylo-iodides. According to Decker (B. 24, 690) the alkylo-iodides B'RI are converted by alkalis into the hydroxides B'ROH which are readily oxidised by the air to crystalline oxy-v-alkyl-quinolines C₆H₄ CH:CH which melt about 100°. The cyanines may be considered as derived from one molecule of alkylquinoline and one molecule of oxy-v-alkyl-quinoline. The alkylo-hydroxides are converted by warming with alcohols R'OH into compounds B'ROR'.

Methylo-chloride B'MeClaq. On heating with ZnCl, at 180° it is converted into a base C₂₀H_mN₂O [72°-75°] (above 360°), crystallising in large trimetric prisms, and yielding a hydrochloride [112°] and the double sults $C_{20}H_{-20}N_{.}OHAuCl_{+}$ and $(C_{20}H_{-20}N_{.}O)_{.}H.PtCl_{+}$ [190°] nearly insol. water (Ostermayer, B. 18, 593).—B',Me,PtCl_{+} [230°]. Yellow plates.—B'MeAuCl_{+} (20°) — B'McCllCl. [112°]. Formed by adding ICl to the methylo-chloride in aqueous solution. Large yellow plates.

Methylo-tribromide B'MeBr₁. [123°]. Orange-red plates. Converted by picric acid solution into B'MeOC₁H₁(NO₂)₂ [164°]. Methylo-iodide B'MeI. [73°] (La Coste, B. 15, 192; Pictet, B. 23, 1903). Large crystals. Converted by moist Ag₂O into a strongly alkaline solution of the hydroxide B'MeOH. Aqueous NaOH in the cold converts B'McI into the oxide B'2Me2O, a white powder, reconverted by HI into B'MeI (possibly oxy-v-methyl-quinoline) (La Coste; Claus, B. 15, 475; Bernthsen, B. 18, 29; Decker, B. 24, 690). Potash, even in cold aqueous solution, forms an oil probably containing methyl-quinoline (lepidine) (Skraup, Sitz. I'v [2] 81, 593). By the action of KOH on a mixture of B'MeI (2 pts.) and the methyloiodide of (Py. 1)-methyl-quinoline (1 pt.) there is formed di-methyl-cyanine iodide C21H19N2I, crystallising in oblong green tablets, [291], sl. sol. water, forming a reddish-blue solution (Hoogewerff a. Van Dorp, R. T. C. 2, 317; 3, 337). The alcoholic solution is violet, with green fluorescence. Its solution in acids is yellow. The aqueous solution is decolourised by CO, the colour re-appearing on boiling. corresponding $C_{21}H_{19}N_{2}Cl$ E_{30} [c. 300] forms $C_{21}H_{18}N_{2}Cl$ (H1*Cl.) and as yellow crystals. Quinoline methylo-iodide is oxidised by alkaline K₃FeCy₆ to oxy-methyl-quinoline or ν-methylquinolone C_6H_1 $\stackrel{CH}{<}$ $\stackrel{:CH}{NMe}$ $\stackrel{:CH}{CO}$ [72°] (324° at 728 mm.) (Decker, J. pr. [2] 46, 31; cf. Bernthsen a. Hess, B. 18, 37, who took it for di-methyl-diquinolyl; Ostermayer, B. 18, 591). This body is also got from carbostyril and MeI (Friedlünder a. Müller, B. 20, 2009). It deliquesces with water, forming an oil. Hydrochloride

 $[112^{\circ}]$ Ethylo-chloride B'EtClaq. [93°]. Large trimetric tables (Claus a. Tosse, B. 16, 1277).—

B'₂Et₂PtCl₆. [226°]. Yellow pp. E'thylo-bromide B'EtBr aq. metric tables. By the action of (Py. 1)-methylquinoline ethylo-bromide it is converted into diethyl-cyanine bromide C22H23N2Br or C23H22N2Br, crystallising in small needles, not melted at 290°. forming a blue solution in alcohol.

Ethylo-iodide B'EtI. [118°] (Spaltcholz, B.16, 1851); [160°] (Hoogewerff a. Dorp, R. T.C. 2, 321). Monoclinic crystals At 280° it yields (γ)-ethyl-quinoline and di-ethyl-quinoline (Reher, B. 19, 2996). Moist Ag₂O forms strongly alkaline B'EtOH, which is sol. water and resinified by atmospheric oxidation. On heating B'EtI (2 pts.) with (Py. 3)-methyl-quinoline ethylo-iodide (1 pt.) and alcoholic potash, there is formed di-ethyl-isocyanine iodide C.H.N.I

(Hoogewerff a. Van Dorp, R. T. C. 3, 344) or C₂₂H₂₈N₂I (Spalteholz, B. 16, 1851). This body forms lustrous green prisms (containing haq or } EtOH or ½ EtOH 1 haq) melting at 152°. It is insol. ether, sl. sol. water, and forms a crimson solution in alcohol. By the action of KOH on a mixture of B'EtI and (Py. 1)-methyl-quinoline ethylo-iodide there is formed di-ethyl-cyanine iodide C₂H₂N₂I [273°], crystallising in green prisms (Hoogewerff a. Van Dorp, R. T. C. 2, 317). Quinoline ethylo-iodide is oxidised by alkaline K₃FeCy₆ to C₈H₄ CH :CH NEt.CO (Decker, J. pr. [2] 47, 36), which body is also got

from carbostyril and Etl (Friedländer a. Weinberg, B. 18, 1530). Solidifies at -20° . $C_oH, NEtIHgCy_x$. [138°]. Needles (from water). $C_oH, NEtBrHgCy_z$. [155°]. Crystals (from alcohol) (Claus, A. 269, 271).

Ethylo-nitrate B'EtNO₃. [89° unc Large trimetric crystals (Claus, B. 16, 1277). [89° uncor.].

Propylo-chloride B'PrCl aq. [c. 95°] (hydrated); [135°] (anhydrous). Colourless crystals (Claus a. Collischonn, B. 19, 2504). Crystallises from chloroform in prisms (containing CHCl₂) [79°]. V. e. sol. water.—B'PrClBr₂. [85° uncor.]. Orange-red radiating crystalline mass. -B'BrClI.

[62°]. Brown crystals.

Propyl-bromide B'PrBr 2aq. [66° uncor.] (hydrated); [148° uncor.] (anhydrous). Formed by heating quinoline with PrBr and a little (10 p.c.) alcohol at 100°. Tables, v. e. sol. water and alcohol. The anhydrous crystals (obtained from absolute alcohol) are very deliquescent. Crystals obtained from chloroform (containing CHCl₃) melt at 65°-129°.—B'PrCl_Br. [c. 60°]. Formed by passing dry Cl into a solution of B'PrBr in chloroform. Small sulphuryellow plates. Unstable.—B'PrBr₄. [93°]. Formed by adding Br to the aqueous or alcoholic solution of B'PrBr. Triclinic garnet-red crystals. Yields (Py. 3)-bromo-quinoline on heating. B'PrBrl₂. [60° uncor.]. Formed by evaporating a mixture of I in ether and B'PrBr in alcohol. Lustrous brown needles. - B'PrBrI. [49°]. Slender, nearly black, needles with green

Propylo-iodide B'PrI. [145°]. yellow crystals. Not hygroscopic. Crystallises from chloroform with CHCl3, partially melting at 92°. — B'PrCl.I. [87°]. Sulphur-yellow needles.—B'PrCl.I. [145°]. Converted by long boiling with water into B'PrCl.—B'PrBr.I. [77°]. Triclinic orange tables.—B'PrBr.I. [480_580] Very unstable orange powder.—B'PrI₃. [62°]. Very stable bronzy brown prisms.—B'PrI₄. [50°]. Stable tables.

Iso-amylo-chloride B'C_sH₁₁Cl.—

 $B'_2(C_bH_1)_2P'Cl_s$. [220°]. Yellow crystalline pp. Iso-amylo-bromide B'O₂H₁₁Braq. [87°] (hydrated); [140°] (anhydrous) (Claus a. Tosse, B. 16, 1277)

 $B'C_3H_{11}I$. Isoamylo-iodide B'C,H,I. [185°]. Yellow monoclinic needles (Perkin, C. J. 14, 246; Nadler a. Merz, J. pr. 100, 129; Greville Williams, C. N. 1861, 219; Hoogewerff a. Van Dorp, R. T. C. 2, 40; 3, 352; Arzruni, R. T. C. 4, 62). Does not form cyanine on treatment with potash unless it contains the isoamyloiodide of (Py. 1)-methyl-quinoline, in which case di-isoamyl-cyanine iodide C₂₂H₃₅N₂I

[c. 100°] is produced. This body crystallises in lustrous green monoclinic crystals (containing $1\frac{1}{2}$ aq); a:b:c=2:379:1:1:669; $\beta=88^\circ$ 45'. It also forms brass-yellow crystals. It is very hygroscopic, nearly insol. ether, sl. sol. CHCl, acetone, and isoamyl alcohol. It is v. sol. alcohol, forming a deep-blue solution. Iodine converts it into C29H35N2I3 [189°], which is sl. sol. alcohol, v. sol. acetone, forming blue solu-tions. The solution of di-isoamyl-cyanine iodide in HClAq is colourless, and deposits on evaporation colourless scales of C29H35N, I2HCl. evaporation colouriess scales or $C_{2p}H_{2p}N_{2}L2HCI_{1}$, which at 100° gives off HCl, leaving bronzed $C_{2p}H_{13}N_{2}IHCI$. Moist Ag₂O forms uncrystallisable $C_{2p}H_{23}N_{2}(OH)$. Alcohol and AgCl produce $C_{2p}H_{23}N_{2}(OI)$ and corpusing in long blue prisms, and yielding $(C_{2p}H_{2q}N_{2}CI)_{2p}PtCI_{2p}$. Alcohol and AgNO₃ give $C_{2p}H_{3p}N_{2}(NO_{3})$ aq, which forms between $C_{2p}H_{3p}N_{2}(NO_{3})$ and $C_{2p}H_{3p}N_{2}(NO_{3})$. lustrous needles giving a blue aqueous solution and yielding colourless C₂₂H₂₃N₂(NO₃)2HCl and blue C₂₂H₃₃N₂(NO₃)HCl. Alcoholic ammonium sulphide converts the nitrate into reddish-yellow monoclinic crystals of C₃₈H_{s8}N₄S₃O₂, which yields $C_{a_3}H_{a_5}N_1S_2Cl_42PtCl_4$ as an orange pp. (N. a. M.). H.SO, converts di-isoamyl-cyanine iodide into $(C_{29}H_{35}N_2)_2SO_4$ 2aq, crystallising from hot water in blue needles.

Allylo-iodide B'C, H,I. [177.5°] (Pictet,

C. R. 95, 300).

Benzylo-chloride B'C,H,Cl 3aq. [65°]. iclinic tablets. It crystallises also as Triclinic tablets. B'C,H,Cl 2aq [130°] in trimetric crystals (Claus, B. 13, 2045; 16, 1279; 18, 1305). V. sol. water and alcohol, insol. ether. KMnO, oxidises it to benzyl-o-amido-benzoic acid and its formyl derivative. By treatment with KOH or Ag.O it is converted into a strong base, v. sol. water. Excess of KOH ppts. an oil which turns red in air. The benzylo-hydroxide yields quinoline on distillation (Bernthsen a. Hess, B. 18, 35). Mercuric chloride yields a crystalline pp. [142°].—(B'C,H,),PtCl_s. [246°]. Yellow pp.—B'C,H,ClBr₂. [92°]. Crystalline.—B'C,H,BrCl_s. [80°]. Yellow needles.—B'C,H,Br,. [100°]. Orange prisms.—B'C,H,BrI,. [110°]. Dark-[100°]. violet needles.

Phenacylo-bromide B'Br.CH.Bz. [1150-165°]. Needles, v. sol. water and alcohol, v. sl. sol. ether (Bamberger, B. 20, 3340).—B'HNO₃.

References .- AMIDO-, BROMO-, BROMO-AMIDO-, Bromo-nitro-, Chloro-, Chloro-nitro-, Iodo-, Nitro-, Oxy-amido-, and Oxy- quinolines.

Diquinoline v. DIQUINOLYL.

Isoquinoline C₀H,N i.e. C_cH₄<CH:OH. [23°].

(241° i.V.). Occurs, as well as quinoline, in coal-tar (Hoogewerff a. Van Dorp, R. T. C. 4, 125, 285; 5, 305).

Formation.—1. By the action of HI at 230° or of zinc-dust in a current of H at a low red heat upon the di-chloro- derivative [123°] obtained by the action of POCl, on the imide of $C_6H_4 < CH_2CO NH$ o-carboxy-phenyl-acetic acid (Gabriel, B. 18, 3470; 19, 1656, 2361; Le Blanc, B. 21, 2299).—2. Together with di-isoquinolyl, which yields B'₂H₂PtCl₄ [177°] by distilling henzylidone-ethyl-amine (Pictet a. Popovici, B. 25, 733).—3. By heating isocarbostyril or its

carboxylic acid with zinc-dust in a current of

hydrogen (Bamberger a. Kitschelt, B. 25, 1146; |

Zincke, B. 25, 1497).

Properties. - Hygroscopic tables. **Vialda** phthalic and cinchomeronic acids on oxidation by KMnO₄. Tin and HClAq give a tetra-hydride. Forms crystalline compounds with HgCl₂ and AgNO₄. Bromine in ether gives C₂H₂NBr₂, [82°], which forms very unstable C.H.NBr.HBr. [c. 133°], converted at 200° into bromo-iso-

[c. 133°], converted at 200° into bromo-isoquinoline [40°] (Edinger, J. pr. [2] 43, 191).

Salts.—B'₂H.PtCl₂2aq. [264°]. Reddishyellow crystals.—B'HAuCl₄. [225°]. Yellow needles.—B'HgCl₂. [165°]. White needles.—B'HgCl₂. [165°]. White needles.—B'HgCl₂. [165°]. Yellow needles.—B'H₂Cr₂O₇: needles.—Picrate B'C₄H₃N₅O₇. [223°]. Yellow needles.

Methylo-iodide B'MeI aq. [160°]. Flat yellowish needles. Treatment with AgCl and yellowish chloride gives (R'MeCl) PtCl [240°].

platinic chloride gives (B'MeCl),PtCl, [240°] (Claus, J. pr. [2] 38, 492). KOHAq added to B'MeI forms an oily base which yields (B'MeCl),PtCl, 6aq. Özidised by alkaline K_xFeCy, to ν -methyl-isoquinoline C,H₄ CH:CH [40°] (319°), sol. water, and yielding B'H,PtCl₆ 2aq (Decker, J. pr. [2] 47, 37). Ethylo-iodide B'EtI. [147°]. Yellowishyielding

red tables. Yields ethyl-phthalimide on oxida-

tion. Gives (B'EtCl), PtCl.

Benzylo-chloride B'C,H,Cl. water and alcohol, sl. sol. ether (Goldschmidt, M. 9, 678). Yields benzyl-phthalimide [115°] on oxidation by KMnO, in a solution kept neutral by HCl.

Phenacylo-bromide B'BrCH2Bz. [205°]. Formed from isoquinoline and ω-bromo-acetophenone dissolved in benzene (G.). Prisms (from alcohoi), v. sol. water. AgNO3 forms B'NO_s(CH₂Bz) crystallising in needles.

Diquinoline v. DIQUINOLYL.

QUINOLINE (B. 1)-CARBOXYLIC ACID

ÇH:C(CO₂H).C.CH:ÇH Quinoline ana-carb-CH:CH ___ C-N:CH oxylic acid. Quinoline-m-carboxylic acid.

[357°].

Formation.-1. Together with a smaller quantity of the (B. 3)-acid by heating m-amidobenzoic acid with glycerin, H.SO., and m-nitrobenzoic acid (Schlosser a. Skraup, M. 2, 518; 7, 519) .- 2. By saponifying its nitrile, which is got by distilling sodium quinoline (B. 1)- or (B. 4)sulphonate with KCy (Bedall a. Fischer, B. 14, 2574; 15, 683, 1980).—3 By heating quinoline (B. 1,4)-di-carboxylic acid (Skraup a. Brunner, M. 7, 153).

Properties .- White crystalline powder, sol. dilute acids and alkalis, insol. ether and benzene,

v. sl. sol. water and alcohol.

Salts.-HA'HCl 11aq: white needles .-(HA'), H, PtCl_s: yellow plates. — CaA', 2aq. — CaHA', 6aq: needles. — HO.CuA' 2aq: minute violet plates, insol. water. - AgA': crystalline pp.

Nitrile C₉H₈N.CN. [88°]. (above 360°). Formed as above and also from (B. 1)-amidoquinoline by diazotisation and treatment with CuCy₂ (Freydl, M. 8, 581). Crystals, sl. sol. Aq. Tetrahydride C₁₆H₁₁NO₂. [147°]. Formed

by reducing the acid with tin and HCl (Fischer by leading active with the late (Present a. Körner, B. 17, 765). Yields a crystalline nitrosamine C₁₀H₁₀N₂O₃. [186°]. ψ-Isomeride C₁₀H₁NO₃. [338°]. Perhaps

identical with the preceding. Formed by warm-

ing quinoline with m-amido-benzoic acid, nitrobenzene, glycerin, and H,SO, (Lellmann a. Alt, A. 237, 318). Got also by saponifying its nitrile which is formed by fusing sodium quinoline ψ-ana-sulphonate with KCy in a current of hot air (Lellmann, B. 20, 1449; 21, 397). Snowy powder. HA'HCl aq. H,A',H,PtCl,: needles.-ZnA'2.-AgA'.

Tetrahydride C10H11NO2. [147°]. by reducing the acid or bromo-quinoline carb-

oxylic acid with tin and HClAq.—HA'HCl aq.

Nitrile .C₉H₄N.Cy. [89°]. Needles (containing 1½aq), melting at 70°. Effloresces, and then contains and melts at 74.5°. —
B'₂H₂PtCl₈: needles.

Quinoline (B. 2)-carboxylic acid
CO₂H.C=CH.C.CH:CH
CH:CH.C-N:CH
CH:CH.C-N:CH

acid. [291°]. Formed by heating p-amidobenzoic acid with glycerin, p-nitro-benzoic acid, and H₂SO₄ (Schlösser a. Skraup, M. 2, 518). Formed also by heating its nitrile with HClAq at 140° (Fischer a. Wittmack, B. 17, 440). Thick prisms, sl. sol. hot water, g. sol. acids and alkalis.—HA'HCl.—(HA')₂H₂PtCl_g.—CaA'₂ 2aq. -AgA'.

Nitrile C, H, N2. [131°]. Formed by distilling potassium quinoline p-sulphonate (from sulphanilic acid) with KCy. Needles, forming a red solution in HClAq.

Quinoline (B. 3)-carboxylic acid

CH:CH.C.CH:CH Quinoline-m-carb-CO.H.C=CH.C-N:CH

oxylic acid. [248°].

Formation. -1. By oxidation of (B)-diquinolyl with CrO, and HOAc (O. Fischer a. Loo, B. 17, 1901; 19, 2473).—2. By oxidation of (B. 3)-methyl-quinoline (Skraup a. Brunner, M. 7, 142).-3. By heating the stannochloride of camido-phthalic acid with c-nitro-phthalic acid, glycerin, and H.SO. (Tortelli, G. 16, 367).

Properties.—Needles (from water).

Salts.—Cu(OH)A' aq.—AgA'.—HA'HCl aq: triclinic prisms.—H.A',H.,PtCl_s: orange prisms.

Quinoline (B. 4)-carboxylic acid CH:CH — C.CH:CH Ouinoline Quinoline-o-carboxylic CH:C(CO₂H).Ö—N:CH

acid. [187°].

Formation. -1. By heating o-amido-benzoic acid with o-nitro-benzoic acid, glycerin, and H₂SO₄ (Schlosser a. Skraup, M. 2, 518).—2. By Lelimann a. Reusch, B. 22, 1392).—2. By heating its nitrile with conc. HClAq at 150° (Lelimann a. Reusch, B. 22, 1392).—3. Together with the (B. 1)-isomeride, by heating quinoline (B. 1,4)-di-carboxylic acid (Skraup a. Brunner, M. 7, 153).

Properties.—Needles, m. sol. cold water and alcohol. FeSO, gives a purple colour in neutral solutions. — HA'HCl: yellowish prisms. — H₂A'₂HCl: golden prisms. — H₂A'₂H.QtCl₃: orange needles.—CaHA's: needles. - AgA': pp.

Methylo-iodide HA'MeI. Slender yellow needles (La Coste, B. 15, 196). Moist Ag₂O forms a solution of the hydroxide which reproduces HA' on evaporation.

Nitrile C₁₀H₈N₂. [84°]. Needles. Yields B'₂H₂PtCl₈, crystallising in orange needles.

Quinoline (Py. 1)-earboxylie acid

C₆H₄C(CO₂H):CH Cinchoninic acid. [254°]. Formation .- 1. By exidation of cinchenine.

cinchonidine. cinchotenine, cinchotenidine, cinchonitine, and cincholepidine (Weidel, A. 173, 84; M. 3, 79; Skraup, A. 201, 303; M. 2, 601; Forst a. Böhringer, B. 14, 436; Schnider-schnitsch, M. 10, 55).—2. By oxidation of (Py. 1)-methyl-quinoline (lepidine) (Hoogewerff a.

Van Dorp, R. T. C. 2, 11).

Preparation.—By boiling cinchonine with nitric acid of S.G. 1.3 (Königs, B. 12, 97; Claus,

B. 18, 362).

Properties.-Slender needles (containing aq) (Skraup) or triclinic crystals (containing 2aq) a:b:c = .746:1:.817; $a = 81^{\circ} 37'$; $\beta = 120^{\circ} 2'$ $\gamma = 86^{\circ} 37'$ (Muthmann a. Nef, B. 20, 637). By slow evaporation of an aqueous solution it is obtained in monoclinic forms (containing 2aq), $a:b:c = \cdot 276:1: \cdot 533; \beta = 98^{\circ} 3'$ (Ditscheiner, A. 173, 84; Claus, B. 20, 1604). V. sl. sol. water and alcohol, insol. ether. Yields quinoline on distillation with lime, and oxy-quinoline carboxylic acid on fusion with potash. On heating with conc. H2SO, it yields quinoline p-sulphonic acid (Georgiovitch, M. 8, 644). Sulphuric acid and P₂O₃ at 1.75° gives an (a)-sulphonic acid C_bH₂N(SO₃H)(CO₂H), which forms very bitter triclinic crystals (containing aq), nearly insol. tricinic crystals (containing aq), nearly insolcold water, giving the salts (NH₁)₂Λ" 2aq, CaA" 2½ aq, BaA" 3aq, PbA" aq, and CuA" aq. H₂SO₄ and P₂O₅ at 260° give a (β)-sulphonic acid C₁₆H₂NSO₅ crystallising in bitter needles (containing 2aq), m. sol. cold water, forming the salts (NH₁)HA" 2aq. BaA" aq, and PbA" 4aq (Weidel, M. 1, 845; 2, 565; Georgievitch, M. 8, 644).—KMnO₄ forms pyridine tricarboxylic acid.

Salts .- HA'HCl .- (HA') 2H2PtCla: triclinic prisms.—HA'HClICl 2aq (Dittmar, B. 18, 1618). —HA'HNO₃. — (HA')₂H₂SO₄: long prisms. — KA' ½aq. — CaA'₂ 1½aq: prisms (Weidel). —CaA'₂ (Skraup). —CuA'₂: dark-violet plates, sl. sol. hot water .- AgA': crystalline pp.

Dibromids C, H, NO, Br, [188°]. Long red needles, decomposed by boiling water (Claus, B. 18, 1307).

Di-iodide C₁₀H,NO_.I₂. [c. 242°]. Steelblue tables, nearly insol. cold water.

Ethyl ether EtA'. [13°]. Trimetric crystals, v. sl. sol. water, v. sol. ether, sl. sol. alcohol (Van der Kolf a. Van Leent, R. T. C. 8, 217).—EtA'HgCl. [153°]. Small needles.— (EtA')₂H₂PtCl_s. [204°]. Orange-yellow needles.

A mide $C_{10}H_{\rm w}N_{\rm s}O$. [181°]. Needles, v. e. sol. hot water. $-B'_{2}H_{2}PtCl_{\rm e}$. [250°-255°].

Benzylo-bromide C10H, NO2C, H, Br. [130°]. Silky needles, v. sol. water and alcohol, insol. ether. By heating the aqueous solution or by treatment with alkalis, it is converted, by loss of HBr, into the anhydride CO-O, which crystallises in dimetric tables (containing 3aq) [84°] and has a bitter taste. This anhydride is converted by alkalis into CaH, N(C,H,)CO2H [218°] (Claus a. Muchall, B. 18, 363, 1310).

Tetrahydride C10H11NO2. Formed from cinchonic acid, tin, and HClAq (Weidel, M. 2, 29; 3, 61). Yields a nitrosamine [137]. — B'HCl 1; aq: monoclinic crystals; a:b:c= ·932:1:1·942; $\beta = 90^{\circ}$ 41'. Heated with H₂SO, it gives disulpho-cinchonic acid and methylquinoline (cincholepidine). -B', H, PtCl.

Acetyl derivative of the Tetrahydride C₁₀H₁₀AoNO₂. [164°]. Trimetric crystals; a:b:c=848:1: 569. Sl. sol. cold water and al-

cohol.—CaA'₂ 2aq: minute needles.
Quinoline (Py. 2)-carboxylic acid
C₈H, CH: CO₂H.
[273°].

Formation .- 1. By heating acridinic acid at 125° (Graebe a. Caro, B. 13, 100). - 2. By oxidation of (Py. 2)-ethyl- (or methyl-) quinoline (Riedel, B. 16, 1609; Doebner a. Miller, B. 18, 1643).

Properties.—Slender needles, sol. alcohol, sl. sol. cold water. Dissolves in acids and alkalis. Oxidised by KMnO, to pyridine tricarboxylic

Salts .- HA'HCl: needles, v. sol. water .-Picrate: [216°]. -CuA'2. - AgA': small prisms. (HA'), H.PtCl.: orange needles.

Quinoline (Py. 3)-carboxylic acid

CH:CH Quinaldinic acid. [156°]. Formed from (Py. 3)-methyl-quinoline by oxidation with chromic acid mixture (Doebner a. Miller, B. 16, 2472). Got also by oxidation of (α)-diquinolyl (Weidel a. Strache, M. 7, 300). Needles (containing 2aq), v. sol. hot water, acids, and alkalis. —CuA'_2aq. —CaA'_2.—AgA': amorphous precipitate.—AgHA'_2HNO, aq: silky needles. — HA'HCl aq. — (HA')_2H_2PtCl, 2aq. — (HA')_4L_2Cr_O,: sparingly soluble red crystals.

Quinoline (B. 1,4)-di-earboxylic acid CH:C(CO₂H).C.CH:CH [270°]. Formed by $CH:C(CO_2H).C.N = CH$ heating amido-terephthalic acid with glycerin, H.SO., and o-nitro-phenol (Skraup a. Brunner, M. 7, 147). Long needles (containing 2aq), v. sl. sol. cold water. Salts.—HA'HCl 1 dq.—(HA').H.PtCl₈.—Cu₃A'₂(HO)₂ aq: bluish pp.
Quinoline (Py. 2,3)-dicarboxylic acid

 $C_0H_1 < CH:C.CO_2H$ $N=C.CO_2H$ Acridinic acid. Formed by oxidation of acridine with KMnO, (Graebe a. Caro, B. 13, 99). Long needles (containing 2aq), sl. sol. cold water, v. sol. alcohol. Does not combine with acids. Decomposed by heat into CO, and a mono-carboxylic acid [2750]

Quinoline (Py. 1,3)-dicarboxylic acid

C₀H, C(CO₂H): CH [246°]. Formed from (Py. 3)-styryl-cinchoninic acid by oxidation with alkaline KMnO, (Doebner a. Peters, B. 22, 3009). Needles, sl. sol. cold water and alcohol.—CuA" aq.—Ag₂A": white pp.

Quinoline (a) dicarboxylic acid C₀H₅N(CO₂H)₂. [270°]. Formed by saponifying its nitrile. Slender needles (containing aq), sl. sol. alcohol and ether.

Nitrile C,H,NCy2 [222°]. Formed by heating potassium quinoline (a)-disulphonate with KCy (La Coste a. Valeur, B. 20, 99). Needles (from alcohol), insol. Aq, v. sol. alkalis.

Quinoline (B. 2, Py. 3)-dicarboxylic acid CO₂H.C=CH.C.CH:CH [275°-280°]. ĊH:CH.Ö.N=C.CO,H

Formed by oxidation of benzylidene-quinoline (B. 2)-carboxylic acid (Von Miller, B. 23, 2261).

References.—Bromo-, Nitro-, and Oxx-QUINOLINE CARBOXYLIC ACIDS.

QUINOLINE (Py. 8).CARBOXYLIC ALDE-HYDE C,H,N.CHO. [71°]. Formed by oxida-

tion of (Py. 3)-quinolyl-acrylic acid with KMnO. (Miller a. Spady, B. 18, 3404; 19, 130). Monoclinic plates (from ligroïn), sl. sol. water. Reduces ammoniacal AgNO₃. Yields a phenylhydrazide C₁₈H₁₃N₂ [198°] crystallising in yellow plates.

QUINOLINE HYDRIDES.

Polymeride of quinoline dihydride C18H18N2. [162°]. Formed by reducing quinoline with zinc-dust and HOAc, zinc-dust and NH₃, zinc and HClAq, or alcohol and sodium-amalgam (Königs, B. 12, 101, 252; 14, 99; Wyschnegradsky, B. 12, 1481; Lellmann, B. 22, 1337). Amorphous powder. Its solution in conc. HClAq is ppd. by water and by NaOAc. Yields a nitrosamine.

Quinoline dihydride (?). (220°-226°). Found in small quantity among the products of the action of KOH on quinoline (O. de Coninck, C. R. 94, 87).—B'₂H₂PtCl₆.

Quinoline tetrahydride C.H., N i.e.

C₈H₄<CH₂,CH₂. [c. 10°]. (240° uncor.).

Formation.-1. By reduction of quinoline with zinc or tin and HClAq (Wyschnegradsky, Bl. [2] 34, 339; B. 12, 1481; 13, 2400), with zinc-dust and NH3Aq, with alcohol and sodiumamalgam (Königs, B. 14, 99; 16, 727), or with sodium (Weidel a. Glaser, M. 7, 328).—2. From carbostyril, alcohol, and Na (Knorr a. Klotz, B. 19, 3302).

Properties .- Needles, sol. water, volatile with steam. Secondary base. ICl forms in presence of HCl an amorphous pp. Colla LN (Dittmar, B.

18, 1619).

Reactions .- 1. The vapour passed through a red-hot tube yields indole and quinoline,—2. Chromic acid mixture yields quinoline.—3. Netro-benzene yields quinoline. p-Chloro-nitrobenzene at 200° does the same (Lellmann a. Reusch, B. 22, 1389).—4. HI and P reduce it to Lengfeld, B. 23, 1159).—5. Br forms cily CyH₁₀, and C₂H₂, and CyH₂, an chloride and NaOH form C,H,ON.SO.C,N, [67°], crystallising in plates, sl. sol. alcohol, water (Schotten a. Schlömann, B. 24, 3695) .-Methyl chloroformate gives C₀H₁₀N.CO₂Me [c. 35°], which may be oxidised by KMnO₄ in the cold to an acid [156°] and at 100° to a compound [175°] crystallising in red needles.-8. Diazobenzene chloride and aqueous NaOAc form $C_9H_{10}N.N_2C_9H_5$, which is split up by dilute H2SO4 into phenol and quinoline tetrahydride.-9. Potassium cyanate acting on the hydrochloride forms C₀H₁₀N.CO.NH₂ [150.5°], crystallising in needles, sl. sol. cold water. It is converted by conc. H₂SO₄ and HNO₃ at 0° into C₂H₈(NO₂)₂N.CO.NH₂ [191°], sl. sol. alcohol, and C₂H₃(NO₂)₂N [161°], v. sol. slochol, which forms a nitrosamine [127°] (Thomas, R. T. C. 10, 148).—10. Benzoic aldehyde and ZnCl₂ yield CHPh(C₉H₁₀N)₂ [153°], while p-nitro-benzoic aldehyde forms a corresponding body [177°] (Einhorn, B. 19, 1243).

Salts. - B'HCl. [181°]. — B',H,PtCl,. Prisms (from alcohol) or B'H₂SO₄. [137°]. tables (from water).

Acetyl derivative C.H. NAc. Yields CO.H.CO.NH.C.H.CO.H [1:2] on oxidation by KNnO.

Bensoyl derivative C.H., NBz. [750]. Tables (from alcohol). Oxidised by KMnO, to benzoyl-isatic acid (Schotten, B. 24, 772).

Nitrosamine C, H, N(NO). Oil. Converted by alcoholic HCl into the isomeric (B. 2)nitroso-quinoline tetrahydride [134°], which separates from benzene in steel-blue crystals, converted by NaNO₂ and HOAc into C,H₃N₂O₂ [98°] (Ziegler, B. 21, 864). Phenyl-hydrazine forms C_vH₁₀N₂O.PhN₂H₃ [120°]. Zinc-dust and HOAc reduce the nitrosamine to the hydrazine $C_0H_{10}N(NH_2)$ [56°] (c. 255°), which crystallises from ligroin, and forms B' H2SO, 2aq, crystallising in yellow plates. The hydrazine is oxidised in ethereal solution by ppd. IIgO to the tetrazone C18H20N4, which forms colourless needles [160°], sol. ether, sl. sol. alcohol.

Methylo-chloride v. Hydrochloride of

v-Methyl-ouinoling tetrahydride.

Ethylo-iodide B'Etl. Changed by alkalis into v-ethyl-quinoline tetrahydride, which is a liquid (254°-258°) yielding (C,H,0NEt), H.CdCl,, [105°], and (C,H,0NEt), H,PtCl, [c.460°) (Wyschnegradsky, B. 13, 2400; Claus a. Stegolitz, B. 17, 1329).

Quinoline tetrahydride C,H1,N. Formed by distilling cinchonine (1 pt.) with KOH (3 pts.) (O. de Coninck, C. R. 94, 87; A. Ch. [5] 21, 478). Got also by distilling brucine with potash (De Coninck, C. R. 99, 1077). Slightly hygroscopic oil, v. sol. acids. Reduces FcCl₃. May be oxidised to quinoline.—B'HCl: deliquescent needles, v. sol. water. - B', H, PtCl, -B'₂H₂PtCl₄: pale orange plates.

Quinoline hexahydride C,H13N. 720 mm. A product of the action of HI and P at 230° on the hydrochloride of quinoline tetrahydride (Bemberger a. Lengfeld, B. 23, 1155). Liquid, turning brown in air, m. sol. hot water. FeCl, gives a brown colour on warming. Diazo benzene sulphonic acid gives a light-red colouring matter. Phosphomolybdic acid gives a white pp. Potassio-mercuric iodide gives no pp. NaNO, in acid solution gives an oily pp. of the nitrosamine.—B'HCl. [170°]. Silky needles. B'HBr. Long silky needles.

Quinoline decahydride C,H,,N i.e.

CH₂·CH₂·CH.CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₃·CH Formed by heating the hydrochloride of quinoline tetrahydride (3 pts.) with HI (16 pts. of S.G. 1.9) for 7 hours at 230° (Bamberger a. Lengfeld, B. 23, 1145). Needles or prisms (from ligroin). Smells like coniine. Fumes with HCl. Sublimes, in needles, in the cold. M. sol. water, v. sol. alcohol and ether, sl. sol. alkalis. Gives no colour with FeCl, or diazo salts. Reduces anmoniacal AgNO, in alcoholic solution. Phosphomolybdic acid gives a white flocculent pp. changing to needles. Potassio-mercuric icidida. iodide added to the acid solution gives scarlet crystals changing to black prisms on warming.

Reactions .- 1. Phenyl-cyanate forms, ethercal solution, C₉H₁₈N.CO.NHPh, crystallising in needles [148°].—2. Phenyl thiocarbimide in ether forms C,H16N.CS.NHPh, crystallising from chloroform in tables [134:5°].—3. An ethereal solution of CS₂ gives C₂H₁₈N.CS.SNH₂C₄H₁₆, crystallising in needles [120°], not decomposed by boiling alcohol, but converted by iodine into

(C.H., N)HI and S₂(OS.NC, H., 2), which crystallises in colourless needles [81°], sol. alcohol.
Salts.—B'HCl. [276°]. Small tables.—
B'HI. [253°]. Silky needles.—B'HAuCl,.
[96°]. Golden needles.—B',H,PtCl,. [207.5°].
Acetyl derivative C,H,gNAc. Oil.

Remacul derivative C.H., NBz. [44°].

Bensoyl derivative C. H₁₆NBz. [44°]. ISOQUINOLINE TETRAHYDRIDE C. H₁₁N. (232°). Formed by the action of tin and HCl upon isoquinoline (Hoogewerff a. Van Dorp, R. T. C. 5, 305). Liquid, smelling like isoquinoline, sl. sol. water. Absorbs CO, from the air. forming a crystalline carbonate. are forming a crystatine caronate. The aqueous solution reduces AgNO₃. Yields an oily nitrosamine.—B'HCl. [196°]. Tables, sol. alcohol. Not hygroscopic.—B'₂H₂SO₄: sol. alcohol.—B'₂H₂PtCl₂. [232°]. Reddish-yellow tables, decomposed by hot water.

QUINOLINE HYDROQUINONE v. DI-OXY-QUINOLINE.

QUINOLINE-IODOFORM Quinoline, Reaction 20.

QUINOLINE-QUINONE C.H.NO., i.e.

CH.CO.C.CH;CH CH.CO.C.N=CH. Formed by the action of cold chromic acid mixture on (B. 4,1)-oxy-amido-quinoline (Fischer a. Renouf, B. 17, 1644). Flat needles with green reflex (from alcohol), decomposing at 110°-120°. Its salts are decomposed by water. Reduced by sulphurous acid to dioxy-quinoline. Aniline in alcoholic solution forms, on boiling, the dianilide C₁₈H₁₀N₂O₂ crystallising from dilute alcohol in small copperred plates with green reflex [c. 190°], forming a

wiolet solution in HClAq.

Mono-oxim CH.C(NOH).C.CH:CH
CH.CO — C.N—CH

Formed by the action of NaNO2 and HClAq on (B. 4)-oxy-quinoline (Von Kostanecki, B. 24, 152). Needles (from alcohol). Gradually blackens below 220°, decomposing completely at 245°.

Di-oxim CH.C(NOH).C.CH:CH CH.C(NOH).C.N=CH. by adding hydroxylamine hydrochloride to an aqueous solution of the mono-oxim (Von Kostanecki a. Reicher, B. 24, 156). Minute crystals. Ac₂O yields a crystalline di-acetyl derivative de-composing below 160° with evolution of gas. Dyes cotton mordanted with iron salts greenishblack.

Quinoline-o-quinone C,H,NO... Formed by oxidising (B. 2) oxy-(B. 1 or 3)-amido-quinoline with FeCl, in acid solution (Matheus, B. 21, 1887). Unstable.—B'HCl: long reddish-yellow needles. Decomposed by Na₂CO₂, forming a brown solution. The sulphate forms yellow plates.

Mono-oxim C,H,N(OH)(NOH). from p-oxy-quinoline, NaNO2, and HCl (M.).

Golden needles (from HOAc), and HCi (M.). Golden needles (from HOAc), sl. sol. ether. Di-oxim C.H., N(NOH). Needles, decomposing at 190° (Von Kostanecki a. Reicher, B. 24, 158). Converted by cone. KOHAq into the anhydride C.H., N(N,O), which forms colourless needles, readily volatile with steam.

QUINOLINE (B. 1)-SULPHONIC ACID CH:0(80.H).C.OH:CH A product of the CH:CH --C.N=CH.sulphonation of quinoline (O. Fischer, B. 15, 6:3, 1979; 20, 731; La Coste a. Valeur, B. 20,

97). Formed also from amido-benzene m-sul phonic acid, nitrobenzene, glycerin, and H2SU at 160° (Lellmann a Lange, B. 20, 1446). Mono clinic needles (containing aq). Yields oxy-quino line [224°] by potash-fusion.—CaA'₂5aq: needles v. e. sol. water. According to Lellmann, there exists an isomeric quinoline (B. 1)-sulphonic acid, also got by sulphonation of quinoline, with H₂SO₄ (containing 50 p.c. SO₃ extra) at 260 (Lellmann, B. 20, 2172). This \(\psi\)-acid is converted by conc. H₂SO₄ at 250°-300° into the (B. 2)-acid (Lellmann, B. 22, 1391). The \(\psi\)-acid forms an hydrous crystals.

Tetrahydride C.H. N.SO.H aq. [315°] Formed by reducing the above acid (B. 4)-bromo quinoline (B. 1)-sulphonic acid and also (B. 4). oxy-quinoline (B. 1)-sulphonic acid with tin and HClAq (Lellmann a. Lange, B. 20, 3087; Claus, J. pr. [2] 42, 344). Trimetric crystals (from dilute solutions) or monoclinic crystals (from cone. solutions). FeCl_s gives a brown colour passing through purple to grass-green on warming.

Quinoline (B. 2)-sulphonic acid

SO,H.C=CH.C.CH:CH

CH:CH.C.N=CH. Formed by heating a mixture of amido-benzene-p-sulphonic acid, glycerin, nitrobenzene, and H₂SO₄ (Happ, B. 17, 191). Formed also (to the extent of 70 p.c.) by heating quinoline with conc. H2SO4 at 240°-300° and by heating the (B. 1)- or $(\beta 4)$ - acid with conc. H2SO at 240°-300° (Georgievitch, M. 8, 578, 639). Monoclinic needles (containing $1\frac{1}{2}aq$), sl. sol. alcohol and cold water. Not melted at 260°. Potash-fusion yields (B. 2)-oxy-quinoline [193°]. Bromine-water gives a yellow pp. of di-bromo-quinoline [126°] and at 100° Br (3 mols.) forms tri-bromo-quinoline [170°] (Claus a. Küttner, B. 19, 2884). Heating with KCy gives C.H.N.Cy [131°] which on saponification yields the carb.

oxylic acid [288°].
Salts. — KA' (dried at 120°). Tables. —
BaA'₂ (dried at 120°).—AgA': slender needles. —
Ag₂HA'₃: needles. — (HA')₁₈K₄I₉ 6aq: lustrous green crystals.

Ethyl ether EtA'2aq. Crystals, v. sol. water (Claus a. Happ, B. 18, 366).—EtA'KI; unstable brown needles, v. sol. water (Claus a. Stegelitz, B. 19, 921).—EtA'KBr.,—EtA'HgCl.,

Benzyl ether C,H,A'2aq. Monoclinic crystals.—C,H,A'KI, needles with blue reflex.

Quinoline (B. 3) sulphonic acid CH:CH.C.CH:CH SO₃H.O=CH.C.N=CH. [above 300°]. Formed by heating quinoline with H2SO4 (containing 15 p.c. SO, extra) at 130° (Claus, J. pr. [2] 37, 260). Small needles, v. e. sol. water, v. sol. alcohol. Potash-fusion yields oxy-quinoline [165°-200°]. Bromine forms di-bromo-quinoline [255°] and tri-bromo-quinoline [199°].—NaA'3aq. KA' 2aq. — CaA', 4aq. — BaA', 4aq. — PbA', CuA', 2aq: dark-green crystalline powder. Ethyl ether EtA'. [275°]. Needles (from

alcohol).

Chloride C.H.N.SO.Cl. Viscid mass. Amide C.H.N.SO.NH. [119°]. Crystalline. Quinoline (B. 4)-sulphonic acid :CH ____ C.CH:CH CH:CH -Quinolins o-sulphonic CH:C(SO,H).C.N=CH acid. Formed, together with a smaller quantity of the p- acid, by heating quinoline with fuming

H.SO, at 170° (O. Fischer a. Bedall, B. 15, 683, 1979; 20, 731; Riemerschmied, B. 16, 721; La. Coste a. Valeur, B. 20, 95; Claus, B. 19, 925, 2882; J. pr. [2] 37, 260). Formed also by heating quinoline with conc. H,SO, at 220° (Georgievitch, M. 8, 641). Monoclinic prisms, v. sl. sol. water. Oxidised by KMnO, to pyridine dicarboxylic (quinolinic) acid (Fischer, B. 17,755) and a small quantity of (1.9.3) and the small quantity of (1.9.3) and (1.9 a small quantity of (1,2,3)-sulpho-amido-benzoic acid (Zürcher, B. 21, 180). Changed by conc. H₂SO₄ at 250° to the (B. 2)-isomeride (Georgievitch, M. 8, 578). Bromine-water forms a yellow insoluble pp. and, at 100°, tri-bromoquinoline [198°].

Salts.—NaA' 5aq (Spies, J. pr. [2] 37, 265). -KA' 2aq. -CaA', 9aq. Monoclinic crystals. PbA', -CuA', 2aq: small green needles.

Ethyl ether EtA'. [66°]. Needles (from chloroform). Decomposed by boiling water.

Chloride C.H., NSO, Cl. [124]. Needles. Amide C.H., N.SO, NH., [184]. Needles Amide C,H,N.SO,NH, (from water) (Hoogewerff a. van Dorp, R. T. C. 8, 184). Converted by Br and KOHAq into C.H.NSO.NBrK 2aq, crystallising in yellow needles, m. sol. water, and converted by HOAc into C,H,NSO,NBrH, crystallising from acctone in needles, yielding (CoH.NSO2NBr)2Ba 2aq.

Quinoline (a)-disulphonic acid $C_9H_b(SO_3H)_2N$. Formed, together with the (β)someride, by heating quinoline (B. 4)-sulphonic acid with fuming H.SO, at 250° (La Coste a. Valeur, B. 19, 995; 20, 98). Yellow needles (containing 3aq), v. sol. water, insol. alcohol.-K₂A"3½aq: satiny plates, v. e. sol. water.—BaA"3aq. S. 4.08 at 15°.

Quinoline (β) -disulphonic acid

C₀H₃N(SO₃H)₂. Formed as above (La Coste a. Valeur, B. 19, 998; 20, 3199). Needles (containing 1 aq), v. sol. water, insol. alcohol .-KA" aq : crusts, sl. sol. cold water .- BaA" 2aq : white powder, sl. sol. cold water (difference from (a) - isomeride).

References. - Bromo- and Oxy-QUINOLINE SULPHONIC ACIDS.

ISOQUINOLINE SULPHONIC ACID

C₂H₂N(SO₂H). Formed by heating isoquinoline (1 pt.) with fuming H₂SO₄ (2 pts.) at 100° (Hoogewerff a. van Dorp. R. T. C. 5, 305).—

BaA', 9aq. Needles, v. sol. water.
QUINOLINIC ACID v. Pyridine Dicarri-OXYLIC ACID. The name is also given by Dewar (Pr. 30, 164) to an acid C₉H₉NO₃ [143°] formed in small quantity in the oxidation of quinoline (derived from cinchonine) by boiling aqueous KMnO. (a)-DIQUINOLYL O₁₈H₁₂N₂ i.e.

 $C_{o}H_{\bullet} < CH:CH:CH:CH:CH > C_{o}H_{\bullet}$ Diquinoline.

[176°]. (above 400°). V.D. 8·73 (calc. 8·86). Formation.—1. By heating quinoline with sodium at 192° (Weidel, M. 2, 491; 7, 327).—2. In small quantity (8 p.c.) by passing dry oxygen into a mixture of quinoline and quinoline hydrochloride in presence of platinum-black (Weidel,

M. 8, 120).

Properties. — Monoclinic plates, a:b:c=1.37:1:1.32; $\beta=109^{\circ}58'$. Insol. water, sol. alcohol, ether, and benzene. Oxidised by KMnO. and HOAc to cyclothraustic (C, H, N,O,), quinoline (Py. 8)-carboxylic, oxyisocinchomeronic (oxy-pyridine dicarboxylic), and o-amido-benzoic

acids (Weidel a. Strache, M. 7, 280, 806; 8, Alkaline KMnO, forms isocinchomeronic, o-amido-benzoio, and pyridanthrillic (C₁₅H₁₆N₃O₄) acid. MeOH and H₃SO₄ form B''MeSO₄H (Ostermayer, B. 18, 333, 597).

Salts.—B''H₂Cl₄ 4aq; white needles.—

B"H,PtCl, aq.—B"HAuCl, 2aq.—B"H,SO, aq. Methylo-chloride B"Me,Cl, 6aq: needles.

B'Me,Cl,2ICl. [238°]. Lemon-yellow pp.

Methylo-iodide B''Mel. [283°].

Ethylo-iodide B''Etl. Yellow needles

(from water), sl. sol. water (Roser, B. 17, 2769).

Sulphonic acid C₁₈H₁₁N₂(SO₂H). Formed by heating diquinolyl with H₂SO₄ (containing 5 p.c. SO₃ extra) (Weidel a. Glüser, M. 7, 308). Minute needles, almost insol. hot water, sol. conc. HClAq and H.SO4. Converted by potashcone. richa and H₂SO₄. Converted by potasniusion into oxy-diquinolyl [208°].—KA'2aq: needles, v. e. sol. water.—Cuh'₂2aq.

(a)-Disulphonic acid C₁₈H₁₀(SO₂H)₂N₂.

Formed by heating diquinolyl (10 pts.) with

H₂SO₄ (11 pts.) and SO₃ (34 pts.) at 170° (Weidel, M. 2, 503). Minute needles, sl. sol. water. Yields, by potash-fusion, di-oxy-di-quinolyl [239°].—K₂A" 5aq: needles.—CuA" 6aq: bluish-green crystals, nearly insol. water.

(β)-Disulphonic acid C18H10(SO3H)2N2 Formed, together with the mono-sulphonic acid, by heating (a)-diquinolyl (100 pts.) with H2SO (332 pts.) and SO, (18 pts.) for 20 hours at 190° (Weidel a. Glüser, M. 7, 322). Small needles, converted by potash-fusion into di-oxy-di-quinolyl [above 305°].—K.A" (dried at 120°): crystalline powder.—CuA" (dried at 120°).

(β)-Diquinolyl

CH:CH.C.CH:C.CH:CH CH:N—C.CH:C.CH:N—C₆H, [192°].

Formation .- 1. By heating quinoline with BzCl at 250° (Japp a. Graham, C. J. 39, 174) .-2. In very small quantity by distilling cinchoninic acid with lime (Weidel, M. 2, 501). -3. By passing quinoline through a red-hot tube (Zimmermann a. Müller, B. 17, 1965).-4. By distilling quinoline (B. 4)-sulphonic acid; the yield being 10 p.c. (O. Fischer a. Loo, B. 17, 1899; 19,

Properties .- Iridescent plates (by sublimation) or colourless prisms (from ether), sol. hot benzene, alcohol, and ether, insol. water. Weak base, the salts being decomposed by water. pase, the saits being decomposed by water. Oxidised by CrO₃ and HOAc to quincline (B. 3)-carboxylic acid. CrO₃ and H₂SO₄ give pyridyl-quincline carboxylic acid C₂H₃N.C.H₃N.CO₂H [273°]. Bromine forms C₁₈H₁₂N₂Br₁ [192°].

Salts.—B"H₂SO₄: sparingly soluble concentric needles.—B"H₂PtCl₆: granular pp.

Ethylo-iodide B"Etl. Very unstable

red crystals, decomposed by hot water.

C18H10(SO3H)2N2. Disulphonic acidFormed by heating the base (1 pt.) with conc. H₂SO₄ (10 pts.) at 180°. V. e. sol. water.— K2A" Baq: prisms.

(γ).Diquinolyl CH:N—C.CH:CH-CH-CH.C.N -CH CH:CH.C.CH:C—C=CH.C.CH:CH Di-p-

quinolyl. [178°].

Formation.—1. By boiling a mixture of benzidine, nitrobenzene, glycerin, and H,SO. (Roser, B. 17, 1817, 2767; O. W. Fischer, M. 5, 418; Colson, C. R. 108, 677). A better yield is got by using o-or p-nitrophenol instead of nitrobenzene (Ostermaver a. Henrichsen, B. 17, 2444). When crude benzidine is used there is also formed a base C_{2.}H₁₈N₂O₃, which yields B'2SnCl₂ [135°] and B''H_{2.}PtCl₂ 2aq (Colson, C. R. 107, 1003; 108, 677).—2. By heating azobenzene with glycerin and H₂SO₄ (Claus a. Stegelitz, B. 17, 2380).

Properties .- Monoclinic crystals, insol. water, sl. sol. ether, v. sol. hot alcohol and benzene. MeOH and H₂SO₄ at 180° form B"(MeHSO₄)₂2aq, crystallising in needles. Bromine in alcohol forms unstable $C_{18}H_{12}N_{.0}Br_{.2}$ and $C_{13}H_{12}N_{.2}Br_{.4}$, converted by HClAq at 190° into C18H11BrN2 [150°-

155°7.

Salts. - B"H2Cl2 4aq: white needles. B"HAuCl, 2aq: slender needles.—B"H, SnCl,: colourless needles. - B"H_PtCl₆ (dried at 105°) B"H₂Cl₂2ICl: cheesy pp. (Dittmar, B. 18, 1618).

-B"H₂SO₄3aq. -B'2H₂SO₄. -B"2H₂Cr₂O₇. -B"C₀H₃(NO₂),OH: minute yellow prisms.

Methylo-iodides B"MeI. Cryst

Crystals. B"Me₂I₂. [c. 300°]. Yellow needles, sol. water. Ethylo-iodide B"2Etl. [270°]. Needles.

Disulphonic acid C₁₈H₁₀(SO₃H)₂N₂. White powder, insol. water and alcohol.—
Na₂A" 5aq: small needles. The same, or an isomeric, disulphonic acid is got by heating benzidine disulphonic acid with o-nitro-phenol, glycerin, and \dot{H}_2SO_4 . It crystallises in plates or needles, and yields \dot{K}_2A'' aq.

(8)-Diquinolyl

CH:N-C.CH:CH CH.CH:CH.C.CH:CH

CH:CH.C.CH:C C.N=CH'
[148°]. Formed by heating o. p-di-amido-diphenyl hydrochloride with nitrobenzene, glycerin, and H2SO, (O. W. Fischer, M. 6, 546). Leaflets, insol. water, sol. hot alcohol and benzene. Bromine in presence of water forms orange bromne in presence or water forms orange needles of C₁₈H₁₂N₂Br₁.—B"H₂Cl₂: needles, v. c. sol. water.—B"H₂PtCl₆ aq: reddish-yellow crystalline pp.—Picrate. [168°]. Yellow needles.

Methylo-iodide B"MeI. [126°]. Needles.

Disulphonic acid C₁₈H₁₀(SO₂H)₂N₂. Four-sided tables, not melted at 300°. Si. sol. hot water. - BaA" 3aq: needles, m. sol. hot water.

(Py. 3, B. 1 or 3)-Diquinolyl $C_{18}H_{12}N_2$. [159°]. Formed (7 pts.), together with the isomeride [115°], by heating a mixture of m-amido-(Py. 3)phenyl-quinoline (20 pts.), glycerin (70 pts.), o-nitro-phenol (15 pts.), and H₂SO₄ (60 pts.) (Miller a. Kinkelin, B. 18, 1910). Small monoclinic tables, sl. sol. ether, cold alcohol, and chloroform.—B"H₂Cl₂2aq: plate's.—B"H₂PtCl₃ $-B''H_2SO_4$: easily soluble needles. $-B''C_6H_3N_3O_7$.

-B'H₂SO₁: easily solution needles. -B'U_eH₂N₂O₁. [240°]. Crystalline powder.

Methylo-iodide B''MeI. [263°]. Needles. (Py. 8, B. 3 or 1)-Diquinolyl C₁₈H₂N₂. [115°]. Formed as above (M. a. K.). Lightyellow triclinic crystals, v. sol. alcohol, ether, and benzene, sl. sol. ligroin. -B''H₂Cl₂3aq: tables, v. e. sol. water .- B"H2PtCla: crystalline.

--C.N=CH \cdot Formed from p-amido-(Py. 3)-phenyl-quinoline, glycerin, nitro-benzene, and H₂SO₄ (Weidel, M. 8, 140). It is also a product of the action of oxygen on a mixture of quinoline hydrochloride, aniline, and platinised asbestos at 180°. Monoelinic tables (from alcohol).—B"H,PtCl,: crystalline powder. B"HCl: yellow. B"H,Cl.

Methylo-iodide B"MeI aq. [232°]. Small needles (from water), sl. sol, boiling water.

Sulphonic acid C₁₈H₁₁(SO₃H)N₂. Insoluble powder. Potash-fusion yields an oxy-

diquinolyl [187°].

diquinolyl [187].

(B., Py. 1)-Diquinolyl C₁₈H₁₂N₂. [122°]. Got by heating (a)-amido-(Py. 1)-phenyl-quinoline [150°] with glycerin, nitro-benzene, and H₂SO₄ (Koenigs a. Nef, B. 20, 632). Large crystals (from benzene). May be distilled. V. e. sol. alcohol, v. sl. sol. ether. Strong base.—
B"H₂PtCl₃: granules, sol. cone. HIAq.

(B., Py. 1)-Diquinolyl $C_{18}H_{12}N_2$. [117°]. Got by heating (β) -amido-(Py. 1)-phenylquinoline [198°] with glycerin, nitro-benzene, and H.SO, (Koenigs a. Nef, B. 20, 634). Tables (from benzene), v. e. sol. alcohol. May be distilled. Strong base. — B'H,PtCl_e: ye needles.—Picrate. [248°]. Bulky flakes. yellow

(Py. 2,3)-Diquinolyl

 C_eH_i CH:C—C=N C_eH_i . [176°]. Formed by the action of (Py. 3)-quinolyl-acetic aldehyde on o-amido-benzoic aldehyde in alcoholic solution (Carlier a. Einhorn, B. 23, 2895).

Plates (rom alcohol).—Aurochloride: [248°].
—Platinochloride: [278°].—B"H₂Cl₂ 4aq.

Methylo-iodide B"MeI.

Diquinolyl tetrahydride C18H16N2. [118°]. Formed by heating (Py. 3)-chloro-quinoline with quinoline tetrahydride (Friedländer a. Weinberg, B. 18, 1533). Crystals, sl. sol. ligroin, insol. water. May be distilled. HClAq forms a deep-yellow solution.

Reference. - OXYDIQUINOLYL.

(Py. 3) QUINOLYL-ACETIC ACID

C₆H₄CH:CII N=C.CH₂CO₂H. [275°]. Formed from the aldehyde by potash-fusion or by oxidation Carlier a. Einhorn, B. 23, 2896). Formed also by oxidation of a-oxy-quinolyl-propionic acid with KMnO₄. Needles (from alcohol).—Hydrochloride: [243°]; needles. — Silver salt: white scales, yielding quinaldine on distilling with lime.

(Py. 3)-QUINOLYL-ACETIC ALDEHYDE C₁₁H_pNO i.e. C₂H₅N.CH₂.CHO. [104°]. Formed by careful oxidation of α-oxy-quinolyl-propionic acid (Einhorn, B. 18, 3467; 19, 908). Crystals (from alcohol). Yields a phenyl-hydrazide [199°].—B'₂H₂PtCl₆2aq.—B'C₆H₃N₃O₇. [212°].

QUINOLYL-ACETONE v. ACETONYL-QUINOL-

(Py. 3)-QUINOLYL-ACETYLENE

C.H.N.C:CH. Formed by distilling a solution of di-bromo-quinolyl-propionic acid with Na, CO, (Carlier a. Einhorn, B. 23, 2896). Volatile oil. Br forms C.H.N.CBr:CHBr.

(Py. 3)-QUINOLYL-ACRYLIC ACID

C₁₂H₂NO₂ i.e. C₈H₄ < CH: OH N=C.CH: CH.CO₂H. [193°]. Formed by the action of boiling potassium carbonate solution upon 'quinolyl-acrylo-trichloride' C.H.N.CH:CH.CCl, aq [145°], which is got by heating (Py. 3)-methyl-quinoline with chloral at 110° (Miller a. Spady, B. 18, 3402, 3465; 19, 130; Einhorn, B. 19, 908). Plates. Oxidised by KMnO, to aldehydo-quinoline. HBr forms acid. - *BaA',: β-bromo-quinolyl-propionic needles, sl. sol. cold water. - *HA'HOl: needles.

OWINGLYL-ACRYLO-TRICHLORIDE

TRI-(B. 2)-QUINOLYL-CARBINOL

(C.H. N), C.OH. [108°]. Formed by oxidising tri-quinolyl-methane with H, CrO, and HOAc (Noelting a. Schwarz, B. 24, 1608). Needles, v. sol. alcohol, sl. sol. ligroïn.

(B. 3, Py. 8)-QUINOLYLENE DIACRYLIC CH:CH.C.CH:CH

ACID

CO,H.CH:CH.C=CH.C.N=C.CH:CH.CO,H. [over 300°]. Formed by boiling tri-chloro-propenyl-quinolyl-acrylic acid with K₂CO₃Aq (Éckhardt, B. 22, 284). Sol. acids and alkalis. Insol.

water, sl. sol. hot alcohol.

DI-(B. 2)-QUINOLYL-ETHANE C₂₀H₁₀N₂i.c. C₃H₆N.OH₂·Ch₂N. [124°]. Formed by heating di-p-amido-di-phenyl-ethane with nitrophonol, glycerin, and H₂SO₄ (Comey, B. 23, 1115). Hexagonal plates, insol. water, sl. sol. ether.—B"H_Cl, 4aq: needles, v. sol. water.—B"H_Cl, - B"H_PtCl, - B"H_PtCl, - B"HAUCl, - Sulphate: prisms, m. sol. cold water.

(Py. 3)-QUINOLYL-ETHYLENE C,1H,N i.e.

 $C_{e}H_{\bullet} < CH:CH > N = C.CH:CH$. Formed by boiling β bromo-quinolyl-propionic acid with ono. K.CO₃Aq (Einhorn, A. 246, 172). Oil. — B'₂H, PtCl₃ 4aq. [187°].—B'HAuCl₄. [159°]. (B. 3, P₂y. 3). Di-quinolyl-ethylene C₆H₁, N₂

Formed by heating m-amido-(Py. 3)-styrylquinoline with o-nitro-phenol, glycerin, and H₂SO₄ (Wartmann, B. 23, 3650). Oil, v. sol. alcohol, sl. sol. ether.

Methylo-iodide B'MeI 13aq. Golden needles v. sol. hot water and alcohol.

Yields C₂₀H₁₁N₂Br₂McI. [210°]

QUINOLYL-DI-ETHYL-PHENOL C10H10NO i.e. C. H. N.C. H. Et. OH. This is probably the constitution of apocinchene (Comstock a. Königs,

B. 20, 2674; \hat{v} . vol. ii. p. 174).

(B. 4)-QUINOLYL-HYDRAZINE $C_0H_0N_3$ i.c.

CH:N-C ____C.N₂H³ [64°]. Formed from (B. 4)-amido-quinoline by diazotisation and treatment with SnCl₂ and HCl (Dufton, C. J. 59, 757; Böttinger, B. 24, 3277). Needler (from ether) or prisms (from ligroin). — B"H₂Cl₂: prisms. Converted by potassium cyanate and HCl into C₂H₈N.NII.NH.CO.NH₂ [235°], and by pyruvic acid into C,H,N.N,H:CMc.CO,H crystallising in orange needles, converted by boiling HClAq into quinindole (a)-carboxylic acid

HClAq into quinindole (a)-carboxylic actu $C_{12}H_{10}N_{.}O_{.2}$ [286°].

(B. 1)-Quinolyl-hydrazine [151°]. Formed in like manner from ana-amido-quinoline (Dufton, C. J. 61, 785). Yellow needles (from water). Yields B'HCl [248°] and is converted by cyanic acid into $C_{1}H_{2}NH.NH.CO.NH_{2}$ [255°], the horseign addition of the N. NH.NH.CO.NH 2005 and the horseign addition of the NH.NH.NH.CO.NH 2005 and the horseign addition of the NH.NH.NH.CO.NH 2005 and the horseign additional to the NH.NH.NH.CO.NH 2005 and the horseign and the NH.NH.CO.NH 2005 and the horseign and the by benzoic aldehyde into C.H.N.NH.N:CHPh [194°], by acetone into C.H.N.NH.N:CMc. [140°] and by pyruvic acid into the acid C.H.N.NH.N:CMc.CO.H [185°], whence boiling HClAq forms the corresponding quinindole carboxylic acid, which decomposes at about 300°.

DIQUINOLYLINE is DIQUINOLYL.

DI.(B. 2)-QUINOLYL KETONE (C.H.N)2CO. [174°]. Formed from di-p-amido-benzophenone, glycerin, H₂SO₄, and pieric acid (Noelting a. Schwarz, B. 24, 1608). Needles, v. sol. alcohol,

gl. sol. hot water. - B"H,Cl. [over 200°]. Needles, v. e. sol. water and alcohol

(Py. 3)-QUINOLYL-MERCAPTAN

CeH. CH: CH [174°]. Formed by heating (Py. 3)-oxy-quinoline with P.S. at 145° (Roos, B. 21, 620). Yellow plates, sl. sol. hot water, v. sol. hot alcohol. Yellow dye. Combines with acids and bases. Does not react with hydroxylamine or phenyl-hydrazine.

Ethyl derivative C.H.N.SEt. Formed from quinolyl-mercaptan, NaOEt, and Etl. Oil, decomposed by distillation .- B'HI. [154°] .-

B',II,PtCl, aq. [c. 190°]. Octahedra. TRI-(B. 2)-QUINOLYL-METHANE

CH(C,H,N), [202°]. Formed from p-rosaniline, glycerin, H,SO,, and pieric acid at 150° (Noelting a. Schwarz, B. 24, 1606). Needles (containing EtOH), melting at 98°. Melts at 202° when anhydrous. — B"'3HCl: plates, sol. water. — B"C₄H₃N₃O₇: yellow needles.—B", H₁₂Pt₃Cl₂₁: yellow crystals.—B""3MeI. [266°].

(B. 2)-QUINOLYL-METHENYL-AMIDOXIM

C(NOH)(NII.).C=CH.C.CH:CII CH:CH.C.N=CH. [105°]. Formed from CoH. N.Cy, hydroxylamine hydrochloride, Na₂CO₃, and dilute alcohol (Biedermann, B. 22, 2761). Yellowish needles, m. sol. hot water. Fehling's solution gives a greyish-green pp. FeCl, gives a deep-red colour. AgNO, gives a white pp. yielding a mirror.

Reactions .- 1. Phthalic anhydride on warming forms $C_9H_6N.C < N.O > C.C_6H_1.CO_2H$ [203°].

2. Ac_O yields $C_{_{0}}\mathrm{H_{_{6}}N.C} { <\!\!\!\! < \!\!\! < \!\!\!\! \stackrel{N.O}{\sim} \!\!\!\! > \!\!\!\! \mathrm{CMe}}$ [175°], crystallising in needles. - 3. The hydrochloride is converted by potassium evanate into $C_0H_1N.C(NOH).NII.CO.NH_2$ [165°]. 4. Chloroformic ether forms $C_0H_0N.C(NII).NO.CO.Et$ [97°], which is converted by NaOIIAq into $C_{\nu}H_{e}N.C \stackrel{N.O}{<_{NH}} > 0$ [155°].

Salts .- B'HCl: needles .- B'2H2PtCle. Acetyl derivative C.H.N.C(NOAc).NH [115°]. Formed by means of AcCl in the cold. Needles, insol. cold water, sl. sol. ether.

Ethyl ether CgH6N.C(NOEt).NH2. Formed from the amidoxim, NaOEt, and Etl. Needles, v. sol. alcohol and hot water.

(Py. 3)-QUINOLYL-PROPIONIC ACID
C_yH_nN.CH_y.CH_y.CO_yH. [116°]. Formed by reducing quinolyl-acrylic acid with sodiumamalgam (Cartier a. Einhorn, B. 23, 2896). Ethyl ether Eth'. [116°]. Needles.

Reference. -- OXY-QUINOLYL-PROPIONIC ACID.

DI-(Py. 3)-QUINOLYL DISULPHIDE [137°]. Formed by oxidising (C,H,N),Š,. quinolyl-mercaptan with H.O. in dilute alcohol (Roos, B. 21, 622). Plates (from alcohol), insol. water and alkalis.

QUINONE C.H.O. i.e. CH.CO.CH. Benzoquinone. Mol. w. 108. [116°]. V.D. (H = 1) 53.4 (calc. 54) (Hofmann, 7. 3, 583). H.C. 659,020. H.F. 45,200 (from diamond) (Berthelot a. Recoura, Bl. [2] 48, 699; A. Ch. [6] 13, 312, 335; C. R. 104, 1572).

Formation.—1. By oxidation of quinic acid with MnO₂ (4 pt.), H₂SO₄ (1 pt.), and water (1 pt.) (Woskresensky, A. 27, 268).—2. By

oxidation of hydroquinone (Wöhler, A. 51, 148).

8. By oxidation of benzidine, of aniline, and of p-phenylene-diamine by MnO₂ and H₂SO₄ (Hofmann, Pr. 18, 4).—4. By action of MnO₂ and H₂SO₄ on amido-benzene p-sulphonic acid and on phenol p-sulphonic acid (Schrader, B. 8, 759).

Preparation.—1. By adding conc. Na₂Cr₂O, Aq to a cold solution of aniline (1 pt.) in H₂SO₁ (8 pts.) and water (25 pts.), and extracting with ether (Nietzki, B. 19, 1467).—2. 20 g. of aniline are dissolved in 600 c.c. of water containing 160 g. of H₂SO₁; 20 g. of finely-powdered potassium bichromate are added by degrees, with constant agitation, keeping the temperature at 10°-15°. After standing over night 33 g. more potassium bichromate are added; the quinone is then extracted with ether, dried over CaCl₂, and the ether removed by distillation. The yield is about 86 p.c. of the theoretical amount (Schniter, B. 20, 2283; cf. Seyda, B. 16, 687; Nietzki, B. 11, 1102; A. 215, 127).—3. From p-amidophenol. p-Amido-phenol sulphate is dissolved in water, some H₂SO₄ added, and then PbO₂ gradually, wich shaking, till the violet colour first formed disappears. The quinone is extracted with ether. Yield theoretical (Schmitt a. Siepermann, J. vr. (2110, 317)

Siepermann, J. pr. [2] 19, 317).

Properties.—Yellow monoclinic prisms (from water) or plates (from EtI) (Hesse, A. 114, 299), or needles (by sublimation). Its odour is characteristic. V. sl. sol. cold water, m. sol. alcohol and ether. The solutions turn the skin brown. Sol. HClAq and cone. HNO₃. Its alkaline solution turns brown in air (Laurent, C. R. 26, 35). An alcoholic solution of hydrocerulignone deposits, even in dilute solutions, crystals of cerulignone with steel-blue reflex.

Reactions .- 1. Chlorine forms tri - chloroquinone.—2. HCl and KClO3 give tetra-chloroquinone (Hofmann, A. 52, 55).—3. Conc. HClAq forms chloro-hydroquinone (Wöhler; Städeler, A. 69, 308) .- 4. HIAq forms quinhydrone and hydroquinone.—5. HBr passed into a solution in chloroform ppts. quinhydrone, and finally forms brome-hydroquinone. HBrAq forms, on heating di-bromo-hydroquinone (Sarauw, A. 209, 99). 6. Bromine. (1 mol.) in CHCl, is instantly absorbed. Excess of bromine (2 mols.) appears to form C.H.Br.O2, which is split up by heat into HBr and two di-bromo-quinones C.H.Br.O. [2:5:4:1] and [2:6:4:1] (Nef, J. pr. [2] 42, 167).— 7. HNO, on heating yields oxalic and picric acids and HCy (Nietzki, A. 215, 138, —8. Ammonia gas forms emerald-green quinonimide C.H.NO, sol. water, the solution soon turning black (Woskresensky). NH, in presence of chloroform produces hydroquinone, quinhydrone, and brown C.H.NO. (Zincke, B. 16, 1556).—9. An alcoholic solution exposed to sunlight yields hydroquinone and aldehyde (Ciamician, G. 16, 111). - 10. Hydrasine hydrate gives hydroquinone and a compound $O_2H_4(OH)_2N_2H_4$ (Curtius a. Thun, J. pr. [2] 44, 191).—11. Heated in a sealed tube alone at 160°, or with water at 100°, it yields hydroquinone and quinhydrone (Scheid, A. 218, 227).-12. PCl, forms a thick oily product, C₁₂H₂O₄P₃Cl₈. Water acting upon this forms C₁₂H,O₄P₂Cl₈. Water acting upon this forms mono- and di-chloro-hydroquinone.—13. Heated with POCl, quinone gives mono- and di-chlorohydroquinone. An amorphous body C₂₁H₁₄O₁₁

is also formed.—14. Alcoholic H.S form C, H, SO, a yellowish crystalline mass, melting below 100°.-15. AcCl forms in the cold the di-acetyl derivatives of chloro-hydroquinone. On warming it also forms CeH2Cl2(OAc)2 (Schulz, B. 15, 652). AcBr, in like manner, gives $C_0H_0Br(OA0)_2$ and $C_0H_0Br_2(OAc)_2$ —16. Ac_O does not act below 200°, when it forms $C_0H_4(OAc)_2$ and a brown mass. 17. Cold dilute NaOAc converts it into hydroquinone (Hesse, A. 220, 365).—18. Aniline in boiling alcoholic solution forms di-phenyl-di-amidoquinone and hydroquinone 3C,H,O2+2NH2Ph quinone and hydroquinone $3U_0H_1U_2 + 2NH_2I^*n = O_0H_2(NHPh)_2O_2 + 2C_0H_1(OH)_2$. Other primary and secondary bases act in like manner.—19. o- and p- Nitro-aniline form red crystals $C_0H_1O_2C_0H_1(NO_2).NH_2$ melting at 97° and 120° respectively (Hobebrand, B. 15, 1976). o-Nitro-aniline in HOAc forms $C_0H_2O_2(NH.C_0H_1NO_2)$. [1:4:2:5] [305°] crystallising from alcohol in red needles (Leicester, B. 23, 2794).-20. o-Amidophenol in hot alcohol forms a base (C₂H₁₈N₁O₁?) which crystallises in violet needles [250°], al. sol. alcohol (Zincke a. Hebebrand, A. 226, 61). In alcohol (Zincke a. Hebebrand, A. 226, 61). In dilute acids it forms a red solution. Ac₂O yields $C_2, H_{16}Ac_2N, O_4$ [285°], while Bz_2O at 150° gives C_2, H_3Bz_2N, O_4 [265°]. Yields a crystalline nitrosoamine $C_2, H_{16}(NO)_2N, O_4$. Forms the salts $B''H_2Cl_2$, crystallising in needles with green lustre, $B''H_2SO_4$, $B''H_2PCl_3$, and a picrate crystallising in steel-blue needles [236°].—21. $C_9H_4(NH_2)(OMe)$ [1:2] forms $C_{20}H_{19}N_2O_4$ or $C_9H_2O_2(NH_2O_4)$. Ome) 2 crystallising in reddishviolet needles [230°], forming a blue solution in H_2SO_4 .—22. p-Amido-phenol hydrochlorids gives H2SO, -22. p-Amido-phenol hydrochloride gives C_bH₂O₂(NH,C_bH₄,OH)₂ crystallising in violet-brown needles, not melted at 290°.—23. (1,3,2). brown needles, not metica at 290°.—25. (1, 5, 2)Anido-o-cresol forms a compound [285°], which
gives a crystalline acetyl-derivative.—24. (2, 4, 1)Nitro-toluidine forms C₆H₄O₂,NH.C,H₆NO₂, decomposing at 300°, and C₆H₂O₂(NH.C,H₆NO₂),
(L.).—25. Acetoacetic ether and ZnCl₂ at 100° form C₁₆H₁₆O₆ [184°], crystallising in needles, insol. water, sol. hot alcohol. Conc. H₂SO₄ forms a deep-blue solution. Alcoholic potash forms $C_{14}H_{10}K_{2}O_{8}$ 2aq, the salt of an insoluble acid $C_{14}H_{12}O_{8}$ (Von Pechmann, B. 21, 3005). — 26. $C_{9}H_{4}(OH)(OMe)$ [1:4] in hot ligroin forms di-methyl-quinhydrone C₂₀H₂₀O₆, crystallising in lustrous greenish-black prisms, decomposed by warm water (Hesse, A. 200, 253).

Mono-oxim CO CH:CH C:N.OH or C(OH) CH.CH C NO no Nitrogo physical

C(OH) CH.CH C.NO. p-Nitroso-phenol. Mol. w. 123.

Formation.—1. By boiling nitroso-di-methylaniline (or nitroso-di-phenyl-aniline) hydrochloride with dilute NaOHAq (Baeyer a. Caro, B. 7, 809, 967; Ter Meer, B. 8, 622; Fischer, B. 19, 2995).—2. By adding KNO2 and HOAo to an aqueous solution of phenol (B. a. C.; cf. Stenhouse a. Groves, A. 188, 360).—8. By adding hydroxylamine hydrochloride to a cold dilute aqueous solution of quinone (Goldschmidt, B. 17, 213).—4. Formed also from aqueous phenol, hydroxylamine hydrochloride and H.O. (Wurster, B. 20, 2631). Free hydroxylamine merely reduces quinone to hydroquinone.

Properties.—Nearly colourless needles or greenish trimetric plates; a:b:a=:598:1:2-469.

M. sol. water, forming a light-green solution

which turns brown on boiling. V. sol. ether, acetone, and aqueous alkalis, sl. sol. HOAc. Decomposes at 120°-130°. Decomposed by hot Decomposes at 120-130. Decomposed by allowood. HClAq. When dissolved in phenol it gives, on addition of H,SO,, a cherry-red solution turned blue on addition of KOHAq. In this reaction the compound C, H, NO, is formed. Polyhydric phenols, containing two hydroxyls in the m-position, give by like treatment fluorescent 'dichroïns'; thus resorcin gives $C_{18}H_{15}NO_8$, $C_{36}H_{28}N_2O_{19}$, and azoresorcin (Brunner a. Chuit, B. 21, 249).

Reactions.-1. Oxidised by alkaline K, FeCy, to p-nitro-phenol.—2. Reduced by tin and HClAq to p-amido-phenol.—3. Nitrous acid gas passed into an ethereal solution forms diazophenol nitrate (Jaeger, B. 8, 894).—4. Gaseous HCl passed into a cooled ethereal solution forms HCl passed into a cooled ethereal solution forms di-chloro-amido-phenol [175°] and tri-chloro-amido-phenol (J.; Hirsch, B. 13, 1908).—5. A solution of HCl in McOH in presence of ice forms C₂H₂Cl₂(NH₂)(OMe) [72°]; while EtOH and HCl give C₂H₂Cl₂(NH₂)(OEt) [46°] (275°). 6. Conc. KOHAq at 180° forms azophenol C₁₂H₁₆N₂O₂ [214°] (Jaeger).—7. KClO₃ and HClAq form C₆H₄ClNO₂, crystallising in yellow needles, v. sol. alcohol, insol. water, and explading at 70° (Möhlen R. 19 281).—8. ploding at 70° (Möhlau, B. 19, 281).—8. ClO Me added to its sodium salt forms C₀H₁(NO).O.CO₂Me [137°], while ClCO₂Et yields C₀H₁(NO).O.CO₂Et [109°] (Walker, B. 17, 400). 9. BzCl added to the sodium salt in ether forms C.H.(NO).OBz, crystallising in yellowish needles [168°-175°], sol. hot alcohol (Walker).—10. Aniline forms azophenine C₆H₂(NPh)₂(NHPh)₂, p-Chloro-aniline forms, in like manner, tetra-chloro-azophenine [205°] (Fischer a. Hepp. B. 21, 677) .- 11. Bromine forms C, H2Br2O(NOH), crystallising in small leaflets, decomposed by water (O. Fischer, B. 21, 674).-12. Phenyl cyanate gives C.H.O.NO.CO.NHPh, crystallising in short yellow prisms decomposed at 160° without melting. It is converted by alkalis into the oxim, aniline, and CO, (Goldschmidt a. Strauss, B. 22, 3105).

Salts.-C.H.(NO)(ONa) 2aq. Red needles (from alcohol), v. sol. water, insol. ether. Decomposed by boiling water. Ppd. by NaOH from aqueous solution.—(C₈H₄(NO).O) Ba (dried at 100°). Red needles (from warm water).— -C_sH₄(NO).OAg aq. Violet crystals with green reflex.

Dioxim C(NOH) CH:CH C(NOH). Formed

by the action of hydroxylamine hydrochloride on the mono-oxim, on hydroquinone, and on pnitroso-aniline (Nietzki, B. 20, 613; 21, 430; Fischer, B. 21, 685). Yellowish needles (from hot water). Decomposes at 240°. Reduced by SnCl, and HCl to p-phenylene-diamine. Oxidised by alkaline K.FeCy, into insoluble di-nitroso-benzene. Ac.O forms a crystalline di-acetyl derivative, sol. hot alcohol.

C,H,<NCI Quinone-chlorimide [85°].

l'ormed by the action of bleaching powder on a solution of the hydrochloride of p-amido-phenol (R. Schmitt, J. pr. [2] 8, 1; 19, 816; Hirsch, B. 11, 1980; 13, 1903; Fogh, B. 21, 890; Andresen, J. pr. [2] 23, 167) or C.H.(NH₂).OEt. Purified by steam-distillation. Golden crystals (from HOAc). Sl. sol. cold water, v. sol. alcohol and ether. Explodes above 86°. Smells like quinone. Stains the skin brown. Turned brown by alkalis. Reduced by tin and HCl to p-amidophenol. Water at 100° forms quinone. Aqueous 80, forms amido-phenol sulphonic acid. HCl gives chlorinated amido-phenols. Gives Liebermann's colour reaction with phenol and H₂SO₄.
Quinone-di-chlorimide C₆H₄N₂Cl₂ i.e.

C₅H₄ NCI. Formed from p-phenylene-diamine hydrochloride and bleaching-powder solution (Krause, B. 12, 47). Needles (from water), decomposing at 124°. Almost insol. cold water. Its solution stains the skin brown. Reduced by SnCl₂ to p-phenylene-diamine. HCl forms tetrachloro-p-phenylene-diamine. Br gives di-chlorodi-bromo quinone. (β)-Naphthylamine forms C_{1s}H_{1s}N_sO, which dyes silk crimson and yields B'HNO₃ (Nietzki a. Otto, B. 21, 1745).

Quinone-phenylimide C₁₂H₁₁NO i.e.

 $C_6H_4<\stackrel{\mathrm{NPh}}{\circ}$ [97°]. Formed by oxidising p-oxydi-phenyl-amine in benzene by HgO (Ban-drowski, M. 9, 134, 415). Red crystals, v. sol. alcohol, ether, and chloroform. Decomposed by water and alkalis. Acids reproduce quinone. Reacts with aniline, forming p-oxy-di-phenylamine and di-phenyl-di-amide-quinone-phenyl-

Quinone-p-tolylimide C, H, NO. Formed in like manner from p-oxy-phenyl-ptolyl-amine (B.). Dark-red scales (from ligroin), sol, most solvents. Di-methyl-amido-phenylimide C14H14N2O i.e.

C.H. C.H. NMe. Phenol-blue. Formed by the action of nitroso-di-methyl-aniline on an alkaline solution of phenol, or by exidation of a mixture of phenol and phenylene-di-methyl-p-diamine (Möhlau, B. 16, 2851; 18, 2913). Formed also from quinone-chlorimide and di-methylaniline (Fogh, B. 21, 889). Steel-blue prisms (from water) (containing aq). Its solution in HClAq is blue. Conc. H.SO, forms quinone and $C_eH_4(NH_2)(NMe_2)$. Boiling NaOHAq forms NMe₂H and C_eH_4 . O. The sulphonio acid C₁₄H₁₄N₂SO₄ ½aq, formed from *p*-amidophenol-sulphonic acid in water by successive treatment with Cl and dimethylaniline, crystallises in bronzed needles, forming a blue solution in NaOHAq.

NaOHAq. Quinone tetrahydride $CO < CH_{r}CH_{2} > CO$. Diketohexamethylene. [78°]. Formed by heating the dihydride of di-oxy-terephthalic acid (succinyl-succinic acid) of 200° and distilling the product under reduced pressure (Hermann, A. 211, 322; Baeyer a. Noyes, B. 22, 2170). Prisms, v. sol. water. FeCl, does not colour its solution. Its alkaline solution turns brown in the air. Bromine forms C₆Br₁O₂. Reduces Fehling's solution. HCy forms C₆H₈(OH)₂Cy₂ [180°]. Yields a di-oxim which when quickly heated melts at 200°; when slowly heated at 192°. The di-phenyl-di-hydrazide C.H.(N2HPh)2 is obtained as a white pp. [125°] crystallising from alcohol in yellow prisms [150°], yielding a crystal-line hydrochloride B"H.Cl.

An isomeride of the tetrahydride CaHaOs, [1707], is got by the action of NaOHAq on succinyl-succinic ether. It crystallises in prisms (containing laq). It changes into the preceding isomeride on distillation. It reduces Fehling's solution.

References .- AMIDO-, BROMO-, BROMO-NITRO-, CHLORO-, CHLORO-NITRO-, IODO-, NITRO-AMIDO-,

Oxy-amido-, and Oxy-quinone.
TRIQUINONE v. BENZENE-TRI-QUINONE.

QUINONE DICARBOXYLIC ACID dihydride v. DI-OXY-TEREPHTHALIC ACID.

Tetrahydride v. Dihydride of DI-OXY-TEREPHTHALIC ACID.

Quinone tetracarboxylic acid. Methylether C₂O₂(CO₂Me)₄. [207°]. Formed by oxidation of C₂(OH)₂(CO₂Me)₄ with HNO₃ (Nef. A. 258, 318). Colourless prisms (containing 2MeOH) (from MeOH) or yellow needles (by sublimation).

Ethyl ether CoO2(CO2Et)4. Formed by oxidising di-amido-pyromellitic ether with conc. HNO₃ (Nef. C. 3:53, 428; A. 237, 28). Golden needles (from alcohol). May be sublimed. On treatment with KOHAq or with H₂SO₄ in HOAc it yields hydroquinone tetra-carboxylic ether. Zinc-dust and HOAc also reduce it to hydroquinone tetracarboxylic ether.

QUINOPHENOL v. OXY-QUINOLINE.

$C_{\mathfrak{s}}H_{\mathfrak{s}} < N > C_{\mathfrak{s}}O_{\mathfrak{s}}.$ DIQUINO-PHENAZINE

Formed by the action of dilute HNO, on CeH.: N2:C6O2(OH)2, which is got from rhodizonic acid and o-phenylene-diamine (Nietzki a. Schmidt, B. 21, 1228). Yellowish needles (containing 3aq), sl. sol. water. Converted by o-phenylene-diamine sulphate crystallising in greenish needles. into C21H12N6,

DIQUINOQUINONE CH/CO.CO\CH. Di-CO.CO

The di-oxim CoH2O2(NOH)2 is diquinoyl. nitrosoresorcin (q.v.) (Goldschmidt a. Strauss, B. 20, 1611; Kehrmann a. Messinger, B. 23, 2816). The dioxim is converted by hydroxylamine into the tetra-oxim, which, on heating amine into the tetra-oxim, which, with Ac₂O, yields the anhydride $C_eH_2N_4O_2$ crystalliaing in needles [61°], sol. ether. The tetraoxim may be reduced by SnCl, and HCl to tetraamido-benzene.

Triquinoquinone v. Benzene TRIQUINONE. Reference. - OXY-DIQUINOYL.

$C_6H_3Me < N > C_6O_4$ DIQUINO-TOLAZINE

Formed from rhodizonic acid and tolylene-odiamine, the product being oxidised by HNO, (Nietzki a. Kehrmann, B. 20, 324). Yellow needles (containing 2aq). On warming with an aqueous solution of a salt of tolylene-o-diamine it is converted into C2, H18O6, which crystallises from chloroform in needles (containing CHCl3).

QUINOVATANNIC ACID C14H18O8? Occurs in the bark of Cinchona nova (Quina nova) (Hlasiwetz, A. 79, 129). Translucent yellow mass, sol. water and alcohol, insol. ether. FeCl₂ gives a dark-green colour. NH₃Aq colours its solution brown. Its alkaline solution absorbs oxygen from the air. Boiling dilute H_2SO_4 splits it up into sugar and 'quinova red' $C_{28}H_{28}O_{12}$ (Rembold, A. 143, 273), which also occurs in the bark. Quinova red is a nearly black resin, nearly insol. water, v. sol alcohol, ether, and alkalis,

gives no colour with FeCl, and yields protocatechuic acid on fusion with potash.

QUINOVIN $C_{10}H_{16}O_{8}$ (Hlasiwetz) or $C_{28}H_{44}O_{11}$ (Oudemans, jun., R. T. C. 2, 160). Quinovabitter. Quinovic acid. $[a]_{b}=+59^{\circ}$. Occurr in false einchona bark from Cinchona nova (Pelletier a. Caventou, J. Ph. 7, 112; Winckler, Rep. Pharm. 51, 193; Buchner, jun., A. 17, 161; Peterson, A. 17, 165; Schnedermann, A. 45, 277; Rochleder a. Hlasiwetz, A. 79, 129; 111, 182). Occurs also in true cinchona bark (Schwarz. A. 80, 330; De Vrij, J. Ph. [3] 37, 255), in all parts of Cinchona Calisaya (from Java), and in

tormentilla root (Rembold, A. 145, 9).

Preparation.—The bark is extracted with boiling milk of lime, the extract ppd. by HCl and the pp. repeatedly dissolved in alcohol

and thrown down by water.

Properties.—Needles (from alcohol), almost insol. hot water, v. sl. sol. ether, v. sol. dilute alcohol. Tastes bitter. Dextrorotatory. Sol. aqueous alkalis. Resolved by acids into quinovic acid and quinovite. Does not reduce Fehling's solution.

Salts.—PbC₃₀H₄₀O₈aq.—(CuO)₃4C₃₀H₄₈O₈. (β)-Quinovin. [c. 235°]. [α]_D = + 28° in a 2·7 p.c. alcoholic solution. Occurs in cuprea bark (from Remijia) (Liebermann a. Gicsel, B. 16, 928). Scales (from dilute alcohol). Insol. ether, v. é. sol. alcohol. Dextrorotatory. Forms with alcohol the compound $C_{as}H_{s2}O_{11}5EtOH$, crystallising in large prisms. Split up by dilute acids into quinovic acid and quinovite.

Quinovite $C_0H_{12}O_4$ i.e. $C_0H_{3}O(OH)_3$. Quinovasugar. (c. 300°). $[a]_0=60^\circ$ (O.); $=+78^\circ$ (I. a. G.). Formed by the action of HCl on a hot alcoholic solution of quinovin; quinovic acid crystallises out, and the mother-liquor is neutralised by BaCO, filtered, and evaporated. Hygroscopic mass, sol. ether. Has a bitterswect taste. Does not ferment with yeast. Reduces Fehling's solution.

Tri-acetyl derivative C,H,O(OAc), [47°]. (c. 303°). White needles (Liebermann,

B. 17, 872).

Quinovic acid C.H.O. (Oudemans, R. T. C. 2, 160); $C_2H_{38}O_1$ (Hasiwetz a. Gilm, A. 111, 182); $C_2H_{38}O_2$ (Liebermann). $[\alpha]_D = +86^{\circ}$. Occurs in tormentilla root (Rembold, A. 145, 6). Formed from quinovin as above. White sandy powder composed of minute trimetric six-sided lamine, insol. water, v. sol. hot alcohol, sl. sol. ether. Tasteless. Ppd. from alkaline solutions by acids in a gelatinous form, gradually becoming pulverulent. Dextrorotatory. H2SO gives off CO and forms novic acid, quinochromin gives to CO and forms now sent, quinterform $C_{30}H_{44}O_2$ (crystallising in needles), quintervene $C_{32}H_{12}(?)$, and apoquinovic acid $C_{14}H_{26}O_4$ (crystallising in needles; whence $C_{16}H_{22}NaO_4$ $3^1_2_3aq$). Salts.—K_C2, $H_{30}O_1$ $1^1_2_3aq$; bulky pp.— $CuA''Ou_3(OH)_6$ 5aq: light-blue pp.— Ag_2A'' :

bulky pp.

Ethyl ether C32H16Et2O6. [127°-130°]. rystals, v. sol. alcohol and ether.

Pyroquinovic acid C₃₁H₃₈O₄. (above 360°). Formed by heating quinovic acid (Liebermann a. Giesel, B. 16, 936). Needles, insol. water, v. sol. alcohol and ether. Its alkaline solution is lævorotatory. On distillation, the distillate solidifies to a clear glassy mass, easily soluble in ether, and resembling gum copal in its proper-

ties. When this substance is heated with HI and P it yields a terpene (quinoterpene) which probably has the formula C_{so}H_{4s}. This terpene is also formed by direct reduction of pyroquinovic acid with HI and P (Liebermann, B. 17,

869).
Salts.—KA' (dried at 110°).—BaA'₂.
Quinoterpene C₃₀H₄₈. (above 360°). Formed

as above. Dextrorotatory.

Oxy-quinoterpene C₉H₁₈O₂ or C₂₈H₃₄O.

Cholestol. [139°]. (above 300°). Accompanies quinovin in false cinchona bark (Liebermann, B. 17, 871; 18, 1803; Hesse, A. 234, 377). Needles (from alcohol). Reduced by HI and P to quinoterpene. Yields an acetyl derivative [126°] and a benzoyl derivative [144°].

QUINOXALINE C.H., N. i.e. C.H., N.CH.

[27°]. (222° uncor.). Formed by the action of o-phenylene-diamine on glyoxal in aqueous solution (Hinsberg, B. 17, 320; A. 237, 334). White crystals, smelling like quinoline and piperidine, miscible with cold water, alcohol, ether, and benzene. Partially separated from aqueous solution by warming or by adding KOHAq. Its aqueous solution gives white pps. with HgCl, and AgNO,. Yields a sparingly soluble oxalate. Little attacked by oxidising agents. Sodium reduces it, in alcoholic solution, to phenylene-ethylene-diamine (Merz a. Ris, B. 20, 1190).- B'HCl: needles, v. sol. water. Decomposes at 184°.—B'H₂SO₄. [187°]. Silvery plates, v. sol. water.—B'₂H₂PtCl₆ (dried at 100°). Needles.

References .- ANIDO- and OXY-QUINOXALINE.

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RACEMIC ACID v. TARTARIC ACID. RACEMIC CAMPHOR v. CAMPHOR.

RADICLE. Lavoisier and his followers regarded an acid as a substance formed by the combination of much oxygen with another body; the body with which the oxygen was combined was called by de Morvoau the radicle of the acid, and the name was used in this sense by Lavoisier. 'Il faut donc distinguer dans tout acide la base acidifiable, à laquelle M. de Morveau a donné le nom de radical, et le principe acidifiant, c'est-à-dire, l'oxigène' (Traité élé-mentuire de Chimie [1789] 1, 69). That the radicle of an acid might be either a simple or a compound substance is evident from de Morveau's use of the term; in speaking of the nomenclature of acids of unknown composition, he says: 'Nous nous sommes contentés de désigner l'être simple qui y modifie l'oxigère par l'expression de base acidifiable, ou, pour abréger, de radicle, de têt acide ' (Mémoire sur le Développement des Principes de la Nomenclature Methodique [1787]). Lavoisier, in 1780, extended the meaning of the term radicle when he said (Traité, 1, 209) that most of the oxidisable and acidifiable radicles of mineral compounds were simple bodies, whereas the radicles of compounds of vegetable and animal origin were generally composed of at least two simple bodies. The notion of radicles was here, and elsewhere, extended by Lavoisier to mean the bases or foundations whereon more complicated bodies were built up, generally by the addition of oxygen.

As organic chemistry advanced, and many compounds were obtained from animal and vegetable sources, attempts were naturally made to find some reason for the existence of so vast a number of compounds all composed of but three or four elements. Lavoisier's assertion that the radicles of organic compounds are themselves composed of two or more elements, was revived, adopted, and developed. Berzelius, Liebig, Dumas, and other earlier workers in organic chemistry were struck by the enormous number of compounds produced by the union

of the four elements carbon, hydrogen, oxygen, and nitrogen. They said the true elements of organic chemistry are the radicles cyanogen, amidogen, benzoyl, cthyl, &c., &c. Dumas (C. R. 5, 300) said: 'In mineral chemistry the radicles are simple, in organic chemistry they are compound; therein consists the whole difference. The laws whereby the compounds are formed and their reactions are regulated are the same in both.' Liebig said: 'Organic chemistry is the chemistry of compound radicles.' In 1832 Liebig and Wöhler made apparent the meaning and wide applicability of the dictum that organic chemistry is the chemistry of compound radicles' by their researches into the constitution of the compounds obtained from oil of bitter almonds. By regarding these bodies as compounds of the radicle benzoyl, C,H,O, they became comparable with the compounds of the radicles potassium and other metals. From this time the conception of the radicle was firmly established.

The elements are the simple radicles, on which, and by the combinations of which, compounds are built up. The reactions of a series of compounds often show such similarities that we are obliged to conclude that the compositions of these compounds are also similar; in many cases this similarity of composition can be made apparent only by supposing that a certain group, or collocation, of elements enters into the composition of all the compounds. Such a group of elements, playing the part of a simple body throughout a series of reactions, but nevertheless separable into two or more elements, is

called a compound radicle.

For an example of the working out of the conception of the radicle v. AMMONIUM COM-DOUNDS, vol. i. pp. 200-201. M. M. P. M.

RADI OIL. The product of the distillation of the wood of a juniper. Contains a sesquiterpene Cl. H₂₁, whose hydrochloride C₁₂H₂₁2HCl melts at 118° (Wallach, A. 238, 82).

RAFFINOSE C₁₂H₂₂O₁₆5aq (Morris a. Brown, C. J. 53, 619; De Vries, R. T. C. 8, 326; C. R.

106, 751; Tollens a. Mayer, B. 21, 1569). Melitose. Gossypose. Melitriose. Mol. w. 528 to 644 (by Raoult's method) (cal. 594); 596 (by rate of osmosis in leaves of Tradescantia). [c. 87°]. S. 17 at 16° (R.); 14 at 20° (Loiseau). S. (80 p.c. alcohol) 1.4 at 70°. [α]_D = 104.6 (M. a. B.). [α]_J = 116.6. H.O. 2,019,700 (Stohmann, J. pr. [2] [4]_D = 104.6. [2]_D = 104.6. [2]_D = 10 45, 320; cf. Berthelot a. Matignon, C. R. 111, 13). Discovered by Johnston (C. S. Mem. 1, 159) in a manna, which drops from various kinds of eucalyptus in Tasmania. Further examined by Berthelot (C. R. 41, 392) and Rischbiet a. Tollens (B. 18, 2611). Occurs also in cotton-seed (Ritthausen, J. pr. [2] 29, 351; Böhm, J. pr. [2] 30, 37), in beet-root molasses (Loiseau, Bl. [2] 26, 365; Tollens, B. 18, 26; A. 232, 201; Lipmann, B. 18, 3087; Lindet, G. B. 110, 705; Blanck, G. 18, 3087; Lindet, C. R. 110, 795; Bl. [3] 3, 682).

Preparation .- Cotton-seed cake is extracted with spirit (S.G. 848). The extract is boiled down to a small bulk, and then shaken with ether (to remove colouring matters). After a time lumps of sugar separate; these are dissolved in 80 p.c. alcohol at 70°, boiled with animal charcoal, and allowed to stand. In a week glittering needles, arranged in hemispherical masses, separate (H. Ritthausen, J. pr. [2]

29, 351).

Properties .- Groups of needles, v. c. sol. hot water, v. sl. sol. alcohol. Has a slightly sweet taste. Does not reduce Fehling's solution. Not turned brown by boiling KOHAq. At 108° it gives off its water of crystallisation without melting; the anhydrous raffinose is not very hygroscopic. A second hydrate (containing 6aq) may be got as lamellee by crystallisation from dilute alcohol (Berthelot, C. R. 109, 548; Bl. [3] 2, 656). Readily ferments, giving with good yeast approximately as much alcohol as cane-sugar, while with feeble yeast only onethird of that quantity is formed. Raffinose can be assimilated by young plants, being converted into starch (Brown a. Morris, C. J. 57, 486).

Reactions.—1. Boiling dilute H.SO, splits it into levulose and 'melibiose' C. H. O. I. which yields with phenyl-hydrazine the osazone $C_{21}H_{22}N_1Q_0$. The mixture of lævulose and melibiose shows $[a]_D=50^\circ$. On further boiling with dilute H2SO, the melibiose is hydrolysed, the product consisting of galactose (1 mol.), lawulose (1 mol.), and dextrose (1 mol.) (Scheibler a. Mittelmeier, B. 22, 1678, 3118; Tollens, A. 238, 508; 249, 227). Melibiose is identical with eucalyn, and may be reduced by sodiumamalgam to melibiotite C12H21O11, a syrup which does not reduce Fehling's solution, but yields galactose on boiling with dilute acids. Invertin also splits up rasilnose first into lævulose (which may be fermented by yeast) and melibiose, and then this melibiose may be split up at 36° by a conc. solution of invertin into dextrose and galactose. The Pneumococcus of Friedländer sets up fermentation in suitable solutions of raffinose (Percy Frankland, C. J. 59, 270). 2. NaOEt gives a compound containing 6 to 7 p.c. sodium.—8. Boiling HNO₃ (S.G. 1·15) gives 23 p.c. of mucic acid. Saccharic acid is also formed.

Salts (Beythien a. Tollens, A. 255, 195) .-

 $\begin{array}{l} -C_{18}H_{28}U_{16}BaO.-C_{18}H_{22}O_{16}2BaO.\\ C_{18}H_{22}O_{16}(CaO)_3 2aq.-C_{18}H_{22}O_{16}8PbO. \end{array}$

Estimation. - In a mixture of cane-sugar and raffinose, the amount of raffinose may be determined by observing the change of rotatory power after hydrolysis (Creydt, B. 19, 3115; Gunning, Fr. 28, 45). The raffinose may also be ppd. by lead acetate from a solution in methyl alcohol, and the effect on the polarising action of the liquid observed (Lotman, Chem. Zeit. 12, 391; Gunning)

RANGIFORMIC ACID C₁₁H₁₈O₂. [106°]. Occurs, together with atranoric acid, in the lichen Cladonia rangiformis (Paterno, G. 12, BANGIFORMIC ACID C11H18O1. 259). Plates (from benzene), sol. other. Its ammoniacal solution gives a flocculent pp. of

AgA' on adding AgNO₃.

RAPIC ACID C18H34O3. Occurs as glyceride, together with the glycerides of erucic and behenic acids, in rape-seed oil (Reimer a. Will, B. 20, 2387). Oil. Yields stearic acid on fusion with potash. The zinc salt melts at 78°. The Na salt is gelatinous, v. sol. water, sl. sol. alcohol.

REDUCINE C₁₂H₁₂N₂O₃ or C₆H₁₁N₃O₄. An alkaloid occurring, as well as para-reducine C₆H₂N₃O, according to Thudichum (C. R. 106, 1803) in urine. It reduces ferric, cupric, mer-curic, and silver salts, and forms an insoluble barium compound.

REDUCTION. This term is used as synonymous with deoxidation in its widest sense. v. DEOXIDATION, vol. ii. p. 377; and cf. OXIDA-

TION, vol. iii. p. 657. REGIANIN v. JUGLONE.

RENNET v. MILK and PROTEÏDS. RESACETIC ACID v. vol. i. p. 18.

RESACETOPHENONE v. DI-OXY-ACETO-

PHENONE.

RESINS. Amorphous substances, occurring in all parts of plants, but especially in the bark (Wiesner, Sitz. W. 52 [2] 118). Frequently associated with essential oils. Resins are also formed from various oils by atmospheric oxidation or by the action of alcoholic potash. Boiling aqueous potash resinifies aldehydes. P.O. converts various aldehydes (e.g. benzoic aldehyde) into resins. These resins are solid, translucent, with conchoidal fracture, insol. water, wholly or partially sol. alcohol and aqueous alkalis. The resins, therefore, contain acids. The resins soften when heated, but are decomposed by distillation. By potash-fusion protocatechnic acid is obtained from guaiacum, benzoïn, dragon's blood, asafœtida, esparto resin, myrrh, acaroid resin, and opopanax. By potash-fusion p-oxy-benzoic acid is got from benzoïn, dragon's blood, aloes, and acaroid resin; phloroglucin from dragon's blood, esparto resin. and gamboge; and resorcin from galbanum, asafætida, gum ammoniac, sagapenum, and acaroid resin (Hlasiwetz a. Barth, A. 134, 265; 138, 61; 139, 83). Dammar, sandarac, mastic, and incense-resin are not attacked by fused potash. Resins containing gum or mucilage, soluble in water, are called gum-resins. Resins mixed with essential oils are termed balsams. The following resins are completely soluble in alcohol of 95 p.c. : benzoïn, caranna, resins and balsams from conifers (colophony), dragon's blood, guaiacum, mani-resin, mastic from Alexandria and from Bombay, black balsam of Peru,

podocarpus resin, sandarac, balsam of Tolu, anthorrhea resin. The following resins are only partially dissolved by alcohol of 95 p.c.; ammoniac, asafœtida, bdellium, Canada balsam, ceradia resin, copaiba balsam, copal, dammar, elemi, euphorbium, euryops resin, galbanum, gamboge, liquidambar, common mastic, Mecca balsam, myrrh, olibanum, opopanax, white balsam of Peru, sagapenum, sonora-lac, and liquid storax (Hirschsohn, Ar. Ph. [3] 10, 481; 11, 54, 152, 247, 312, 434). Ether dissolves completely: caranna, Canada balsam, conifer resins, copaiba balsam, dragon's blood, elemi, guaiac-resin, mani-resin, mastic, podocarpus resin, and sandarac. Most other resins are partially soluble in ether. FeCl, gives in alcoholic solution a blue colour with guaiacum and caranna, a dark-green colour with benzoin and some sorts of asafeetida, and a black colour with gamboge, balsam of Peru, opopanax, storax, sagapenum, shellac, and xanthorrhœa resin. FeCl, gives in an alcoholic solution of Canada balsam and of some sorts of dammar, a pp. which disappears on heating, and with copal and sonora-lac a pp. which does not disappear on heating. Alcohol containing HCl is coloured brick-red by white balsam of Peru and ceradiaresin; red to violet by common myrrh and euryops-resin; blue to violet by some sorts of elemi; yellowish-brown to green by guaiacresin; yellow, changing through brown to cherryred, by benzoin and balsam of Tolu; crimson by xanthorrhoa resin; greenish, changing to dingy violet, by asafœtida; yellow by gamboge and caranna; light rose-coloured by podocarpus resin; and brown by other resins. Conc. H., SO. forms a cherry-red solution with benzoin from Siam and with balsam of Tolu; a yellow solution with gamboge; a solution with yellowishbrown fluorescence with asafeetida; and brown with other resins. A drop of H,SO, added to a solution of pine-wood resin in HOAc gives a red or violet colour as the liquids mix (Morawski, C. C. 1888, 1630). Fossil resins (e.g. amber) are often found in beds of coal and lignite, being clearly derived from plants. Schmidt a. Erban (M. 7, 655; cf. Kremel, Fr. 26, 262) have determined, for a great variety of commercial resins, the quantity of alkali necessary to neutralise an alcoholic solution, and the amount required for saponification, and also the amount of iodine the resins can take up. They also base a method of separation upon the relative solubilities of resins. A classification of red resins according to their solubility in chloroform, benzene, and CS₂ is given by Dobbie a. Henderson (Tr. E. 30, 624). Colophony softens under boiling water, while powdered shellac, mastic, elemi, and dammar agglomerate, and sandarac, copal, and amber remain unchanged (Kliebhau, C. C. 1888, 87). The products of distillation of colophony have been examined by many chemists (Fremy, A. Ch. [2] 59, 13; A. 15, 284; Pelletier a. Walter, A. Ch. [2] 67, 267; Thénard, Robiquet, a. Dumas, C. R. 1838, i. 460; Schiel, A. 115, 96; Couerbe, J. pr. 18, 165; Curie, C. N. 30, 189; Kelbe, B. 13, 1157; B. 14, 1240; A. 210, 1; B. 15, 808; Renard, C. R. 91, 416; B. 18, 2000; Bl. [2] 36, 215; Tilden, B. 13, 1604; Anderson, C. N. 20, 76; Mills, 'Destructive Distillation,' 31; Tichborne, Ph. [8] i. 302; Morris, C. J. 41,

167) by whom the following substances have been described as constituents: water, reti-Taghthou as constituents: water, real-maphtha C,H_a (108°) (P. a. W.), retinyl C,H_a (150°) (P. a. W.), retinol C,H_a (150°) (286°-246°) (P. a. W.), retisterene [67°] (325°) (T. R. a. D.), (P. a. W.), retisterene [67°] (325°) (T. R. a. D.), carbonic acid, carbonic oxide, ethylene (S.), replene (S.), heptane [37°) (T.), octane (S.), a valerylene (50°) (C.), cymenes (170°–178°) (K.), heptinene C, Π_a (104°) (R.), colophenone $C_{11}H_{18}O_a$ (S.) (97°), a terpene (160°) (S.), abietic acid (K.), isobutyric and methyl-propyl-acetic acids (K.), hydrocarbons $C_{11}H_{10}$ (190°–200°) (K.), and iso-butyric aldehyde (T.). Renard (A. Ch. [61, 1, 223]) found among the products of distillations. [6] 1, 223) found among the products of distillation of colophony (rosin oil), pentane, amylene, hexane, hexylene, toluene, toluene tetrahydride, toluene hexahydride, xylene, xylene tetrahydride, xylene hexahydride, m-ethyl-propyl-benzene, terpenes, isobutyric aldehyde and acid, and valeric aldehyde and acid. Lwoff (B. 20, 1017) found, in resin cel, valeric, heptoic, ennoic, and hendecoic acids. Resin oil is coloured violet by Il₂SO, of S.G. 1.53 (Holde, C. C. 1888, 952).

Resin of Pinus Laricio (Poir). [c. 100°]. V. sol. alcohol, ether, and oil of terpentine; insol. ligroin. Contains much methoxyl (Bamberger, M. 12, 441). Turned red by air, and finally brown. It contains a little free caffere acid C. H. (OH) . CH: CH. CO. H [195°] and ferulic acid [4:3:1] C. H. (OH) (OMe). CH: CH. CO. H [169°]. 4 p.c. of caffere and 1 p.c. of ferulic acid may be extracted by boiling with water. The resin also contains some vanillin Calla(OH)(OMe).CHO. The resin yields pyrocatechin and protocatechuic

acid on fusion with potash.

Resin of Picca vulgaris (Link). [c. 100°]. Contains methoxyl (Bamberger, M. 12, 456). Contains p-coumaric acid and vanillin. Potashfusion gives protocatechuic and p-oxybenzoic . acids.

Resin of Pinus sylvestris contains an acid $C_{10}H_{20}O_5$ [143°], insol. water, v. sol. alcohol, ether, and HOAc. $[a]_j = -74^\circ$. It yields the salts $C_{20}H_{20}A_5O_3$, $(C_{20}H_{20}O_3)_2Ba$ 2aq, $(C_{20}H_{20}O_3)_2C_4$, and $(C_{20}H_{20}O_{3})_{2}Cu$, and oily $C_{20}H_{20}EtO_{3}$, which on distillation forms oily $C_{20}H_{2}$, EtO_{2} . Alcoholic HCl converts the acid into an isomeride [160°]. $[\alpha]_i = -93^{\circ}$ (Shkateloff, J. R. 20, 477).

Resin from Ficus rubiginosa contains 'sycoceryl acetate ' C₃₄H₃₀O₂ [121°] which on saponification gives acetic acid and sycoceryl alcohol C₃₂H₅₄O [114°] (De la Rue a. Müller, *Tr.* 1860,

43; Kennie a. Goyder, C. J. 61, 916).

References. - ABIETIC ACID, ALDEHYDE RESIN, Amber, Arbol-a-brea resin, Asafætida, As-PHALT, BENZOÏN (gum), CANADA BALBAM, COLO-PHONY, COPAIBA BALSAM, COPAL, DAMMARA RESIN, Dragon's blood, Elemi, Euphorbium, Gal-Banum, Gualacum, Gum ammoniac, Gutta percha, JALAP, LAC, LARCH FUNGUS, LARREA RESIN, MASOPIN, Mastic, Maynas Resin, Mecca Balsam, Myrre, Olibanum, Opopanax, Palisander Besin, Podo-CARPIC ACID, PODOPHYLLIN, SAGAPENUM, SAM-DARAC, SCAMMONY, and STORAY.

DARAC, SCAMMONY, and STORAX.

RESORCIN C₆H₆O₂ i.e. C₆H₄(OH)₁ [1:8].

[112°]. (267°) (Kopp). S. 86·4 at 0°; 147·3 at 12·5°; 228·6 at 30° (Calderon, Bl. [2] 29, 234).

V.D. 3·85 (calc. 3·81) (Troost, C. R. 89, 351.

H.C.v. 683,100. H.C.p. 683,400. H.F. 87,600 (Stohmann, J. pr. [2] 45, 335). S.V. 108 (Lossen, A. 254, 59]. S.V.S. 93·05.

896 RESINS.

Formation.-1. By potash-fusion from galbanum (Hlasiwetz a. Barth, A. 130, 354), m-iodo-phenol (Körner, Bl. [2] 7, 261), phenolp-sulphonic acid (Glutz, Bl. [2] 8, 361), p-chloro-benzene sulphonic acid (Oppenheim a. Vogt, A. Suppl. 6, 376), from umbelliferone (Hlasiwetz a. Grabowski, A. 139, 99), from asafætida, from gum ammoniac, from sagapenum, from acaroid resin (Hlasiwetz, A. 130, 354; 138, 63; 139, 78), from o., m., and p. bromo-phenol (Fittig a. Mager, B. 8, 362), from p.-chloro-phenol (Faust, B. 6, 1022), from p-iodo-phenol above 165° (Nölting a. Wrzesinsky, B. 8, 820), from phenol (Barth a. Schreder, B. 12, 420), and from benzene m. or p. disulphonic acid (Barth a. Senhofer, B. 8, 1483; Fahlberg, Am. 2, 195).-2. By dry distillation of brazilin (E. Kopp, B. 6, 446). 3. By the action of nitrous acid on m-amidophenol (Bantlin, B. 11, 2101).

Preparation .- By fusing benzene m-disulphonic acid with NaOH (Müllhäuser, D. P. J.

263, 154).

Properties .- Colourless trimetric tables (from water, alcohol, or ether); $a:b:c = 912:1:1\cdot059$ (Calderon, C. R. 84, 779) or needles (from benzene). V. sol. water, alcohol, and ether, insol. chloroform and CS. Acquires a reddish tint on exposure to air. Neutral to litmus. Has a sweet taste. FeCl, colours its aqueous solution dark violet. Its ammoniacal solution, exposed to the air, becomes rose-red and finally brown. The ammoniacal solution leaves on evaporation a dark-blue mass, which forms a blue solution, turned red by acids. Bleaching-powder gives a transient violet colour. A drop of a solution of NaOCl gives a violet colour, quickly changing to yellow, and on heating to dark-red or brown (Stark, Ph. [3] 21, 848; Boddé, Ar. Ph. [3] 27, 656). Resorcin reduces boiling ammoniacal AgNO, and boiling Fehling's solution. On heating resorcin with a few drops of nitro-benzene and conc. H,SO, a blue mass is got which, when poured into water and made alkaline, gives a solution with vermilion fluorescence. If resorcin is added to conc. H.,SO, and a little NaNO,, and the mixture is heated to 100°, a product is got which, when mixed with water and rendered alkaline by NH_s, imparts to fusel oil a crimson colour with vermilion fluorescence (Bindschedler, M. 5, 168). Resorcin fused with phthalic anhydride forms fluorescein, which dissolves in aqueous alkalis with strong green fluorescence (Baeyer, A. 183, 8). Resorcin heated with alcohol, beet-sugar, and HClAq gives a reddish-violet colour (Ihl, Chem. Zeit. 13, 264). A solution of resorcin (1 pt.) in absolute alcohol (2 pts.), mixed with an aldehyde and a few drops of conc. HClAq, gives, after standing for some hours and then pouring into water, a resinous or crystalline pp. (Michael a. Ryder, Am. 9, 134). A mixture of resorcin and furfuraldehyde touched with a drop of HCl gives an indigo-blue substance, which dissolves with green colour in water, and is ppd. by HCl in blue flakes (Baeyer, B. 5, 25). On warming a liquid containing chloral or chloroform with resorcin and NaOH s yellowish-red colour with green fluorescence is got (Schwarz, Fr. 27, 668). Cupric sulphate and excess of ammonia form a deep-black liquid, which dyes wool black (Wagner, D. P. J. 220,

Titration.—1. Bromine-water is run in until all the resorcin is converted into tribromo-resorcin, which is ppd.: $C_6H_4(OH)_2 + 3BF_8 = C_6HBr_4(OH)_2 + 3HBr$. The excess is determined by adding KI and titrating with hyposulphite (Degener, J. pr. [2] 20, 322).—2. Potash and potassium iodide are added to the solution, and then a neutral solution of bleaching-powder is run in. On adding HCl a pp. of tri-iodo-resorcin is formed, and the excess of iodine is

titrated by hyposulphite (Degener).

Reactions.—1. Soda-fusion gives phlorogluein (65 p.c.), some pyrocatechin (3 p.c.), and tetra-oxy-diphenyl (1 p.c.) (Barth a. Schreder, B. 12, 503).—2. Exhaustive chlorination in presence of I forms CCl₄ and CO₂ (Ruoff, B. 9, 1483) .- 3. ICl forms tri-iodo-resorcin (Michael a. Norton, B. 9, 1752).-4. An alkaline solution gives with KI a violet-red pp. of C6H2I3KO2 (Messinger a. Vortmann, B. 22, 2320).-5. A solution of resorcin (10 g.) in water (100 c.c.) gives a purple colour with 5 c.c. of very dilute solutions of nitrates, to which a drop of 15 p.c. HClAq and 2 c.c. of H₂SO, have been added (Lindo, C. N. 58, 176).—6. Resorcin (15 g.) dissolved in water (70 c.c.) and warmed with a mixture of (60 c.c. of) HBrAq (S.G. 1.47) and (20 c.c. of) HNO₃ (S.G. 1.39) gives C₄₈H₃₃BrN₂O₁₃ as a lustrous violet mass, which forms a red solution in alcohol, changed by alkalis to a blue liquid (Brunner a. Krämer, B. 17, 1873; 21, 2481). It yields C4, H20Ac6BrN2O13 as an orangered amorphous powder [120°], v. sol. hot alcohol.

7. Resorcin (15 g.) heated with water (60 g.),
HNO₃ (20 c.c. of S.G. 1·39), and HCl (60 c.c. of S.G. 1.2) for half an hour on a water-bath forms a violet mass $C_{ss}H_{4s}ClN_{s}O_{1s}$, insol. chloroform, sol. alcohol and ether. It yields yellowish-brown flocculent $C_{66}H_{10}Ac_{g}ClN_{3}O_{18}$ (Brunner, B. 21, 2479).—8. A blue colouring matter (lacmoid) is got by heating resorcin (55 pts.) with NaNO₂ (18 pts.) at 130°, dissolving in NH3Aq and reppg. by HCl (Benedikt a. Julius, M. 5, 534).—9. Bromine in CS₂ forms C₆H₂Br₂(OH)₂ [111°] (Zehenter, M. 8, 293).—10. With Al₂Cl₈ it gives the compound (C₆H₄O₂)Al₂Cl₄, which is v. sol. hot CS₂, less sol. cold CS₂; decomposed at once by water into resorcin, Al₂O₃, and HCl (Claus a. Merklin, B. 18, 2934).—11. Dry ammonia passed into a solution of resorcin in dry ether forms (CaHaO2)NH2, which separates as a liquid, solidifying as colourless deliquescent crystals, turning green and afterwards blue in the air (Malin, A. 138, 80).-12. H₂O₂ and NH₂Aq give, after acidification, a brown pp. ('lacmoid') which forms an indigo blue solution in alkalis (Zulkowsky a. Peters, M. 11, 243; cf. Wurster, B. 20, 2934).—13. Animonium carbonate solution at 125° forms (4,2,1)and (6,2,1)- di-oxy-benzoic acid (Senhofer a. Brunner, Sitz. W. [2] 80, 504).-14. Ammoniacal CaCl₂ at 300° forms a brownish-red colouring matter [72°], insol. water and alkalis, sol. alcohol (Seyewitz, C. R. 109, 946).-15. Sulphur and NaOHAq form, on boiling, C₆H₄O₂S₂, a yellow powder, sol. alkalis, insol. water, and decomposing before fusion (Lange, B. 21, 263) .-16. K₂S₂O₇ acting on potassium resorcin forms C₅H₄(OH)(O.SO₂K) and C₅H₄(O.SO₃K)₂. The latter salt is converted, by heating in the dry state at 160°, into a salt of resorcin disulphonic acid (Baumann, B. 11, 1911). -17. COCl. forms

C.H.: CO, a red amorphous substance, insol. water, v. sol. alcohol (Birnbaum, B. 14, 1753).-18. An alcoholic solution of potassium xanthate forms $C_0H_1(OH)_2CS_2H$, crystallising in yellow needles [131°], sol. hot water (Lippmann a. Fleissner, M. 9, 296).—19. Acctone dicarboxylic acid and conc. H.SO, form (8) umbelliferone acctic acid C(OH): CH.Cl.O.CO CH = CH.Cl.C.(CH₂CO,H) CH [202], crystallising in needles (containing aq), insolether (Michael, J. pr. [2] 37, 469).—20. Benzene sulphonic chloride added to a solution kept slightly alkaline forms CoH4(O.SO2CoH5)2, crystallising from hot alcohol in needles [70°] (Georgesen, B. 24, 417).—21. Hydrogen ammonium o-sulphobenzoic acid forms C13H13NSO 2aq as pale-yellow crystals, v. sol. water and alcohol. Its alkaline solutions are slightly fluorescent. Conc. HClAq at 220° reconverts it into the parent substances (Fahlberg a. Barge, B. 22, 754). Resorcin (4 mols.) heated with o-sulphobenzoic acid (1 mol.) forms C31H20NSO8 4aq.-22. Chloro-acetic acid forms C.H.(O.CH, CO.H) [194°], which yields a di-bromo- derivative (Gabriel, B. 12, 1640).—23. ClCo₂Et acting on C₆H₄(OK)₂ forms C₈H₄(O.CO₂Et)₂, a thick oil (300°) (M. Wallach, A. 226, 84).—24. Dry oxalic acid (1 mol.) in a scaled tube at 200° forms 'resorcin-oxalein' C₂₀H₁₄O₂, a hygroscopic red powder, sol. alcohol and ether (Claus, B. 10, 1305; 14, 2563). At 100° it becomes $C_{20}H_{12}O_{6}$, which is less sol. alcohol. Dilute alkaline solutions are yellow, with dark-green fluorescence. Bromine gives $C_{20}H_1Br_2O_g$. HNO, forms $C_{20}H_0(NO_g)_Q$. H_2SO_g yields $C_{20}H_0(SO_g)H_0O_g$. Ac. O forms red $C_{20}H_{10}Ac_1O_g$ and colourless $C_{20}H_0Ac_1O_g$. $C_{20}H_0Ac_1O_g$. $C_{20}H_0Ac_1O_g$. $C_{20}H_0Ac_1O_g$. $C_{20}H_0Ac_1O_g$. $C_{20}H_0Ac_1O_g$. heated with resorcin (2 mols.) at 120° yields two compounds C14H2O3 one of which fluoresces green in alkaline solutions (Gukassianz, B. 11, 1184). 26. HOAc and ZnCl₂ at 145° form di-oxy-acetophenone. Resorcin (100 g.) boiled with HOAc (200 g.) and ZnCl₂ (300 g.) for two hours forms 'acetiluorescein' $C_{2}H_{18}O_{3}$ and 'resacetein' $C_{1e}H_{12}O_{4}$. Resacetein crystallises by spontaneous evaporation of its ammoniacal solution in red needles. Its solution in KOHAq is red, but soon turns brown. It yields the salts B'HCl 2aq and B'2H,SO, (dried at 110°) and a triacetyl derivative C₁₆H₉Ac₂O, [229°]. Acetiluorescein forms minute brownish-red crystals. Its dilute alkaline solutions exhibit green fluorescence (Nencki a, Sieber, J. pr. [2] 23, 540; Rasiński, J. pr. [2] 26, 58).—27. Resorcin (20 pts.) heated with formic acid (10 pts.) and ZnCl₂ (20 pts.) for 30 minutes at 140° forms 'resaurin' $C_{19}H_{14}O_6$ or $(C_6H_3(OH)_2)_2C < \stackrel{V}{C_0H_3(OH)}$. Resaurin is a brick-red hygroscopic powder, forming a red solution in alkalis, sol. alcohol, insol. ether and acids (Nencki a. Schmid, J. pr [2] 23, 517) .- 28. On heating with ZnCl, and [2] 23, 547).—28. On heating with 2nU₁ and acctoactic ether or oitric acid 'resocyanin' is formed (Wittenberg, J. pr. [2] 24, 125; 26, 74; Schmid, J. pr. [2] 25, 81). Resocyanin can be prepared by heating dry citric acid (60 g.) with resorcin (60 g.) and H₂SO₄ (150 g.) for an hour at 180°. Resocyanin C₂H₁O₂ [185°] is insol. cold water, sl. sol. ether, v. sol. alcohol. Its alkaline solutions are colourless with blue fluorescence. Its solutions are not

coloured by FeCl₂. It yields $\mathbf{C}_{21}\mathbf{H}_{12}\mathbf{Br}_{4}\mathbf{O}_{6}$ [250°] and $\mathbf{C}_{21}\mathbf{H}_{14}\mathbf{k}\mathbf{c}_{2}\mathbf{O}_{6}$ [150°]. Resocyanin yields resord when fused with potash. It may be reduced to a hydride C₂₁H₂₀O₆ [259°] which yields C₂₁H₁₈Ac₂O₆ [222°]. NaOMe and MeI give $C_{21}H_{18}Ac_2O_6$ [222°]. NaOMe and MeI give $C_{21}H_{18}Me_2O_6$ [159°].—29. A cold alcoholic solution of sodium malonic ether forms C, H,O [191°], which is v. sol. hot alcohol, insol. cold water. Its alkaline solutions are fluorescent. It splits up when heated above 191° into CO, and methyl-umbelliferone (Michael, Am. 5, 434 J. pr. [2] 35,455; 37,469).—30. Resorcin (7 pts.) heated with phthalic anhydride at 200° forms FLUORESCEÏN (vol. ii. p. 557).—31. Resorcin (2 mols.) heated with phthalimide (1 mol.) and H₂SO, at 100° forms C₂₀H₁₃NSO,, a light-yellow powder, insol. benzene and ether, v. sol. alcohol. It forms $C_{20}H_{12}NaNSO$, 7aq and $C_{10}H_{11}Ac_{2}NSO$, a yellowish-green crystalline powder (Ostersetzer, M. 11, 425).—32. g-Benzoyl-benzoic acid forms, on heating, di-oxy-tri-phenyl-carbinol carboxylic anhydride (v. vol. iii. p. 738) .- 33. Maleic anhydride forms, on heating, maleïc-fluorescein $CH:CH > C < C_0H_3(OH) > O$, which exhibits deep green fluorescence in alkaline solution and gives crystalline C₁₆H₈Et₂O₅ and C₁₆H₈Ac₂O₅ [157°] (Burckhardt, B. 18, 2864).—34. Succinic acid (13 g.) heated with resorein (20 g.) and H.SO₄ (40 g.) at 195° forms 'succinyl-fluorescein' $C_{ls}H_{12}O_s$ or $CH_{...}CH_2 > C < C_sH_{...}(OH) > O$, which is crystalline (containing 3aq) and fluoresces in alkaline solution. It yields $G_nH_nBr_nO_s$ (Nencki a. Sieher, J. pr. [2] 23, 153).—35. Tartaric acid 1 mol.) heated with resorcin (2 mols.) and H2SO, (1 p.c.) at 165° forms resorcin-tartrein, a dark olive-green powder, which fluoresces in alkaline solution (Fraude, B. 14, 2558).-86. Na₂CO₃ added to a solution of resorcin and quinone forms a deep-green solution changing through yellow to brownish-red on shaking with air (Wurster, B. 20, 2934).—37. Heated with aniline and CaCl₂ it yields m-oxy-di-phenylamine. With aniline and ZnCl, it yields diphenyl-m-phenylene-di-amine (Calm, B. 16, 2786; cf. Merz a. Weith, B. 14, 2345).—88. Aldehyde in presence of weak acids forms C1.H1.O4 or CH₃.CH(O.C₅H₄.OH)₂, yellow crystals, insol. water and other, sol. alcohol. At 120° this body is converted into brown crystalline C22H23O7. By heating the compound C₁₄H₁₁O₄ with zinc-dust in a current of hydrogen at 300°, resorcin is produced. Ac₂O at 140° gives C₁₄H₁₂Ac₂O₁ [282°] (Causse, Bl. [2] 47, 89; J. Ph. [5] 13, 354).—39. Chloral hydrate in aqueous solution containing NaHSO, forms silky needles of C14H12O6, insol. water and benzene, sol. ether and alcohol. Its alkaline solutions are fluorescent. It yields a diacetyl derivative [252°] (Causse, Bl. [3] 3, 861). Resorcin and glyoxylic acid yield the same $C_{11}H_{12}O_2$. By boiling chloral hydrate (5 pts.) with resorcin (10 pts.) and water (40 pts.) there is formed $C_0H_0O_3$ crystallising from dilute alcohol in yellowish needles, and yielding C_bH_bAc_bO_b [159°] and C_bH_bBc₂O₃ [165°] (Michael a. Comey, Am. 5, 350).—40. Benzoic aldehyde, alcohol, and a little HCl give C28H20O, xaq [above 330°], a colourless resin, insol. water, v. e. sol. alcohol. Its alkaline solution absorbs oxygen from the air. Ac O and NaOAc form Con Hi Ac O. HCl

converts it into the isomeric C26H20O4 4aq crystallising from alcohol in dimetric tables, reduced by sodium-amalgam to C₂₈H₂₂O₄ crystallising from alcohol in prisms, and converted by Ac.O and NaOAc into C_{2a}H_{1a}Ac.O crystallising from xylene in prisms (Michael, Am. 5, 840).—41. CH₂,CCl₂ and caustic soda form OH_3 . $C(O.C_6H_1.OOI_3$ and caustic soda form OH_3 . $C(O.C_6H_1.OOI_3$ [159°], v. sol. alcohol, sl. sol. hot water (Heiber, B. 24, 3684).—42. Camphor forms the compounds $C_6H_6O_2(C_{10}H_{10}O)$ [29°], $[a]_0 = 22\cdot5^\circ$, crystallising in hygroscopic rectangu-Lar plates, and C₂H₂O₂(C₁₀H₁₆O₁₂, a syrupy liquid, S.G. ¹⁶ 1.037; [a]_D = 25° (Léger, C. R. 111, 110).

48. Phenyl-hydrazine (2 mols.) rubbed with powdered resorcin (1 mol.) forms C₂H₂O₂N₂H₂Ph, crystallising in unstable satiny needles [76°], v. sol. benzene alcohol, and ether. It is decomposed by water and alkalis (Baeyer a. Kochendörfer, B. 22, 2195).—44. Quinone (1 mol.) added to a solution of resorcin (1 mol.) in hot benzene forms C₁₂H₁₀O₄ [c. 90°] crystallising in dark-red needles with green reflex, m. sol. water (Nietzki, A. 215, 136).-45. Cyanic acid passed into an ethereal solution of resorcin forms into an ethereal solution of resorein forms $C_8H_8N_2O_4$ [120°], sl. sol. ether, m. sol. hot water (Traube, B. 22, 1579).—46. Phenyl cyanate forms at 100° C_8H_4 (O.CO.NHPh)₂ [164°] (Snape, C. J. 47, 772).—47. Urea (2 pts.) in a current of CO_2 at 250° forms $C_{29}H_{29}N_1O_8$ (5aq, an olive-brown amorphous powder, melting above 360°, v. sl. sol but HOA2 and alkalis (Birnhamm, B. 13. sol. hot HOAc, sol. alkalis (Birnbaum, B. 13, 1619).—48. Heated with aqueous KHCO₃ or ammonium carbonate it yields di-oxy-benzoic acid.—49. Resorcin (1 pt.) mixed with acetone (2 pts.) and fuming HClAq (1 pt.) forms C₁₅H₁₀O₄ or CMe₂(O.C₆H₄.OH)₂, which crystallises in small prisms [213°], insol. water and ether, sol. KOHAq and Na CO Aq. It is decomposed by heat into acetone and resorcin. It forms a crystalline hydrate $C_{13}H_{16}O_{1}$ aq. Ac₂O yields $C_{13}H_{14}Ac_{2}O_{4}$ [126°] while BzCl gives $C_{13}H_{14}Bc_{2}O_{4}$ [115°] (Causse, Bl. [3] 7, 563).—50. Resorcin (20 g.) heated with K.CS, under pressure at 100° forms CH.S.O. [150°-155], sl. sol. CS., converted by potash-fusion into resorcin and (4,2,1)-di-oxybenzoic acid [205°] (Pribram a. Glücksman, M. 13, 626).

Mono-methyl ether C.H.(OH)(OMe). (244°). V.D. (H=1) 62·2 (obs.). Formed by heating resorcin (1 mol.) with KOH (1 mol.) and KMeSO, at 160° (Habermann, B. 10, 868). Formed also from resorcin, NaOMe, and MeI (Tiemann, B. 13, 2362; 14, 2019). Prepared by heating resorcin with MeOH and KHSO, for 10 hours at 180° (Wallach, B. 16, 151). Liquid, NaOHAq. Slightly volatile with steam. FeCl. colours its solution violet. Acetic anhydride forms C.H.(OAc)(OMe) (255°). KOH and K.S.O. form C₆H₄(OMe)(SO₄K), crystallising in plates, sol, water and hot alcohol.

sol. water and hot alcohol.

Di-methyl ether CaH4(OMe)x (215°)

**R. Schiff, B. 19, 562); (224°) (Stohmann).

**V.D. 68°8 (obs.). S.V. 157°13. S.G. 2 1°075.

**H.F.p. 74,034 [C,O₂ = 94,000; H₂₁O = 69,000]

(Stohmann, J. pr. [2] 35, 27). S.V. 157°1.

**Prepared by heating resorcin (1 pt.) with MeOH, KOH (1°5 pts.), and MeI (3 pts.) for 6 hours at 250° (Oechsner de Coninck, Bl. [2] 34, J49).

Oil, v. sol. alcohol and ether. Volatile with steam. Nct coloured by FeCl.

Methyl ethyl ether C.H.(OMe)(OEt). (216°). Formed from C,H,(OH)(OMe), KOH, and KEtSO, at 165°; the product being distilled with steam (Spitz, M. 5, 488). Liquid.

Methyl propyl ether C.H.(OMe)(OPr). (226°). Colourless liquid.

Methyl isobutyl ether C.H.(OMe)(OCH,2Pr). (234°). Liquid. Methyl isoamyl ether C.H.(OMe)(OC,H1). (236°). Liquid. Mono-ethyl ether C.H.(O

Mono-ethyl $C_oH_1(OH)(OEt)$. Liquid. HNO, saturated with nitrous acid added to its ethereal solution at 0° forms C_uH_z(NO₂)(OH)(OEt) and two colouring matters: C₂,H₂₀N₂O₂ [230°] crystallising in red needles, insol. water, sl. sol. boiling alcohol, forming a purple solution in H₂SO₄; and C₁₁H₁₁NO₂ [228°] crystallising in orange-red needles, forming a bluish-violet solution in H.SO, (Weselsky a. Benedikt, M. 1, 891).

 $C_{\epsilon}H_{\iota}(OEt)_{2}$. Diethyl ether (229°) (Pukall, B. 20, 1140); (235°) (Herzig a. Zeisel, M. 11, 300). Formed from resorcin, KOH, and Etl. Colourless prisms, volatile with steam. On adding one drop of KNO, solution followed by HClAq to its solution in HOAc, an intense emerald green colour is produced. Yields two di-bromo-derivatives [101°] and [77°]. Converted by dissolving in HOAc, adding NaNO₃, and passing in HCl into C₆H₃(NO)(OEt)₂ [123°] and C₈H₈(NO)(OH)(OEt), whence BzCl forms yellow crystals of C.H.(NO)(OEt)(OBz) [155°] (Kraus, M. 12, 374).

Hexa-chloro-di-vinyl ether

C₈H₁(OC₂Cl₃)₂. [54°]. Formed by heating C₈H₁(OAc)₂ with PCl₃ at 100° (Michael, Am. 9, 210). Long prisms, insol. hot water.

Di-propyl ether C₆H₄(OPr)₂. (251°). V.D. 702 (obs.). Liquid, m. sol. hot water, sol. alcohol, ether, and ligroin (Kariof, M. 1, 258; B. 13, 1677). Br forms C₆H₃Br(OPr)₂ [70°].

Mono-benzyl ether C.H.(OH)(OC,H.). Formed from resorcin, KOH, alcohol, and benzyl bromide (Schiff a. Pellizzari, A. 221, 376; G. 13, 504).

Di-benzyl ether $C_0H_4(OC_7H_7)_2$. [76°]. Glittering tables (from alcohol).

Tetra-nitro-di-phenyl ether
C_sH₁(O.C_sH₂(NO₂)₂)₂. [184°]. Formed from resorcin, NaOEt, and (1,2,4)-chloro-di-nitro-benzene in alcohol (Nietzki a. Schündelen, B. 24, 3586). Colourless plates. Converted by HNO, into a penta-nitro- derivative [68°], and by H2SO, and HNO, into the hexa-nitro-diphonyl ether [220°].

Di-acetyl derivative C₈H₄(OAc), (273°) (Nencki, J. pr. [2] 23, 147); (278° i.V.) (Typke, B. 16, 552). Formed from resorcin and AcCl (Malin, A. 138, 78). Oil.

Di-bensoyl derivative C.H. (OB2). [117°]. H.F. 124,598 (Stohmann, J. pr. [2] 36, 10). From resorcin (5 g.), benzoic acid (11 g.) and POCl. (13 g.), the latter being added slowly (Rasiński, J. pr. [2] 26, 64). Formed also by shaking resorcin with BzCl and NaOHAq (Hinsberg, A. 254, 254). Plates (from ether).

Anhydride C₁₂H₁₀O₂ i.e. O(C₂H₄·OH)₂. Resorcinyl oxide. Resorcin ether. Formed by heating resorcin with NaOH and CO₂ (Böttinger, B. 9, 182), with Na and CO₃ (Barth, B. 9, 308), with HClAq under pressure (Barth a. Weider, B. 10, 1464), or with H₃SO, (Barth, A. 164, 122; Kopp, B. 6, 447; Annaheim, B. 10, 976). Formed also by heating resorcin at 195° with the disulphonic acid of resorcin or of phenanthrene (Hazura a. Julius, M. 5, 191). Brownishred amorphous powder, acquiring by pressure a green metallic lustre. Nearly insol. water, v. sl. sol. cold alcohol and ether. KOHAq forms a dark red solution with green fluorescence. Potash-fusion reconverts it into resorcin. Oxidised by nitric acid to isophthalic acid. Yields C₁₂H₄Ac₂O₃, which forms a reddish-violet solution in alkalis, and C₁₂H₄Br₂O₃. Formed, together

Anhydride C₂₁H₁₈O₅. Formed, together with C₁₂H₁₀O₅, by heating resorein with HClAq at 180°. Brick-red powder, v. sol. alcohol and ether. Its alkaline solution is brownish-yellow with violet-blue fluorescence. Yields C₂₄H₁₆Ac₂O₅ and C₂₄H₁₂Br₂O₅. Oxidised by nitric acid to

isophthalic acid.

Resazurin C₁₂H₀NO₄ (B. a. K.), or C₁₂H₇NO₄ (Nietzki, B. 22, 3021; 24, 3366). Diazoresorcin. Azoresorcin. Resazoin. Formed by the action of nitrous acid on an ethercal solution of resorcin (Weselsky, B. 4, 613; M. 1, 889; 5, 607). Formed also by the action of MnO, and H,SO, on an alcoholic solution of resorcin and nitroso-resorcin. Prepared by adding furning HNO, (6 c.c.) to resorcin (10 g.) dissolved in ether (500 c.c.) at -7° , Dark-red prisms with green reflex. Insol. water and ether, v. sl. sol. cold alcohol and HOAc. Its alkaline solutions are bluish-violet. Conc. H2SO4 forms a red solution. HCl forms a crystalline hydrochloride. Yields Ba(C12H6NO4)2 crystallising in brown needles, and a sodium salt, which forms greenish needles, v. sol. water, sl. sol. NaOHAq, fluorescing brick red in dilute alcoholic solution. Resazurin forms C₁₂H₃Br₄NO₄ on bromination. Reactions.—1. AcCl in a sealed tube at 100°

forms C₁₂H₉Cl₂NO₃ (?) crystallising from HOAc in golden plates and amorphous $C_{26}II_{21}Cl_3N_2O_6$ (?) (Weselsky, A. 162, 288; Brunner a. Krämer, B. 17, 1854).—2. Conc. H₂SO, at 210° and conc. HClAq at 100° form resorufin.-3. On heating with tin and conc. HClAq an emerald-green solution is got, from which on cooling 'hydrodiazoresorufin hydrochloride ' separates as colourless leaflets or needles, which, when exposed to air, acquire a coppery lustre, and when heated in a current of air produce resorufin. Hydrodiazo-resorufin is dioxyphenoxazine, the formula being $C_8H_3(OH) < \stackrel{O}{\underset{NH}{\longrightarrow}} C_8H_3OH$ (Nietzki, B. 22, 3020). 4. Hot conc. HNO, forms 'tetrazoresorcin nitrate' C₁₈H₆N₇O₁₅ (?), crystallising in lustrous garnet-red needles, sol. water, alcohol, and ether with indigo-blue colour. According to Brunner a. Krämer (B. 17, 1864; 18, 587) these crystals are tri-nitro-resazurin $C_{12}H_a(NO_2)_3NO_4$. By heating them with conc. HNO, Weselsky obtained 'tetrazoresorufin nitrate' $C_{23}H_aN_{12}O_{21}(?)$, crystalliging from NHO in deals red conditions of from lising from NHO, in dark-red needles, and from wet ether in purple needles (containing 11 aq). Tin and HClAq acting upon either of these bodies form a red body, probably tri-amido-resorufin hydrochloride, and a colourless body, probably tri-amido-di-oxy-phenoxazine. By passing air through an ammoniacal solution of the colourless body there are formed lustrous green crystals of 'hydroimidotetrazoresorufin' C₃₈H₂₈N₁₄O, aq (W.) or C₁₈H₈(NH₃)₃NO₄ (B.) (possibly tri-amido-resorutin). — 5. Bromins added to its solution in NaOHAq forms (C₁₂H₃Pr₂NO₄)HBr as a lustrous green mass, forming a blue alcoholic solution with red fluorescence (Brunner a. Krämer, B. 17, 1862). Nietzki obtained C₁₂H₃Pr₄NO₄, which gave C₁₂H₃MaBr₄NO₄ 2aq, crystallising from dilute alcohol in lustrous green prisms.—6. Oxidised in KOH solution by H₂O, to oxyresazurin C₁₈H₂N₂O, (?), which forms almost colourless crystals giving a reddish-yellow solution in alkalis. This compound is also formed by alkaline KMnO₄. It is reduced by zinc-dust to C₁₈H₁₈N₂O, (?), crystallising in colourless needles (Ehrlich, M. 8, 425).

Acetyl derivative C₁₂H₆AcNO₄. [222°]. Formed by heating the sodium compound with NaOAc and Ac₂O at 100° (Nietzki, B. 22, 3024).

Ruby-red needles.

Ethyl ether C₁₂H_eEtNO₂. [215°]. Formed from the Ag salt, alcohol, and EtI. Dark-red needles. According to Weselsky the formula of the ether [202°] got from resazurin, alcohol, and HCl at 100° is C.H.Et.N.O.

HCl at 100° is C_{1s}H_sEt₂N₂O₆.

Resorufin C₁₂H₇NO₃ i.e.

CO.CH:CO.C.CH:COH CH:CH.C:N.C.CH:CH

resorufin.

Formation.-1. By heating resazurin with conc. H2SO, at 210 .- 2. By heating resorcin with a solution of nitrous acid in H.SO. (Brunner a. Krämer, B. 17, 1847).—3. By warming nitrosoresorcin with resorcin and H.SO, (Fevre, Bl. [2] 39, 593) .- 4. By heating resordin with nitrobenzene and H.SO, at 170°. -5. By the action of zinc-dust on an ammoniacal solution of resazurin (Weselsky a. Benedikt, M. 5, 608) .-6. By boiling resazurin (1 pt.) with FeCl. (2 pts.) and furning HClAq (10 pts.) and ppg. with water (W. a. B.).-7. By action of nitroso-phenol on resorcin or of nitroso-resorcin on phenol in presence of H.SO, (Nietzki, B. 22, 3020; 23, 718).-8. By adding MnO, to a solution of pamido-phenol and resorcin in conc. H2SO.

Properties. — Small dark-red grains (from dilute HClAq), insol. water and ether, sl. sol. alcohol. Forms a bluish-violet solution in H.SO. Alkalis form a crimson solution with scarlet

fluorescence.

Reactions.—1. Reduced by tin and HClAq or by zinc and HClAq to dioxy-phenoxazine C₁₂H₂NO₃, exystallising in nearly colourless needles, which soon become green in the air, and yielding C₁₂H₄Ac₂NO₃ [216*] crystallising in colourless needles, sl. sol. hot alcohol.—2. Bromine added to the alkaline solution yields the sodium salt C₁₂H₂Br₁NO₃Na 2aq, crystallising in lustrous green needles.—3. Nitric acid (8.G.1·37) forms a body crystallising in green needles, forming a purple solution in water, alcohol, and ether. This body is probably tri-nitro-resorufia. 4. Fuming HCl at 100° forms 'azoresorufyl chloride' C₂₁H₁₀Cl₁N₂O₃ (?) crystallising in red plates, sol. ether (Brunner a. Krämer, B. 17, 1857). Its alkaline solution exhibits red fluorescence.

Acetyl derivative C, H. AcNO. [228]. Formed by heating resorutin with Ac.O and NaOAc. Orange scales, v. sol. acetone, sl. sol. alcohol ar i ether.

Ethyl ether C, H, EtNOs. [225°]. Orangered needles (Nietzki).

Nitroso-resorcin v. vol. iii. p. 619. Diresoroin v. Tetra-oxy-diphenyl.

References .- AMIDO-, AMIDO-DI-IMIDO, BROMO-, DI-BROMO-AMIDO, BROMO-NITRO-, CHLORO-, IODO-, DI-IODO-NITRO-, NITRO-, NITRO-AMIDO-, and NITROSO-BESORCIN.

RESORCIN-AZO- v. AZO- COMPOUNDS DISAZO- COMPOUNDS.

RESORCIN-BENZEÏN TETRA-OXY-TRI-PHENYL-CARBINOL.

RESORCIN CARBOXYLIC ACID v. Dr-oxy-BENZOIC ACID.

Resorcin (a)-dicarboxylic acid

C₆H₂(OH)₂(CO₂H)₂. [276°]. Formed, together with di-oxy-benzoic acid, by heating resorcin (1 pt.) with ammonium carbonate (4 pts.) and water (5 pts.) in a sealed tube (Senhofer a. Brunner, Bn. 2, 1266). Minute tables (from water), v. sl. sol. hot water. FeCl₃ colours its aqueous solution red. K1A"aq: needles.—K_2A"Baq: needles, v. e. sol. water.—BaA" 5½aq: needles.—CuA" 5 aq.—Ag.A": amorphous pp.

Resorcin (8)-dicarboxylic acid C_aH_a(OH)_a(CO_aH)₂. [250°]. Formed by heating (1,3,5)-di-oxy-benzoic acid with ammonium carbonate and water (S. a. B.). Four-sided prisms (containing aq), sl. sol. cold water. FeCl, colours its solution violet. - K2A".-Ba(HA")2 7aq.-BaA"4aq: needles. — Ba,C₈H,O₆2aq (dried at 160°). —PbC,H₄O₆ 1½aq.—Ca,M° 3½aq.

Resorcin dicarboxylic acid

 $C_6H_2(OH)_2(CO_2H)_2[4:2:5:1]$ (?). [192°]. Formed by oxidising the corresponding aldehyde [127°] (Tiemann a. Lewy, B. 10, 2212). Slender needles. Diresorcin dicarboxylic acid v. Tetra-oxy-

DIPHENYL DICARBOXYLIC ACID.

RESORCIN ALDEHYDE v. DI-OXY-BENZOIC

Resorcin dicarboxylic aldehyde v. Dr-oxy-

ISOPHTHALIC ALDEHYDE

RESORCIN-INDOPHANE C,H,N,O. Ppd., as K salt, by warming potassium tri-nitro-resorcin with aqueous KCy (Schreder, A. 163, 297). Small lustrous needles, forming a bluishviolet aqueous solution.—Na₂C₅H₂N₁O₆aq. — K₂C₅H₂N₁O₆aq: dark-brown lustrous crystals, exploding when heated.—BaC₁H₂N₁O₆aq. — DIRESORCIN-PHTHALEIN C₂H₂O₁O₅J₅laq

(Link, B. 13, 1654) or C₂₀H₁₂O₅ (Benedikt a. Julius, M. 5, 182). [245°]. Formed by heating diresorcin (tetra-oxy-diphenyl) with phthalic anhydride and SnCl₄ or H₂SO₄ at 115°. Silvery plates or needles, forming an indigo-blue solution in alkalis. Converted by heating with zincdust and caustic soda into diresorcin-phthalin C₃₂H₂₄O₁₀8½aq (L.) or C₂₀H₁₄O₆2aq (B. a. J.), crystallising from water in colourless plates [238°], forming a colourless solution in alkalis.
RESORCIN SULPHONIC ACID

C_eH₃(OH)₂(SO₃H). Formed by potash-fusion from the disulphonic acid (H. Fischer, M. 2,

337).-KA' 2aq : crystals.

Resorcin disulphonic acid C,H2(OH)2(SO3H)2. Prepared by sulphonation of resorcin (Piccard a. Humbert, B. 9, 1479; Tedeschi, B. 12, 1267). Deliquescent needles (containing 2aq), sol. water and alcohol, insol. ether. FeCl, gives a red colour. Gives phloroglucin on fusion with

potash. Bromine forms tri-bromo-resorcin even Pb_C,H_S,O, 4aq.

Resorcin disulphonic acid

C_eH₂(OH)₂(SO₃H)₂. Formed from di-amido-benzene disulphonic acid by the diazo- reaction (Limpricht, B. 8, 290). Long four-sided needles. BaA" 2aq : crystalline pp., got by adding alcohol to its aqueous solution.

Resorcin trisulphonic acid C₆H(OH)₂(SO₃H)₃. Formed by heating the disulphonic acid with fuming H₂SO₄ at 200° (Piccard a. Humbert, B. 10, 182). In neutral solution it gives a violet colour with FeCl.-Ba, A", 3!aq. Insol. water and HClAq.

References .- IODO-, NITRO-, and NITROSO-RESORGIN SULPHONIC ACID.

RESORCYLIC ACID v. DI-OXY-BENZOIC ACID. RESORCYLIC ALDEHYDE v. DI-OXY-BENZOIC ALDEHYDE.

Resorcylic dialdehyde v. DI-OXY-ISOPHTHALIC ALDEHYDE.

RETENE C₁₈H₁₈ i.e. CH.C₆H₁ [1:2] CH.C₆H₂MePr[1:2:6:3] Mol. w. 234. [98·5°]. (394°) (Schweizer, A. 264, 195). V.D. 8.3 (calc. 8.1) (Knecht, B. 10, 2074). S. (95 p.c. alcohol) 3 in the cold; 69 at 78°. S.G. (solid) 1.13 at 16°. H.C.v. 2,323,600. H.C.p. 2,326,100. H.F. -13,100 (Berthelot a. Vieille, A. Ch. [6] 10, 447). Occurs in scales in fossil pine-stems, accompanying fichtelite in peat bogs, and is a product of the distillation of wood (Fritsche, J. pr. 75, 281; Fehling, A. 108, 388; Wahlforss, Z. [2] 5, 73; Krauss, A. 106, 391; Ekstrand, Bl. [2] 24, 53; A. 185, 75; Bamberger a. Hooker, A. 229, 115). Produced by passing acetylene through a red-hot tube (Berthelot, J. 1866, 516). White plates, sol. alcohol, v. sol. hot HOAc, ether, and CS₂. Not attacked by potash-fusion or by alkaline KMnO₄. Dissolved by fuming HNO. It is not attacked by sodium-amalgam or HIAq at 200°. Reactions.—1. Absorbs chlorine, forming

C18H18Cl2, which splits up on heating into HCl and chloro-retene $C_{18}H_{17}Cl$, a crystalline body.— 2. Bromine and water form di-bromo-retene C18H16Br2 [180°] crystallising from CS2 in colourless tables. Excess of Br at 100° forms viscid $C_{18}H_{16}Br_4$ and crystalline $C_{18}H_{14}Br_4$ [212°].— 3. Oxidised by chromic acid mixture to retenequinone, phthalic acid, and HOAc. CrO, in HOAc forms retenequinone, retenic acid C18H18O2, and an acid C₁₆H₁₆O₃ crystallising from hot alcohol in plates [139°], forming NaA' and BaA'₂, both crystallising in plates.

Compound with picric acid C₁₈H₁₈C₄H₂(NO₂)₃OH. [124°]. S. (95 p.c. alcohol) 2·3 at 10°; 20 at 78°. Orange-yellow needles (from alcohol). Decomposed by water. Crystallises as $(C_{18}H_{18})(C_{6}H_{6})C_{6}H_{2}N_{2}O_{7}$ from benzene.

Compound with di-nitro-anthra-Dark orange-red needles (from quinone. HOAc).

Tetra-hydride C18H22. (280° at 50 mm.). Formed by adding Na to a solution of retene in isoamyl alcohol (Bamberger a. Lodler, B. 20, 3076). Pale-yellow liquid.

Dodeca-hydrids C₁₂H₃₀. (336° uncor.). Formed by heating retene with HI and P at 260° (Liebermann a. Spiegel, B. 22, 780). Colourless oil with bluish fluorescence. Vields no retenequinone when oxidised by HNO

Perhydride C₁₈H₃₂. [48°]. 719 mm. V.D. 8·69 (calc. 8·58). (335° i.V.) at This is probably the constitution of fichtelite (Bamberger a. Strasser, B. 22, 3361; Spiegel, B. 22, 3369; cf. vol. ii. p. 548). By heating with iodine it is converted into C₁₈H₃₀ (346° cor.) at 714 mm.

RETENE-FLUORENE v. METHYL-ISOPROPYL-

RETENE-GLYCOLLIC ACID C18H18O3 i.e. C₁₀H₁₀:C(OH).CO₂H. Formed by boiling retenequinone with NaOHAq (Bamberger a. Hooker, A. 229, 132). White crystals, sl. sol. hot water. -AgA': flocculent pp., sl. sol. hot water.
RETENE KETONE v. METHYL-ISOPROPYL-

DIPHENYLENE KETONE.

RETENEQUINONE C18H16O2 i.e.

 $CO.C_6H_4$ $CO.C_6H_2MePr$ Dioxy-Retistenequinone. relistene. [192°]. S. (95 p.c. alcohol) 15 at 0°; 2·2 at 78°. Formed by oxidising retene 0°; 2.2 at 78°. with CrO, in HOAc (Wahlforss, Z. [2] 5, 73; Ekstrand, A. 185, 75; Bamberger a. Hooker, B. 18, 1024; A. 229, 117). Orange-red prisms, v. sl. sol. cold alcohol and ether, sl. sol. aniline and HOAc, sol. benzene and chloroform. Not attacked by Cl in the cold. Not affected by hot HNO. Conc. H.SO, forms a green solution. Alcoholic potash imparts to its alcoholic solution a claret colour which disappears on shaking with air, but reappears on warming in absence of air.

Reactions.-1. Bromine forms C18H14Br2O2 [252°], crystallising from HOAc in orange prisms. 2. Cold NaOHAq does not dissolve it, but on boiling converts it into retene-glycollic acid.- On distillation with baryta it yields reteneketone and oily C_nH₂₄ (215-220°).—4. Distillation with zinc-dust forms retene.—5. HI and P reduce it to retene. - 6. In boiling alcoholic solution it is reduced by sodium-amalgam to retene diphenic acid $C_{16}H_{16}(CO_2H)_2$, an unstable resin yielding Ag_2A'' .—7. KMnO, forms oxy isopropyldiphenylene ketone carboxylic acid. -8. Phenyl-

ene-o-diamine forms $C_{1e}H_{1e} < \stackrel{C:N}{C:N} > C_0H_4$, crystallicing in really lising in needles [164°], insol. water, sl. sol. alcohol, v. sol. ether, resinified by strong acids. -9. Alcoholic ammonia added to a solution of the quinone in chloroform slowly forms the imide C18H18O(NH), crystallising in unstable golden needles.—10. Aqueous SO, forms hydroretene-quinone $C_{10}H_{10} < \begin{array}{c} C_{10}H_{1} \\ C_{10}H_{1} \end{array}$ crystallising in white

plates, sol. alcohol and alkalis. The same body is got by reducing the quinone with Zn and NaOHAq. It is oxidised by air to retenequinous.

Oxim C₁₈H₁₈O(NOH). [128.5°]. Golden

needles (from alcohol), decomposed by acids into the quinone and hydroxylamine. Forms green compounds with iron mordants (Von Kostanecki, B. 22, 1347).

RETENE DISULPHONIC ACID

C18H16(SO3H)3. S. c. 40 in the cold. Formed by sulphonation (Ekstrand, A. 185, 86). Needles (containing 10 aq), v. sol. water and alcohol. Its aqueous solution is ppd. by H₂SO₄, forming YOL IV.

H2A"5H2SO4, crystallising in hair-like needles .-K,A" aq (dried at 100'). S. c. 18. Small silky needles.—Na,A" aq (dried at 100'). S. c. 40 in the cold.—BaA" aq. S. 16.—SrA" 1 aq. S. 4.— CaA"8aq. S.5.—MgA"2aq (dried at 100°). S.4.-CuA' 5aq: long needles. S. c. 30.—PbA"aq (dried at 100°). S. 2.

Chloride C18H18(SO2Cl)2. [175°]. Prisms (from HOAc).

Retene trisulphonic acid C18H15(SO3H). Got by heating retene with fuming II.SO, at 100°. Crystalline mass, v. sol. water, alcohol, and ether; not ppd. by H₂SO₄.—Ba₂A'''₂18aq. Needles. S. 7.—Pb₃A'''₂18aq: slender needles. RETENIC ACID C₁₆H₁₆O₂. [222°]. A product of oxidation of retine (Ekstrand, A. 185, 111). Needles (from alcohol), v. sol. alcohol, ether, and HOAc. May be sublimed.-NaA: plates, m. sol. water.

RETINAPHTHA, is TOLUENE. RETINDOLE v. INDOLE.

RETISTENE is RETENE.

RHAMNETIN is the Methyl ether of

QUERCETIN (q.v.).

RHAMNITE $C_6H_{14}O_5$ i.e.

CH₃.CH(OH).CH(OH).CH(OH).CH(OH).CH₂OH. [121°]. [a]_D = 10.7°. Formed by reducing isodulcite with sodium-amalgam in a solution kept nearly neutral by H.SO. (E. Fischer a. Piloty, B. 23, 3104). Triclinic crystals, with sweet taste, v. sol. water and alcohol, sl. sol. chloroform, v. sl. sol. ether. Dextrorotatory. Does not reduce Fehling's solution.

RHAMNOHEPTOSE C,H1,O, СН(ОН).СН(ОН).СН(ОН).СН.

 $\frac{\mathrm{CH(OH).CH(OH).CH(OH).CHO}}{\mathrm{CH(OH).CHO}} \quad [\alpha]_D = 8^{\circ}.$ Formed by the action of sodium-amalgam on the lactone, [c. 160°], [a]_D = 55·6°, of hexa-oxy-octoic acid, which is formed from rhamnohexose by successive treatment with HCy and nexose by successive treatment with fley and baryta (Fischer a. Piloty, B. 23, 3106). Sweet syrup. Dextrorotatory. Yields C,II, O₆(N₂HPh) [200°] and C₈H₁O₅(N₂HPh)₂ [c. 200°]. Converted by treatment with HCy, followed by saponification, into hepta-oxy-ennoic acid CH(OH).CH(OH CH(OH).CH(OH).CH(OH).CH(OH).CO₂H the CH(OH).CH(OH).CH(OH).CH(OH).CO₂H the lactone of which [c. 172°] is levorotatory [a]_p = -51° .

RHAMNOHEXITE C.H.₁₁O₆ i.e.

ÇH(OH).CH(OH).CH(OH).CH3 [c. 173°]. CH(OH).CH(OH).CH₂(OH)

[a]₀ = 11.6°. Formed by reducing rhamnohexose with sodium-amalgam (Fischer a. Piloty, B. 23, 3106). Small colourless prisms (from hot alcohol). Does not reduce Fehling's solution.

RHAMNOHEXOSE C. $H_{14}O_{g}$ i.e. $GH_{a}CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CHO$. [181°]. [a]_D = -61°. Formed by reducing the lactone of isodulcite carboxylic acid with sodiumamalgam in acid solution at a low temperature (Fischer a. Piloty, B. 23, 3104). Small tables, sl. sol. alcohol. Its aqueous solution tastes sweet. Yields a di-phenyl-di-liydrazide [200°].

RHAMNOSE V. ISODULGIES.
RHATANINE C₁₀H₁₂NO₂. S. 8 at 100°.
S (alcohol) 01 at 15°; 04 at 76°. Occurs in the extract of rhatany root (Wittstein, J. 1854, 656; Ruge, Viertelj. d. nat. Ges. in Zürich, 6, Hett 3; Gintl, Sitz. W. [2] 60, 668; Kreitmair, 4. 176, 69). Spherical groups of white needles,

insol. ether. Not ppd. by lead acetate or subacetate. Resembles tyrosine. On heating with a little solution of Hg(NO₃)₂ it becomes rose-red, and gives a brown pp. on further addition of Hg(NO₃)₂. Boiling HNO₃ gives a red colour changing to blue, and finally to a fluorescent green. Sulphuric acid forms a sulphonic acid $C_{10}H_{12}NO_3(SO_3H)$ aq crystallising from alcohol in

Salts.—H₂\(\alpha''\)HCl: monoclinic prisms, decomposed by treatment with water or alcohol.— (H₂A")₂H₂PtCl_e.—Na₂A": deliquescent amorphous mass.—K₂A".—BaA" 2aq.—SrA" 2aq. phous mass.—A.A. .—Ban zuq.—Gra zuq.—CaA".—MgA".—Ag.A": minute needles, sl. sol. cold water.—H.A"H.YO.,: trimetric crystals.—H.A"H.,PO.; small prisms.

RHATANITANNIC ACID C.,0H.20, (Raabe,

J. 1880, 1060). Occurs in rhatany extract from the root-bark of Krameria triandra (Wittstein, J. 1854, 656; Grabowski, A. 143, 274). Amorphous, sol. water. Reduces Fehling's solution. Gives a dark-green colour with FeCl. Yields phloroglucin and protocatechuic acid on fusion with potash. 'Boiling dilute H2SO, forms 'rhatania-red ' C20H18O8, which yields pyrocatechin on distillation.

RHINACANTHIN C14H18O4. Occurs in the root of Rhinanthus communis (Liborius, J. 1881, 1022). Tasteless resin, sol. alcohol. Does not

form glucose on boiling with HClAq.

RHINANTHIN C29H32O20 (L.) or C81H38O400 A glucoside occurring in the seeds of the yellow rattle (Rhinanthus crista-galli), and giving rise to the violet colour of bread prepared from rye contaminated with these seeds. Occurs also in the seeds of Alectrolophus hirsutus (Ludwig, Z. [2] 5, 303; Ar. Ph. [2] 142, 199), and in the leaves and stalks of the snap-dragon (Anti-rhinum majus) (Phipson, C. N. 58, 99). Stellate groups of prisms, with bitter-sweet taste, v. sol. water and alcohol. Gives a bluish-green solution on warming with alcoholic HCl. Resolved by dilute HClAq into brown amorphous rhinanthogen and a sugar.

RHIZOPOGONIC ACID C25H36O4. [127°]. Obtained from the mushroom Rhizopogon rubescens by extracting with ether (Oudemans, R. T. C. 2, 155). Red needles, insol. water, v. e. sol. ether, chloroform, and boiling alcohol. alkaline solutions are intensely violet.—KA' aq:

minute dark-violet crystals.

RHODAMMINES RHODIUM-AMMONIUM COMPOUNDS, p. 405.

RHODANIDES, another name for Sulpho-

cyanides (q. v. vol. ii. p. 348).

RHODÂNIC ACID C,H,NS2O i.e.

HS.CH,CO.S.CN or CH2

CO.NH (Andreasch, M. 10,73). [169°]. Formed by warming an aqueous solution of chloro-acetic acid (1 mol.) with ammonium sulphocyanide (3 mols.) (Nencki, J. pr. [2] 16,1; B. 17, 2279; Ginsberg a. Bondzynski,
 B. 19, 113). Formed also by passing HCl into an alcoholic solution of thioglycollic acid and otassium sulphocyanide (Freydl, M. 10, 82). potassium suipnocyanius (riejui, Yellow six-sided prisms and tables, v. sl. sol. cold water, v. sol. alcohol and ether. Acid in reaction. Boiling baryta-water splits it up into HCyS and thioglycollie acid. Water at 200° forms CO₂, H₂S, NH₃, and thioglycollie acid. Reacts with aldehydes in presence of HCl, form-

ing compounds of the type R.CH:C(SH).CO.S.CN. Ethylidene-rhodanic acid C,H,NS,O [148°] forms yellow needles, sol. hot water. Benzylidene-rhodanic acid C10H,NS2O [200°] also forms yellow needles, converted by hot H2SO4 (4 pts.) into C10H7NS2O3, crystallising in needles, yielding NaA', KA', and NH,A', and converted by HNO₃ nto C₁₀H_aN₂S₂O₇, crystallising in yellow needles yielding NaA' aq. o-Nitro-benzylidene-rhodanic acid C₁₀H_aN₂S₂O₃ [189°] crystallises from dilute alcohol, and may be reduced to o-amido-benzylidene-rhodanic acid, which yields C₁₀H₁AcN₂S₂O [280°-285°] and C₁₀H₆Ac₂N₂S₂O [189°]. p-Nitro-benzylidene-rhodanic acid [252°] is also crystalline (Bondzynski, M. 8, 357). FeCl, added to a hot solution of rhodanic acid forms a brown pp., from which alcohol extracts C₂H₃N₃S₅O₃ as a brownish red powder, forming a red solution in alkalis.

Salts.—CuA', aq: yellowish-green amorphous pp.—(C₃H₃NS₂O), CuCl: golden needles. RHODATES. No salts have been isolated the acidic radicle of which is composed of Rh and O; but there is some reason to think that such salts exist in the solution obtained by passing Cl into an alkaline solution of Rh2(OH),; v. under Hydrated rhodium dioxide, p. 405.

RHODINOL C₁₀H₁₈O i.e. CH₂·C(C₂H₂).CH:CH.CH.Me.CH₂OH. (217°). S.G. 1¹⁵·88. Occurs in German and Turkish oil of roses (Eckart, B. 24, 4205). Oxidised by chromic acid mixture to an aldehyde, rhodinal, and rhodinolic acid. P2Os yields a terpene. KMnO4 forms valerio, butyrio, acetic, oxalic, and carbonic acids and C₆H₁₄O_a, possibly an alcohol.

RHODIUM. At. w. 102-7. Mol. w. unknown. Melts at c. 2000° (Pictet, C. R. 88, 1317). S.G. 12·1 (Deville a. Debray, J. 12, 240). S.H. 05803 (10° to 97°; specimen contained trace of Ir) (Regnault, A. Ch. [3] 63, 1). C.E. 0000085 at

40° (Fizeau, C. R. 68, 1125).

Occurrence.-With the other Pt metals in platinum-ore; the p.c. of Rh varies from 0 to c. 5; as much as 12.3 p.c. was found in a South American ore by Deville a. Debray (A. Ch. [2]

29, 137; cf. Kern, C. N. 35, 88).

Del Rio (v. D. a. D., l.c.) found an alloy of Rh and Au in Mexico, containing from 34 to 43 p.c. Rh. Rhodium was separated from the other Pt metals in 1803 by Wollaston (T. 1804. 419), at the same time as he isolated Pd. The name rhodium was given by W. because of the rose-

colour of the salts (ρόδον = a rose).

Formation.—1. By reducing RhCl, 3NaClAq by Zn, H, formic acid, &c .- 2. By strongly heat-

ing RhCl 3.3NH Cl.

Preparation.—Rh is generally prepared by adding iron to the mother-liquors from which Pt has been extracted (v. Platinum, this vol. p. 286), and then treating the solid so ppd. The processes for the treatment of this residue are many; that described here is the one employed by Claus (J. pr. 85, 129), and by Gibbs (J. pr. 84, 65; 94, 19), and is a modification of Claus's older method (cf. Deville a. Debray, C. R. 78, 1782). The platinum-residue-which contains Rh, Ru, Pd, Ir, Cr, Cu, and Pb-is fused at a bright red heat with 1 pt. Pb and 1 pt. PbO; the regulus, after separation of slag, is treated with nitric acid (equal vols. conc. acid and water); the insoluble residue is washed, dried, and mixed

with its own weight of NaCl, and this mixture is heated to low redness, in a large porcelain tube, in a stream of Cl, for some time; the treatment with NaCl and Cl is repeated; after cooling, the contents of the tube are lixiviated with water, when RhCl₃.3NaCl dissolves with small quantities of the corresponding salt of Ir and traces of some of the other metals. The solution is heated with HNO3Aq, to transform IrCl, into IrCl, and Ir is then removed, as IrCl, 2AmCl, by fractional ppn. with conc. The filtrate from the last pp. of AmClAq. IrCl..2AmCl, which is almost quite free from all metals except Rh, is evaporated to dryness with HNO, Aq, to decompose the AmCl; the residue is mixed with 3 or 4 times its weight of S, and heated to bright redness in a covered porcelain crucible, which is packed in powdered charcoal in a larger earthen crucible. The regulus thus obtained is boiled for some time with aqua regia, and then with conc. H₂SO₄; it is then fused, at a low red heat, with 3 or 4 pts. Zn, whereby an alloy of Rh and Zn is formed, with the production of so much heat that part of the Zn is volatilised. After cooling, the alloy is digested with conc. HClAq, to remove impurities, and is then dissolved in aqua regia. NH, Aq is added to this solution till the pp. which forms has dissolved: the solution is boiled, and evaporated until yellow Rh2(NH3)10Cla separates; the whole is then evaporated to dryness at 100°, and the residue is treated with warm dil. HClAq until the washings show no yellow colour; the residue is dissolved in boiling water, and the liquid is filtered, hot, into dil. HClAq; the small yellow crystals of Rh2(NH3)10Cle which separate are re-crystallised several times from hot, dil. NH3Aq, whereby the salt is obtained quite pure. The pure Rh2(NH3)10Cl6 is decomposed by heating strongly in a graphite crucible, and the Rh thus obtained is fused in a lime crucible in the O-H flame (v. vol. iii. p. 642). The fusion removes the last traces of Os and Si. For other methods of preparing Rh v. Bunsen, A. 146, 265; Fremy, C. R. 38, 1008; Lea, Am. S. 38, 81, 248; Schneider, P. Supp. 5, 261; Philipp, D. P. J. 220, 95; Martius, A. 67, 357; Wilm, Bl. [2] 34,

Properties.—A very hard, white metal, with a tinge of blue-grey; about as ductile and malleable as Ag. Melts only in the full O-H flame, without volatilising; spits on cooling; is superficially oxidised when very strongly heated in air. Insoluble in acids when compact, but the finely divided metal ppd. from solutions is sol. HNO,Aq, and also sl. sol. HClAq in presence of air (Wilm, Bl. [2] 34, 679). Alloys of Rh with Bi. Cu, Pb, Pt, or Zn are attacked by HNO,Aq. Rh is obtained as a black porous solid by reducing solutions of Rh compounds by Zn, Hg, EtOH, or HCO,H (v. Claus, J. pr. 85, 139; Wilm, lc.). The finely divided Rh obtained by heating the purpureochloride takes up c. 13 p.c. O when heated in a stream of air (RhO requires 13-5 p.c. O), and the O is given up by heating in H.

In its chemical relationships Rh is closely allied to Ru and Pd, and less closely to Os, Ir, and Pt; v. Noble metals, vol. iii. p. 628.

The at. w. of Rh has been determined (1) by analyses of RhOl, 3KCl (Berzelius, P. 18, 442 other occupies when the reagents are added, [1828]); (2) by analyses of a large number of and comparing the two, 00019 g. Rh can be

different Rh compounds (Claus, J. pr. 85, 139 [1862]); (3) by analyses of Rh₂(NH₃)₁₆Cl₄ and Rh₂(NH₃)₁₆Cl₅ (Jörgensen, J. pr. [2] 27, 433, 489 [1883]); (4) by reducing pure Rh₂(NH₃)₁₆Cl₄ in H, and determining the residual Rh (Seubert a. Kobbé, A. 260, 314 [1890]); (5) by determining S.H. of Rh (Regnault, A. Ch. [3] 63, 1). No compound of Rh has been gasified. The older values for at. w. of Rh varied from 104'3 to 103. Seubert a. Kobbé have shown that the true value is less than 103.

Reactions and Combinations .- 1. Rhodium black heated in air combines with O to form RhO, according to Wilm (B. 15, 2225). Leidié (Bl. [2] 50, 664) says that the products contain from 14.5 to 17.8 p.c. O (RhO requires 13.5 p.c. O). -2. Oxidised to Rh₂O₃, and then to RhO₂, by fusion with potash and nitre (Claus, l.c.); also by heating strongly with barium peroxide (D. a. D., l.c.) .- 3. Fusion of Rh black with potassiumhydrogen sulphate produces what is probably a double Rh-K sulphate (Claus, l.c.). 4. Heated in chlorine to c. 400°, RhCl₃ is formed (v. Leidić, Bl. [2] 50, 664) .- 5. Mixed with scalium-chloride and heated in chlorine, RhCl, 3NaCl is produced; KCl and Cl, and BaCl, and Cl, act similarly (Berzelius, P. 13, 435; Bunsen, A. 146, 266).— 6. RhS is formed by heating Rh black in vapour of sulphur (B., l.c.).—7. Rh dissolves in molten phosphoric acid (Fischer, P. 18, 257), also in molten acid phosphates (Rose-Finkner, Hand. d. anal. Chem. 6th ed., 1,354). -8. Finelydivided Rh dissolves in molten zinc (Jörgensen, J. pr. [2] 27, 433, 489).—9. Hydrogen is absorbed in large quantities by Rh. The finely divided metal obtained by heating RhCl.3AmCl becomes sensibly hot when H is passed over it (Wilm, l.c.) .- 10. Rh black decomposes chlorine water, forming HClAq and O, and solutions of hypochlorites, forming chlorides and O (Jörgensen, l.c.). It also decomposes hydrogen peroxide, giving off O .- 11. Rh black decomposes formic acid solution to H and CO.; alcohol in presence of alkali is oxidised to alkali acetate, and H is given off, at c. 30° (D. a. D., A. Ch. [2] 29, 137; 56, 385; cf. Hoppe-Seyler, B. 16, 117).—12. When Rh black obtained by heating RhCl, 3AmCl is heated in coal-gas, or in ethylene, the volume of the Rh increases and C is absorbed (Wilm, Bl. [2] 34, 679).

Detection .- Rh may be brought into solution in water, either by repeated fusion with KHSO. or by mixing with NaCl and heating to low redness in Cl. To detect Rh in solution, Demarcay (C. R. 101, 951) recommends to add AmCl to a neutral, or an almost neutral, solution which has been boiled with HClAq, then to add fairly conc. freshly prepared NaClOAq, and then a 20 p.c. acetic acid solution, drop by drop, with constant shaking, till any pp. formed by the NaClOAq dissoves to an orange-coloured solution; on standing, this solution decolourises, deposits a greyish pp., and finally acquires an intense sky-blue colour, which remains for some time. Free HNO₃ or H₂SO₄ should be absent, not much acetic acid should be added, and the temperature should not be raised. By taking two equal portions of the liquid to be tested. diluting one with water to the same bulk as the other occupies when the reagents are added, detected in 3 c.c. liquid. The other Pt metals ! give no reaction with NaClOAq under the above conditions.

Rhodium, alloys of. Rh alloys with many metals, by fusion with them. Some of the alloys seem to have definite compositions, e.g. Rh.Pb and RhZn₂. Descriptions of the alloys will be found in the papers referred to:—As (Wollaston, T. 1804. 419); Bi (W., l.c.); Au (W., l.c.; van Riemsdyk, J. 1880. 1269); Fe (Faraday a. Stodart, G. A.: 66, 167); Pb (Debray, C. R. 90, 1195; Deville a. D., C. R. 44, 1101; 94, 1557); Pt (D. a. D., l.c.); Ag (W., l.c.); Sn (D., l.c.; Leidié, C. R. 106, 1076); Zn (D. a. D., l.c.; Bunsen, A. 146, 271; Jörgensen, J. pr. [2] 27,

Rhodium, ammonio-salts of, v. Rhodium-

AMMONIUM COMPOUNDS, p. 405.

Rhodium, chlorides of. The only chloride of Rh which has been isolated with certainty is RhCl. The lower chloride RhCl, probably exists.

RHODIUM DICHLORIDE RhCl2. This chloride probably exists. Berzelius obtained a greyishred powder, to which he gave this composition, by heating Rh in Cl, warming the product with KOHAq, and treating the hydrated oxide so formed with HClAq, when RhCl₃ dissolved and RhCl₂ (?) remained (P. 13, 437). According to Fellenberg (P. 50, 63) RhCl₂ is obtained, as a rose-red powder, insol. water, HClAq, or HNO, Aq, undecomposed by KOHAq, by heating RhS in Cl. Claus (J. 1855, 423) and Leidié (C. R. 106, 1076; 107, 234) regard the existence of RhCl2 as unproved. According to L., no substance of constant composition is obtained by F.'s method.

(?) Double salt, Am, RhCl, xH2O. The compound to which Wilm gave this composition, and which he said was obtained by adding AmCl to RhCl, Aq in presence of much aqua regia (B. 16, 3033), is almost certainly identical with Am, RhCl, NH, NO, 3, ILO, obtained by Leidié (v.

AMMONIUM CHLOR-RHODITE, infra).

REDDIUM TRICHLORIDE RhCl, (Rhodo-chloride, Rhodo-rhodic chloride, RhCl, RhCl, RhCl, is Rhodium sesquichloride, Rh2Cl6). the simplest formula possible, but it is not necessarily molecular. Leidić (C. R. 106, 1076; 107, 234) prepared RhCl, by heating the alloy RhSn, in a rapid stream of dry, airfree Cl at the B. P. of S, until SnCl, ceased to be formed, allowing to cool, and removing Cl by a current of CO₂. The chloride is thus obtained as a sealing-wax-red powder. The alloy RhSn, is formed by fusing 1 part finely divided Rh with 30 to 50 parts Sn, and treating the product for a day or two with fairly conc. HClAq at 0° (Debray, C. R. 104, 1470, 1577). RhCl, was also formed by Jörgensen (J. pr. [2] 27, 433) by heating Cl.Rh₂(NH₃)₁,Cl₄ in a stream of Cl. Leidié (Bl. [2] 50, 664) says that RhCl₃ is not obtained pure by Claus' method of heating Rh in Cl, as part of the RhCl₃ is decomposed at the temperature which must be employed to cause combination of Rh and Cl. Leidié (l.c.) could not obtain pure RhCl, by heating Rh,S, in Cl, nor by heating the double chlorides of Rh and alkali metals with H2SO4, as recommended by Claus; in the latter reactions L. obtained alkali sulphate and Rh₂(SO₄)₃. RhCl₃ is a red powder, insol. water and acids; decomposes to Rh and

Cl at c. 450°-500° (L., l.c.). When moist RhCl. is heated in vacuo, or in a stream of N, it is partially decomposed at 100°, and wholly at 360°, to Rh₂O₃ and HCl (L., l.c.). Slowly reduced by H at low redness (v. Claus, J. 1855, 423).

TRICHLORIDE HYDRATE RHODIUM OF RhCl.,4H.O. Said to be formed by Claus (l.c.) by dissolving freshly ppd. Rh(OH), in HClAq, and evaporating; by Berzelius (P. 13, 437) by decomposing K,RhCl₈Aq by H₃SiF₈Aq, filtering, and evaporating. Described as a dark-red, glassy, deliquescent solid; e. sol. alcohol, insol. ether. Leidié (Bl. [2] 50, 664) could not obtain this. nor any definite, hydrate of RhCls.

Double salts. Chloro-rhodites

RhCl₃·3MCl, or M_3 RhCl₅. M = Am, $\frac{1}{2}$ Ba, $\frac{1}{2}$ Pb, Hg, K, Ag, Na. Also M_2 RhCl₅; M = ?Am, and K.

Ammonium chlor-rhodite 2Am, RhCl, 3H, O (Ammonium-rhodium trichloride). Large, red, rhombic prisms (v. Keferstein, P. 99, 275); by adding cone. HClAq to Na,RhCl,Aq, filtering from NaCl, and adding conc. AmClAq (Claus, l.c.; Wilm, B. 16, 3033; Leidié, l.c.). Sol. water, or dil. AmClAq; insol. alcohol. The salt Am, RhCl., H.O. said to be formed by heating a solution of the preceding salt (Vauquelin, A. Ch. 93, 204), could not be obtained by Leidié (l.c.).

Double salt with ammonium nitrate, 2(Am,RhCl, NH,NO,).7H,O. Obtained, as violet-red crystals, by adding HNO, Aq to Am, RhCl, Aq, and then excess of AmClAq, concentrating, and drying the crystals in vacuo. Scarcely sol. HNO, Aq; when boiled with water gives off same gases as are obtained by boiling

AmClAq with aqua regia.

Potassium chlor-rhodites (1) K,RhCl, 3H,O. Dark-red triclinic prisms; by adding conc. KClAq to RhCl,Aq, and allowing to evaporate (Claus, l.c.). Obtained by Seubert a. Kobbé (B. 23, 2556) by saturating the filtrate from the salt K₂RhCl₃ (infra) with HCl, filtering from KCl, and evaporating. Leidić (l.c.) failed to obtain this salt.

(2) K2RhCl3.H2O (no water, according to L.). Brown triclinic prisms, sl. sol. water. Gives Rh, KCl, and Cl when heated to redness. Formed by heating a mixture of 1 part spongy Rh with 2 parts KCl, in a stream of Cl, so long as Cl is absorbed, dissolving in water, filtering, and evaporating under reduced pressure (S. a. K., *l.c.*).

Sodium chlor-rhodite Na, RhCls.9H,O. Prepared like the K salt (Berzelius, Claus, Leidié).

The lead, mercurous, and silver salts are obtained by adding Pb(NO₃),Aq, HgNO₃Aq, or AgNO Aq, to solution of an alkali salt (Claus, I.c.). The barium salt is obtained like the K and Na salts (Bunsen, A. 146, 276). Compounds of RhCl, with methylamine chlorides are described by Vincent (Bl. [2] 44, 513).

Rhodium, cyanides of, and derivatives, v. vol.

ii. p. 346.

Rhodium, hydrosulphide of, $RhS_3H_3(=Rh_2S_3.3H_2S).$ A brownish - black, voluminous pp., obtained by passing H2S into solution of a Rh salt at c. 100° (Leidié, Bl. [2] 50, 664). Insol. acids, or alkali sulphide solutions; decomposed by Br and aqua regia. Gives off H.S. and forms Rh.S. when boiled with much water in N, or when heated with water in a sealed tube to 100°.

Rhodium, hydroxides of, v. Rhodium oxides AND HYDRATED OXIDES.

Rhodium, iodide of. The black substance obtained by Jörgensen in making Rh2(NH3)10I4 (v. Iodopurpureorhodium iodide, p. 406) was probably RhI₃; analysis gave 21.8 p.c. Rh, the formula requiring 21.3 p.c. According to Claus (l.c.) an iodide of Rh is formed when KIAq is added to solution of a salt of Rh.

Rhodium, oxides and hydrated oxides of. Rh and O combine, when Rh is strongly heated in O, probably with formation of RhO. only oxides of Rh which have been isolated with certainty are Rh₂O₃ and RhO₂; RhO also probably exists, and there are indications of the formation of RhO₃. The hydrated oxides, or hydroxides, are Rh₂O₃SH₂O [=Rh(OH)₃], and $RhO_{2}.2H_{2}O = Rh(OH)_{1}$.

RHODIUM MONOXIDE RhO (Rhodous oxide). Probably formed when Rh black is heated in a stream of air (Wilm, B. 15, 2225). Leidić (Bl. [2] 50, 664) says that from 14.5 to 17.8 p.c. O is taken up; RhO requires 13.5 p.c. O. The grey powder obtained by heating Rh(OII), was looked on by Claus as probably RhO. Deville a. Debray (A. Ch. [3] 61, 83) obtained what they regarded as RhO containing a little PbO by melting Rh with PbO, Pb, and borax, cupelling, and treating the residue with IINO3Aq. RhO is said to be fairly easily reduced to Rh by heating in H.

RHODIUM SESQUIOXIDE Rh2O3 (Rhodo-rhodic This oxide may be formed when Rh oxide). black is heated to redness in air. Leidié found from 145 to 17.8 p.c. O taken up (BL [2] 50, 664); Rh₂O₄ requires 18.92 p.c. O. Rh₂O₃ was obtained by Claus (J. pr. 76, 24; 80, 282; 85, 129) by heating Rh(NO₄); in a Pt crucible till revides of N consell to the particular till. oxides of N ceased to come off; also by fusing Rh with BaO2 and Ba(NO3)2. Fremy (A. Ch. [3] 44, 385) says that Rh₂O₃ is produced by heating Na₃RhCl₆ to redness in a stream of O. Rh₂O₃ is also formed by heating RhO3H3. Rh2O3 forms a grey solid; insol. acids; reduced by H to Rh (Claus, l.c.). Fromy obtained it as lustrous, metal-like, crystais, somewhat volatile when heated in a stream of O, which decomposed ClAq giving HClAq and O.

HYDRATED RHODIUM SESQUIOXIDE. Rh2O3.3H2O (Rhodo-rhodic hydroxide, RhO3H3). A black gelatinous pp. formed by adding excess of KOHAq, and a little alcohol, to Na₃RhCl_cAq. Sl. sol. conc. HClAq (Claus, l.c.). (2) Rh₂O₃.5H₂O (Hydrated rhodo-rhodic hydroxide, RhO, H₂.H.O). Obtained by adding KOHAq to solution of IthCl, the latter being in excess, allowing to stand till the pp. is citron-yellow (the first rosc-red pp. contains the hydrate mixed with K_sRhCl_e), and washing with hot water (Claus, l.c.). The whole of the KOH cannot be removed from the pp. by washing. Sol. HClAq, HNO, Aq, H,SO, Aq, H,SO, Aq, and when freshly ppd. also in acction Also sol. conc. KOHAq, but reppd. on acid. dilution (Descotils, Gm.-K. 3, 1261). Said by Leidié (C. R. 107, 234) to be sol. in solution of alkali hydrogen oxalates. Solutions of this hydrate in acids yield the salts Rh,3X on evaporation; $X = 2NO_3$, C_2O_4 , SO_4 , SO_3 , &c.

RHODIUM DIOXIDE RhO, (Rhodi- or rhodic oxide). A brown solid; obtained by repeatedly

Insol. soids, or boiling KOHAq. Reduced to Rh by H at a high temperature (Claus, L.c.)

HYDRATED RHODIUM DIOXIDE RhO, 2H,O (Rhodic hydroxide, RhO, H4). Obtained by Claus (l.c.) by leading Cl into a solution of $Rh_2O_3.5H_2O$ in KOHAq till a dark-brown gelatinous pp. was formed, then adding pieces of KOH from time to time, and continuing the passage of CI until pp. became more compact, and green, and the solution became blue-violet. A greenish solid, sol. HClAq, forming a greenish-blue solution, which evolves Cl and becomes the deep-red colour of RhCl, solution (cf. Jörgensen, J. pr. [2] 27,

Rhodic acid and rhodates (?). blue-violet solution obtained by passing Cl into Rh₂O₃.5H₂O in KOHAq (supra) is fairly permanent, but after some time it ppts. a blue powder, gas is given off, and the liquid becomes colourless. When the blue powder is dried it becomes green RhO.2H2O. A blue pp. is also obtained by carefully neutralising the blue-violet solution by HNO, Aq; this powder, when moist, is sol. HClAq, with evolution of Cl; on heating, more Cl is evolved, and the liquid becomes the red colour of RhCl, solution. Claus (l.c.) regarded the blue-violet solution as containing potassium rhodate, and the blue pp. he looked on as rhodium trioxide or rhodic anhydride, RhO3.

Rhodium, salts of. But few salts are known obtained by replacing H of oxyacids by Rh; the chief are nitrate, nitrite, oxalates, phosphates, and sulphates; a few double salts are also known.

Rhodium, sulphides of. Rh and S combine when heated, probably forming RhS. Rh, S, is formed by ppn. from Rh salts.

RHODIUM MONOSULPHIDE RhS (Rhodous sulphide). Said by Berzelius to be formed by heating finely divided Rh in S vapour; also, accord ing to Vauquelin (A. Ch. 88, 167), by heating Am, RhCl_a with S. Fellenberg (P. 50, 63) obtained RhS by heating dry Rh, S_a in CO₂(?). A white-blue, lustrous solid; heated in air gives spongy Rh; heated in Cl forms RhCl, and S2Cl, (F., I.c.). RhS is insol. aqua regia, according to Debray (C. R. 97, 1333.) (v. also Gibbs, J. pr. 91, 171; Lecoq de Boisbaudran, C. R. 96, 152).

RIDDIOM SESQUISULPHDE Rh_S, (Rhodo-rhodic sulphide). Formed, by passing H,S into solution of a Rh salt, as a black pp. according to Leidić (C. R. 106, 1076, 1533) the pp. is Rh_S, 3H_S (p. Rhodium, hydrosulphide of, p. 404), which becomes Rh_S, by heating for some time with water at 100°, in a closed vessel or in N. Leidić (Lc.) obtained Rh_S, in black crystalling tablets by heating RhCl. to 360° in a stream line tablets, by heating RhCl₃ to 360° in a stream of H.S; according to L., this is the only method whereby pure Rh,S, can be prepared. Loses 8 p.c. S when heated in N to dull redness; all S expelled only in O-H flame (L., l.c.). Insol. alkali solutions; not acted on by HClAq, HNO,Aq, BrAq, or aqua regia (L., l.c.). Forms the double salt Rh₂S₃.3Na₂S, by adding excess of conc. Na₂SAq to Na₂RhC₁₈Aq; decomposed by water, stable in presence of excess of alkali M. M. P. M. sulphide (Leidié, l.c.).

RHODIUM - AMMONIUM COMPOUNDS. (Rhodammines. Ammoniacal rhodium bases.) When a solution of Rh in aqua regia is evafusing finely divided Rh with KOH and KNO, porated with excess of NH, Aq a compound Rh.Cl. 10NH, is obtained. By treating this body with moist Ag₂O and water in the cold Rh; Ol, O. H. 10NH, is formed; if heat is used, the product is Rh,O,H,.10NH, These compounds react as definite salts, which exchange their more negative radicles without losing Rh or NH. The classification of the rhodiumammonium compounds generally adopted is similar to that used for the Cr and Co compounds (v. vol. ii. pp. 158 and 222). In the following general formulæ M and X represent negative radicles, which may be the same or different

M₂.Rh₂.10NH₃.X₄ or N₄H₆(NH₄)₅(Rh₂M₂).X₄ Purpureo-rhodium series.

Rh. 10NH, X. 2H2O or N, Ha(NH4), Rh2. X6. 2H2O Roseo-rhodium series.

Rh2.12NH3.X6 or N4H4(NH1)8Rh2.X6 Luteo-rhodium series.

The Rh compounds were investigated by Berzelius (Lehrbuch, 5th ed., 3, 956); Vauquelin der Platinmetalle, Dorpat, 1854); and more recently by Jörgensen (J pr. [2] 27, 633; 34, 894; 44, 48).

L. PURPUREO-RHODIUM COMPOUNDS M.Rh. 10NH. X4. Changed to roseo salts, without loss of NH, by boiling with alkali solution. The two atoms of radicle represented by M., are not removed by the ordinary reagents for removing this radicle from salts.

Chloro-purpureo- series (Jörgensen, l.c.).

Chloropurpurcorhodium chloride Cl₂Rh₂10NH₃Cl₄. This salt is prepared by dissolving the alloy RhZn₂ in aqua regia, evaporating to dryness, treating the residue with water, filtering, adding excess NH₂Aq, evaporating to dryness at 100°, heating with dil. HClAq, and filtering while hot; the insoluble salt is washed with dil. HClAq, dissolved in boiling water, and the hot solution is filtered into HClAq (1:1 by volume); the purpureo-chloride which separates is washed with dilute HClAq, and then with alcohol. Small lustrous yellow rhombic crystals; isomorphous with chloropurpureo-cobalt chloride (v. Topsöe, J. pr. [2] 27, 433; Keferstein, A. Ch. 99, 275). S.G. 2.079 at 18°. S. 56 cold water, considerably more sol. hot water. Sol. without decomposition in hot cone. H2SO, also in boiling NaOHAq. Easily reduced to Rh, but not acted on by such exidisers as aqua regia or HClAq and KClO₃. Heated in CO₂ gives Rh, NH₄Cl, NH₃, and N; heated in H, gives Rh, NH₄Cl, and NH₃; heated in HCl gas, gives Rh and NH,Cl; heated in Cl gives RhCl, and NH,Cl. Reacts with various substances to exchange Cl, for equivalent quantities of other negative radicles. Combines with PtCl, to form the double salt Cl.Rh.10NH.Cl.2PtCl.
Chloropurpureorhodium hydroxide

Cl2.Rh2.10NH3. (OH)4. Known only in solution, which is obtained by rubbing the chlorochloride with a little water and moist Ag2O for a few minutes, and filtering. Reacts strongly alkaline; gives salts by neutralisation with various acids. After warming, the solution contains roseo-chloride, and hydroxide Rh₂.10NH₂.Cl₂(OH)₄, along with Rh₂.10NH₄.(OH)₆, and gives a pp. with AgNO, Aq.

The other salts of this series are the

 $M = Cl_2 \cdot Rh_2 \cdot 10NH_3$.

Bromopurpureo- series (Jörgensen, l.c.). Bromopurpureorhodium bromide

Br₁Rh₂10NH₂Br₄. Deep-yellow rhombic crystals; S.G. 2.65 at 17.5°; scarcely sol. water. Prepared similarly to the chlorochloride, using HBrAq in place of HClAq; also by dissolving the chlorochloride in 7 p.c. hot NaOHAq, digesting for about an hour at 100°, adding excess conc. HBrAq, washing the pp. which forms with dil. HBrAq and then with alcohol; also by saturating solution of roseo-hydroxide, Rh₂.10NH₃.(OH)₆, with dil. HBrAq and heating for some time at Forms a double salt with platinic bromide, Br., Rh., 10NH., Br., 2PtBr., The bromo-nitrate, Br., Rh., 10NH., (NO.)., and bromo-silicofluoride, Br., Rh., 10NH., 2SiF., have been isolated.

Iodopurpureo. series (Jörgensen, l.c.).
Iodopurpureorhodium iodide I.,Rh.,10NH,.I. Prepared by heating the roscohydroxide with excess of HIAq for some time; then transforming the impure product into iodochloride by washing with water, then with alcohol, rubbing repeatedly with dil. HClAq, dissolving in hot water, and filtering into dil. HClAq. The iodochloride is then dissolved in hot wafer and poured into KIAq; the ppd. iodo-iodide is crystallised from hot water. Reddish-yellow, rhombic crystals; S.G. 3:11 at 14:8°; very sl. sol. cold water. Forms a double salt with 2PtI. The other salts of this series are the iodo-chloride MCl₁, iodo-nitrate $M(NO_3)_1$, iodo-silicofluoride $M(SiF_0)_2$, and iodo-sulphate $M(SO_4)_2$.6aq. $M=I_2.Rh_2.10NH_3$.

Nitratopurpureo-series (Jörgensen, J. pr. [2] 31, 49). Nitratopurpureorhodium nitrate (NO₃)...Rh₂·10NH₂·(NO₃)₄. Formed by heating the roseonitrate Rh₂·10NH₃·(NO₃)₈ to 100°; also by adding an equal vol. cone. HNO₃Ag to an aqueous solution of the rosconitrate, and heating at 100°. Yellowish-white crystals; deflagrates when heated. The other salts of this series are nitrato-chloride MCl, and nitrato-dithionate M(S₂O₆)₂. 2aq. M = (NO₃)₂. Rh₂. 10NH₃.

Nitritopurpureo- series or Xantho-

series (Jörgensen, J. pr. [2] 31, 49). Nitritopurpurcorhodium nitrate

(NO₂)₂·Rh₂·10NH₂·(NO₃)₄ (Xanthorhodium nitrate). 5 g. chlorochloride are heated with 50 c.c. water and 30 c.c. NaOHAq (7 p.c.) till dissolved; after cooling, 10 g. crystallised NaNO, are added and then a slight excess of dil. HNO,Aq (1 acid: 2 water). The powder which separates after a time is washed with dil. HNO, Aq, and then with alcohol, and is crystallised from hot water. Octahedral crystals, isomorphous with corresponding Co salt. Insol. alcohol and dilute HNOsAq; sl. sol. cold water; easily sol. hot water and conc. HNO, Aq. No reaction with ordinary reagents for nitrites, e.g. KIAq, KMnO,Aq, &c. Conc. H2SO, does not evolve NO₂.

The other salts of this series are: xantho-

bromide MBr., xanthochloride MCl., xantho-dithionate M(S₂O₄), 2aq, oxalate M(C₂O₄), silicofluoride M(SiF₃), sulphates M(SO₄), and $M(SO_4)_3.8H_2SO_4$. $M = (NO_4)_2.Rh_2.10NH_2$.

11. ROSEORHODIUM COMPOUNDS

Rh., 10NH, X, 2H,O. All the atoms of the negative radicle in these salts react similarly; e.g. AgNO, Aq ppts. 6Cl from the chloride. Heated to 100° 2H2O is given off, and purpureo- salts remain. These compounds are generally formed by treating the chloropurpureo- compounds with hot alkali solutions. Many are prepared from the hydroxide by the action of acids (Claus, l.c.; Jörgensen, l.c.).

Roseorhodium hydroxide Rh, 10NH, (OH) Prepared by heating chloropurpureochloride with excess of moist Ag2O and water for some days, filtering from AgCl, and evaporating in vacuo. A yellow deliquescent solid, with strongly alkaline reaction; ppts. metallic hydroxides from salts; decomposes NH, salts, giving off NH, Neutralises acids, forming roseo- salts.

Roseorhodium bromide Rh., 10NH, Br g. 2H, O. Ppd. by adding cone. HBrAq to solution of the hydroxide; also by boiling chloropurpureo-chloride with NaOHAq, and then adding excess of conc. HBrAq. Pale-yellow crystals; changes to the purpurco- salt at 100°, or by crystallising from hot water. The other salts of this series MI₂(SO₄)₂; nitrate M(NO₃)₃, and the double salt M(NO₃)₂. PtOI₅; phosphate M(IIPO₄)₃,4aq, and the sodium pyrophosphate M(NaP₂O₃)₂.23aq; sulphate M(SO₄)₃.3aq, and the double salt M(SO,)2.PtCl.

III. LUTEORHODIUM COMPOUNDS Rh., 12NH ,. X .. These salts are very stable. Their colours are the same as those of corresponding roseo- salts. The chloride can be prepared by heating the chloropurpureochloride with conc. NH3Aq; most of the other salts are obtained from the chloride (Jörgensen, J. pr. [2] 44, 48, 63). The negative radicles are all acted on similarly by reagents.

Luteorhodium chloride Rh 12NH 3.Cl . Prepared by heating chloropurpurcochloride with c. 30 times its weight NH3Aq (25 p.c. NH3) for several days at 100°-102°, dissolving in hot water, and ppg. by cone. HClAq. S. c. 12 at 8°. Not and ppg. by conc. HClAq. S. C. 12 at 5. Av. Changed to chloropurpureochloride by digestion with HClAq at 100°. Forms the double salt Rh. 12NH., Cl. 3PtCl., Gaq. The other salts of this series described by Jörgensen are: bromide MBrs., nitrates M(NO₂), and M(NO₂), the head of the MCPO. phosphate M(PO₄), 28q and sodium luteopyrophosphate M(NaP₂O₇), 23aq, and sulphate M(SO₄), 5aq.

Rhodium-pyridine compounds. Compounds of Rh with pyridine, C,H,N, and negative radicles have been prepared by Jörgensen (J. pr. [2] 27, 433). The compounds examined contain 8C₅H₃N, and correspond with the chromtetrammonium series of ammoniacal compounds (vol. ii. p. 159), and with the octammine series of ammoniacal Co compounds (vol. ii. p. 225). The composition of these pyridine compounds is represented by the formula M,Rh,(C,H,N),X,; where M = Cl and X = Br, Cl, OH, NO, and SO. The salts resemble the NH, compounds generally. The chloride (X = Cl) is prepared similarly to chloropurpureorhodium chloride, using pyridine in place of ammonia; the other salts are prepared from the chloride by the action of acids. AgNO, Aq ppts. one-third of the halogen only from the chloride and bromide. M. M. P. M. RHODIZONIC ACID v. DI-OXY-DIQUINOYL.

RHEADINE $C_nH_nNO_a$. [232°]. S. (80 p.c. alcohol) 09. S. (ether) 08 at 18°. An alkaloid occurring in all parts of the red poppy Papaver Rhaas, and in the white seed capsules of the white poppy Papaver somniferum (Hesse, A. 140, 145; 149, 35; 153, 47). Small white prisms, nearly insol. water, alcohol, and ether. May be sublimed. Tasteless, and not poisonous. Its solution in very weak HCl is colourless, but in conc. HClAq and in H₂SO₄ it forms purple solutions, the base being partially decomposed. The colourless solution is ppd. by tannin and by HgCl2.

Salts.-B'2H2PtCl62aq: yellow amorphous pp.-B'HI 2aq: mass of minute prisms.

Rheagenine $C_{21}H_{21}NO_{6}$. [223°]. S. (80 p.c. alcohol) '07. S. (ether) '06. Formed by boiling rhoadine with dilute H.SO. Small crystals (from alcohol), sl. sol. ether, alcohol, and water, v. sol. dilute acids. Its alcoholic solution turns litmus blue. Cannot be sublimed. Not coloured by acids. Its salts taste bitter. - B'2H2PtCla-B'HI: short prisms, m. sol. hot water.

RIBONIC ACID C,H₁₀O₄ i.e. CH₂(OH).CH(OH).CH(OH).CH(OH).CH(OH).CO₂H.

Tetra-oxy-valeric acid. Formed by heating CH2(OH).CH(OH).CH(OH).CH(OH).CO2H, arabonic acid, with pyridine in a closed vessel at 130° (E. Fischer a. Piloty, B. 24, 4216). When set free from its salts it changes into the lactone .-

HgA'₂: needles.—CdA'₂: $(a|_{\rm p}=0.6^{\circ})$. Needles.

Lactons C₃H₃O₅. $(72^{\circ}-76^{\circ})$. $(a|_{\rm p}=-18^{\circ})$.

Colourless prisms, v. e. sol. water and alcohol, v. sl. sol. ether. Converted by heating with yridine and water at 135° into arabonic acid. HNO, yields tri-oxy-glutaric acid. Phenyl hydrazine forms C₂H₂O₂(N₂H₂Ph) [164°].

RIBOSE *C₃H₁O₃. Formed by reducing the lactone of ribonic acid with sodium-amalgam

(Fischer a. Piloty, B. 24, 4220). Colourless syrup. Yields a phenyl-hydrazide [155°] and a p-bromo-phenyl-hydrazide C₁₁H₁₅O₁N₂Br [165°].

RICINELAIDIC ACID C18H34O3. [58°]. Formed by the action of nitrous acid on ricinoleic Formed by the action of nitrous sons on action (Boudet, A. 4, 16; Playfair, A. 60, 322; Bouis, A. Ch. [3] 44, 82; Ulrich, Bl. [2] 9, 225). Got also by saponifying ricinelaidin. silky needles, v. sol. alcohol and ether. Reddens litmus. Yields n-heptoic acid on oxidation with HNO₃ (Krafft, B. 21, 2735). Alkaline KMnO₄ yields two tri-oxy-stearic acids [120°] and [116°] (Grüssner a. Hazura, M. 10, 196; Mangold, M. 13, 326). Forms oily $C_{18}H_{31}Br_2O_3$, converted by KOHAq in the cold into $C_{18}H_{33}BrO_3$, whence alcoholic potash forms an acid melting at 71°.

Salts.—BaA'; unctuous powder.—AgA'; white powder, sol. NH₄Aq.

Ethyl ether EtA'. [16°]. Crystalline.

Anide C₁₈H₃₃NO₂. [93°] (Rowney, Chem. Gas. 1855, 361).

Reference. BROMO-RIGINELAIDIC ACID.

BICINELAIDIN. [45°] (Bouis); [66°] (Boudet). Formed by the action of nitrous fumes on castor oil. Solid, v. sol. alcohol and ether. Split up by boiling KOHAq into glycerin and potassium ricinclaidate. Yields heptoic aldehyde (enanthol) on dry distillation (Bertagnini, A. 85, 282). Yields octyl alcohol and potassium sebacate on distillation with potash (Bouis). **RIGINIC ACID** C₁₈H₃₁O₃ i.e. C₁₇H₃₂(OH).CO₂H. [81°]. (252° at 15 mm.). Formed by distilling barium ricinoleate in vacuo (Krafft, B. 21, 2736). Plates (from dilute alcohol). Yields, on oxidation by HNO₃, n-heptoic acid and an acid [c. 103°] not volatile with steam. Converted by HCl into diricinic acid Steam. Converted by HCI into difficults acid C₁,H₂₂(OH).CO.O.C₁,H₂₂.CO.2H, triricinic acid C₁,H₂₂(OH).CO.O.C₁,H₂₂.CO.O.C₁,H₂₂.CO.2H, and polyricinic acids. Sulphuric acid forms these acids, as well as SO₃H.O.C₁,H₂₂.CO.2H, SO₃H.O.C₁,H₃₂.CO.2H, &c. II₂SO₃ acting on castor oil forms the compound

acids, constituting Turkey red oil. The polyricinic acids are converted by boiling KOHAq but not by Na CO, into ricinic acid. Hot water decomposes the polyricino-sulphuric acids into H.SO, and polyricinic acids (Juillard, Bl. [3] 6,

RICININE. An alkaloid occurring, according to Tuson (C. J. 17, 195; C. N. 22, 229; cf. Werner, C. N. 22, 203), in the seeds of the castor oil plant (Ricinus communis). Rectangular prisms or laminæ, insol. water, nearly insol. ether, sol. alcohol.

RICINISOLIC ACID v. TRI-OXY-STEARIC ACID.

RICINOLEÏC ACID C_{In}H_{ai}O₃ i.e. CH₂.[CH₂]₃.CH(OH).CH:CH[CH₂]₈.CO₂H (?) [17°]. Occurs as glycoride in castor oil (Bussy 108; Svanberg a. Kolmodin, J. pr. 45, 431; Bonis, A. Ch. [3] 44, 103; 48, 99; Petersen, A. 118, 69). Prepared by saponification of castor oil by KOH or HCl and purified by means of its Ca or Ba salt (Claus, B. 9, 1916; Krafft, B. 21, 2731). Crystalline mass, miscible with alcohol and ether. Its alcoholic solution is alkaline in reaction. Does not absorb oxygen from the air. Yields C₁₈H₃₃AcO₅. Yields polymerides when heated with water in closed vessels (Scheurer-Kestner, C. R. 113, 201).

Reactions .- 1. Oxidised by HNO3 to azelaic acid C_pH₁₀O₄, oxalic acid, and heptoic acid.— 2. Alkaline KMnO₄ forms two isomeric tri-oxystearic acids (Dieff, J. pr. [2] 39, 345; B. 20, 1211; Hazura a. Grüssner, M. 8, 475; Mangold, M. 13, 326).—2. Nitrous acid forms ricinelaidic acid.—3. Yields methyl hexyl ketone (173°) and an acid C₁,H₂,O₂ [81°] on distillation of the Ba salt.—4. The Na salt on distillation with NaOH salt.—4. The Na salt on distillation with NaOH yields methyl hexyl ketone, sec-octyl alcohol and sodium sebacate Na₂C₁₆H₁₆O₁,—5. Bromine forms oily C₁₆H₁₃Br₂O₂, converted by alcoholic potash into C₁₈H₁₃Br₂O₃, whence Br forms oily C₁₆H₂₃Br₂O₃, converted by alcoholic potash at 120° into ricinostearolic acid C₁₈H₂₂O₃, which combines with bromine forming unstable oily C₁₈H₂₂Br₄O₂.—6. PCl₃ forms C₁₈H₂₂Cl₂O.—7. HI and P give C₁₈H₂₃IO₂.

Salts.—BaA'₂: soft scales (from alcohol), sl. sol. water.—SrA'₂: small grains (from alcohol).—CaA'₂ (dried at 100°). [80°].—MgA'₂: slender needles, v. sol. alcohol.—PbA'₂. [100°]. Crystalline mass, v. sol. ether.—ZnA'₂.—AgA': ourdy pp.

ourdy pp.

Ethyl ether EtA'. Oil. Amide C, H3: CONH. Nodules [66°]. (from alcohol).

References .- Bromo- and Oxy- RICINOLSIC ACID.

RICINOLIC ACID v. TRI-OXY-STEARIC ACID. RICINOSTEAROLIO ACID C₁₈H₃₂O₃. [51°]. Formed by heating the dibromide of ricinoleic acid with alcoholic potash (Ulrich, Z. 1867, 547). Groups of needles (from alcohol), v. sol. ether. Volatile.-BaA'2: plates (from alcohol)

[135°].—AgA': granular pp. RICINOSTEAROXYLIC ACID [78°]. Formed by heating ricinostearolic acid with moist Ag₂O (Ulrich, Z. 1867, 550). Dendritic groups of needles (from alcohol), v. sol. ether.—BaA'₂.—AgA'; granular pp. decomposed by hot alcohol.

ROBININ C₂₅H₃₀O₁₆. [195°]. Occurs in the blossoms of the acacia (Robinia pseudacacia) (Zwenger a. Dronke, A. Suppl. 1, 257). Thin yellow needles (containing 51 aq). Neutral in reaction. Tasteless, sl. sol. cold water and alcohol, insol. ether. Sol. alkalis, forming yellow solutions. The ammoniacal solution turns brown in air. FeCl, gives a brown colour. Its alcoholic solution is ppd. by lead subacetate. Reduces hot Felling's solution. HNO, forms oxalic and pieric acids. Split up by boiling dilute acids into quercetin and a sugar.

ROCCELLIC ACID C₁, H₃₂O₄. [132°]. S. (boiling alcohol of S.G. 819) 55. Occurs in various species of Roccella (Hecren, S. J. 59, 346; Liebig, P. 21, 31; Schunck, A. 61, 64; Hesse, A. 117, 332). Four-sided prisms, insol. water, v. sol. alcohol and ether, sl. sol. warm benzene.

Sol. Na CO Aq and borax.

Salts.-BaA" (dried at 100°).-CaA" aq: amorphous pp. -Pb, A"2(OH), 2aq: white powder.

 $Anhydride C_1, H_{10}O_3$. Got by heating the acid above 220°. Oil, v. sol. hot alcohol and ether.

Anilide C₁, H₃₀O₂(NHPh)₂. [55°]. Got by heating the acid with aniline at 190°. Colourless laminæ (from alcohol), insol. water, NH,Aq, and HClAg

ROCCELLININ C18H16O. Occurs in Roccella tinctoria (Stenhouse, A. 68, 69). Silky needles (from alcohol), nearly insol. cold alcohol and other. Its solutions in alkalis are not coloured by air. Not decomposed by boiling KOHAq. Does not pp. metallic salts.

ROCHELLE SALTS, Potassium-sodium tar-

trate; v. TARTRATES.

ROSANILINE $C_{20}H_{21}N_{2}O$ *i.e.* ([4:1] $C_{20}H_{1}(NH_{2}))_{2}C(OH).C_{4}H_{3}M_{2}(NH_{2})[1:3:4].$ Tri-amido-di-phenyl-tolyl-carbinol. Formed by oxidation of a mixture of aniline, o-toluidine, and p-toluidine (Hofmann, J. pr. 77, 190; 87, 226; Pr. 12, 2; Mühlhäuser, D. P. J. 266, 455, 503, 547). SnCl., As.O., HNO., Hg(NO.), FcCl., and nitrobenzene may be used as oxidising agents. For the production of a red colouring matter it is essential that there should be present a base with methyl in the p-position to amidogen (p-toluidine, (1,3,4)-xylidine, or mes-idine), and also a base with H in the p- position to amidogen (e.g. aniline, o-toluidine, or (1,3,2)xylidine) (Rosenstiehl, C. R. 82, 415; 94, 1319; 95, 238; 98, 433; A. Ch. [6] 2, 360). When nitro-benzene is used as oxidising agent it appears to be itself reduced to benzene and nitrogen, and not to take part in the formation of rosaniline. Thus, when chloro-nitro-benzene, nitro-aniline, or di-nitro-benzene is used, a substituted rosaniline (e.g. chloro-rosaniline) is not formed (Lange, B. 18, 1918). Colourless needles or plates, obtained by ppg. a solution of one of its salts with NH₂Aq and recrystallising. Nearly insol. water, sl. sol. NH₂Aq, m. sol. alcohol, insol. ether. Turns red in air. Dyes silk and wool in acid, neutral, and even in slightly ammoniacal solutions.

Reactions.-1. Reduced by ammonium sulphide or powdered zinc to tri-amido-di-phenyltolyl-methane (leucaniline) (Hofmann, Pr. 12, 2) .- 2. Yields alkyl derivatives on heating with alkyl iodides and phenyl derivatives on heating a salt with aniline (Hofmann, Pr. 13, 9). Benzyl chloride, methyl iodide, and MeOII form $C_{20}H_{16}(C,H_{,)_4}N_3MeI$, crystallising in lustrous green needles (Hofmann, B. 6, 263).—3. The hydrochloride, heated with water at 235°, forms NH,Cl, phenol, red crystals of C20H20N2O2 [176°], and colourless crystals, which turn red in air and then crystallise from alcohol in red needles C₂₀H₁₉NO₃ (Liebermann, B. 5, 144; 6, 951).-4. The hydrochloride, heated with dilute HClAq at 240°, yields aniline and toluidine (L.).—
5. Water at 270° forms di-oxy-benzophenone, di-amido-phenyl-tolyl-ketone, oxy-amido phenyltolyl-ketone, phenol, and NH₃ (Liebermann, B. 6, 951; 11, 1435; 16, 1927).—6. Potassium cyanide added to rosaniline acctate in alcohol yields $C_{21}H_{20}N_4$, a white crystalline powder, sol. HClAq, and reppd. by NII₃Aq. 1t separates from alcohol in monoclinic crystals. It forms crystalline salts .- 7. A solution of a rosaniline salt is decolourised by SO2, and the solution is turned red, and afterwards violet, by aldehydes, and gradually deposits copper-coloured scales of alkylidene derivatives (Schiff, Bl. [2] 7, 518). C.H. CH: C.H., N., Thus cenanthol forms yields B'IIAsO, which yields B'HAsO, and B'H.PtCl_s.-8. *Œnanthol* reacts with rosaniline acetate in the cold, forming $(C_7H_{11})_3(C_{20}H_{16}N_3)_2$ (Schiff, $D\bar{l}$. [2] 5, 291) .- 9. By exhaustive chlorination it yields CCl, and per-chloro-benzene (Merz a. Weith, B. 16, 2876).—10. Boiling Ac₂O yields a tetra-acetyl derivative as a reddish am uphous powder. The same body is got by treating triacetyl-tri-amido-di-phenyl-tolyl-methane acetyl-tri-amido-di-phenyl-tolyl-methane with K.Cr., and HOAc (Renout, B. 16, 1303). A mono-acetyl derivative C20H18AcN3, got by heating rosaniline hydrochloride with acetamide, is reddish brown and yields dark-blue B'HCl with metallic lustre (Beckerhinn, J. 1870, 768).-11. May be sulphonated by H.SO, containing SO, at 130° (Schoop, Chem. Zeit. 11, 572).—12. By diazotisation followed by reduction with tin and HCl in the cold it is converted into 'roshydrazide,' the nydrochloride of which forms green crystals, and dyes cotton brownish-red (Ziegler, B. 20, 1557). -13. Br forms a tetra-bromo-rosaniline (?) crystallising from benzene in prisms (Caro a. Graebe, A. 179, 203).—14. Aldehyde forms a blue product which is converted by Na₂S₂O, into aldehyde green C₂₂H₂₇N₃S₂O, an amorphous green mass, sol. alcohol and ppd. by ether (Cherpin; Usebe, J. pr. 92, 337; Hof-

mann, B. 8, 761; Gattermann, B. 22, 227).

Salts.—These are derived from the anhydrous base C,H,N:C(C,H,NH_2),—C,H,,N,HCl.

Red crystals with green lustre. Insol. ether, sl. sol. water, m. sol. alcohol. Its solution in water or alcohol is crimson. Dyes wool and silk magenta. The absorption-spectrum has been studied by Hartley (C. J. 51, 169) .- C, H, N. 3HCl. Ppd. by conc. HClAq. Yellowish-brown needles. more sol. alcohol and water than B"HCl .-Decomposed by much water, forming B"HCl.-C₂₀H₁₉N₃4HCl or (C,H₆NH₃Cl).CCl(C,H₄NH₃Cl). Got by passing dry HCl into rosaniline powder (Rosenstiehl, Bl. [3] 9, 122). Reddish-brown and hygroscopic, forming a magenta solution. Fumes in air, giving off HCl. After keeping it is not completely soluble. - C20H19N34HBr. Resembles the preceding salt.—C₂₀H₁₉N₃HOAc. Large crystals with green metallic lustre; v. sol. water tals with green metallic lustre; v. sol. water and alcohol. $-(C_{20}H_{19}N_3)H_*PtCl_9$. Amorphous. $-(C_{20}H_{19}N_3)H_*PtCl_9$. $-C_{20}H_{19}N_3HBr$. Sl. sol. water. $-C_{20}H_{19}N_3HH$. Green needles, v. sol. water. $-C_{20}H_{19}N_3HNO_3$: small crystals. $-(C_{20}H_{19}N_3)H_2SO_1$ (dried at 130°). Crystals with green lustre. Does not form an alum with Al_(SO,)3 (Wood, C. N.38,1).-C20H1,0N3C,H3N3O,0 Red needles, very slightly sol. water. — $(C_{20}\Pi_{19}N_3)_2\Pi_2C_2O_4$ aq. — Tannate: ppd. by adding tannin to an aqueous solution of a salt of rosaniline. Red mass, insol. water, sol. alcohol and HOAc (E. Kopp, J. 1862, 694) .-Aurinate: Got by heating equivalent quantities of resamiline and aurin with alcohol (Dale a. Schorlemmer, C. J. 43, 186). Hexagonal crystals with green lustre (Dyson, C. J. 43, 471). More sol. alcohol than either constituent. Dyes silk magenta.—Phenate C₂₀H₁₂N₂C₃H₄O. Got by heating rosaniline with phenol, dissolving in alcohol, and ppg. with water (Dyson, C. J. 43.

Para-rosaniline C₁₀H₁₀N₃O i.e. ([1:4]C₀H₄(NH₂))₃COH. Tri-amido-tri-phenyl-carbinol.

Formation. - 1. From tri-nitro-tri-phenylmethane by exidation by CrO₃ and HOAs followed by reduction of the resulting tri-nitro-triphenyl-carbinol with zinc-dust and HOAc (E. a. O. Fischer, B, 11, 195, 473, 612, 1079, 1598; A. 194, 242) .- 2. By heating a mixture of aniline and p-toluidine with arsenic acid (Rosenstiehl, A. Ch. [5] 8, 192); formed therefore in the preparation of resamiline (Graebe, B. 12, 2241).-3. By heating p-nitro-di-amido-tri-phenyl-methane with FeCl₂ at 170° (O. Fischer, B. 15, 678).—4. By heating p-nitro-benzylidene bromide with aniline (Zimmermann a. Müller, B. 17, 2936). 5. Hy heating aurin with NH, Aq at 180° (Dale a. Schorlemmer, B. 10, 1016).-6. By heating di-amido-di-phenyl-methane (from aniline and formic aldehyde) with aniline, aniline hydrochloride, and nitro-benzene or arsenic acid.

Properties. — Crystallino plates. Nearly colourless; sl. sol. water; absorbs CO₂ from air. Its solution in conc. HClAq is coloured grassgreen by a crystal of KClO₂.

Reactions.—1. Yields o-toluidine and diamido-benzophenone [237°] on boiling with HClAq for a long time (Wienelhaus, B. 19, 110). 2. HIAq at 190° forms aniline and p-toluidine 3. Nitrous acid forms the tri-diazo-derivative, which on boiling is converted into aurin.—4. Reduced by sinc-dust and HClAq to tri-amido-triphenyl-methane.—5. KCy added to its hydrochloride in presence of alcohol forms 'hydrochloride in presence of alcohol forms 'hydro-

eyanpararosaniline ' C, H,, N, HCN, crystallising from hot alcohol in colourless prisms, forming sonverted by conc. HClAq (55 g.), water (55 g.), and aldehyde (22 g.) in the cold into aldehyde blue, a dark-blue hygroscopic powder, ppd. by adding NaCl to the product after dilution with water (Gattermann, B. 22, 227). Aldehyde blue yields, on distillation, a solid base C10H, N.

Salt .- C10 H18 N3 Cl. S. . 24 at 90

Tri-methyl-rosaniline v. TRI-METHYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL.

Hexa-methyl-pararosaniline v. Hexa-methyl-TRI-AMIDO-TRI-PHENYL-CARBINOL.

Phenyl-resamilines v. HEXA-PHENYL-TRI-AMIDO-TRI-PHENYL-CARBINOL and TRI-PHENYL-TRI-

AMIDO-DI-PHENYL-TOLYL-CARBINOL.

ROSEINE. A name for salts of Rosaniline. **ROSEMARY OIL.** S.G. 15.905. a = +42'to +9° 48' in 100 mm. (Schimmel, Ph. [3] 21, 940; 22, 328). Obtained by steam-distillation from Rosmarinus officinalis (Kane, Trans. Irish Acad. 18, 135; Lallemand, A. 114, 197; A. Ch. [3] 57, 404; Gladstone, J. 1863, 549; Montgolfier, Bl. 1816, 18; Bruylants, J. Ph. [4] 29, 508). Contains a terpene (165°), dextrorotatory camphor, borneol, and cineol C₁₀H₁₈O (176°-179°) (Weber, A. 238, 89). The cineol forms a hydrochloride (C₁₀H₁₀O) HCl, a tetra-bromide [124°], and the iodide C₁₀H₁₀I₂ [79°].

ROSE OIL. Obtained by steam-distillation from rose leaves. Contains a stearoptene $C_{16}H_{31}$ [34°] (365°) which is not attacked by chromic acid mixture and appears to be a paraffin (Maracia mixture and appears to be a parainn (Markownikoff, B. 23, 3191; J. pr. [2] 48, 311; cf. Blanchet, A. 7, 154; Gladstone a. Dale, C. J. 17, 1; Salkülünski, N. R. P. 24, 129; Bauer, D. P. J. 204, 253; Flückiger, Z. [2] 6, 126; Panajotoff, B. 24, 2700; Eckart, B. 24, 4205). Rose oil also contains rhodinol (q.v.). Bulgarian oil of roses contains roseol C10H20O (225° cor.), which is oxidised by KMn₀, to C₁₀H₁₀(OH)₁ (240°) S.G. ⁹₆ 1·0445; ²⁰₁ 1·0343; and is reduced by HI to C₁₀H₂₂ (159°) S.G. ⁹₆ ·7700; ²⁰₇₅₅₄ (Ladenburg, J. pr. [2] 48, 293).

ROSEOCOBALT SALTS v. COBALTAMINES,

vol. ii. p. 226.

ROSEOCHROMIUM SALTS v. CHROM-AMMO-NIUM SALTS, vol. ii. p. 160.

ROSEORHODIUM SALTS v. RHODIUM-AMMO-

NIOM COMPOUNDS, this vol. p. 407.

ROSEWOOD OIL. The oil got by steamdistillation from the wood of Convolvulus scoparius contains a terpene C₁₀H₁₆ (249°) (Gladstone a. Dale). Rosewood also contains a black resin $C_2H_{2i}O_6$ [95°] S.G. 15 1.266, which is insol.

water, sol. alcohol, and gives a blood-red colour with H.SO. (Terreil a. Wolff, Bl. [2] 33, 435).

ROSINDOLES. Red colouring matters, greatly resembling rosaniline, formed by heating indoles with BzCl, and by oxidation of benzylidene derivatives of indoles (E. Fischer a. Wagner, B. 20, 815). Thus methyl-ketole yields dimethyl rosindole, C₂₅H₂₀N₂, which may possibly be CPh(C,H,NH) NC,H.

 $\begin{array}{lll} \textbf{ROSINDONE} & \textbf{C_6H_4} \diagdown \begin{matrix} \textbf{CO.CH:C.NPh} \end{matrix} \begin{matrix} \textbf{C_6H_4} \\ \end{matrix} \\ \end{array}$ Rosindulone. [262°]. Formed by heating rosin-

duline with conc. HClAq at 170° under pressure (Fischer a. Hopp, A. 256, 238; 262, 244).

Formed also from oxy-naphthoquinone and phenyl-o-phenylene-diamine (Kehrmann, J. pr. [2] 43, 269; B. 24, 586). Red hexagonal tables, insol. hot water, m. sol. boiling alcohol, forming a scarlet solution with brick-red fluorescence. Reduced to naphthophenazine by distilling in a current of H over zinc-dust. Converted by p-toluidine at 130° into p-tolyl-rosinduline. Oxidised by CrO, to rosindonic acid C₂₂H₁₁N₂O₃, which crystallises in colourless needles, sl. sol. alcohol, insol. water, v. sol. ether.

ROSINDULINE C₂₂H₁₂N₃ i.e.

CH

CH

CH

 $C_eH_4 < \overline{C(NH).CH:C.NPh} > C_eH_4.$ Г199°7. Formed by heating benzene- azo- (a)-naphthylamine with aniline and alcohol at 1650 under pressure (Fischer a. Hepp, A. 256, 236). Formed also by heating phenyl-o-phenylene-diamine with oxy-naphthoquinone imide, HOAc, and alcohol at 100 (Kehrmann, J. pr. [2] 43, 269; B. 24, 587). Reddish-brown plates, v. sol. alcohol and ether, insol. water. Conc. H2SO, forms a green solution, becoming red on dilution. The alcoholic solutions exhibit reddish-yellow fluor-

escence.—B'HCl 3 aq: red needles.

Rosinduline. This name has also been given to the phenyl derivative of the preceding body

(v. vol. iii. p. 9).
ROSOLIC ACID v. TRI-OXY-DI-PHENYL-TOLYL-CARBINOL and TRI-OXY-TRI-PHENYL-CARBINOL.

ROTTLERIN C₁₁H₁₀O₂? [200°]. A yellow substance occurring in the fruit of Rottlera substance occurring in the fluit of Institution in the fluit of Institution in India (Anderson, N. Ed. P. J. [2] 1, 300; Jawein, B. 20, 182). It is identical with Mallotoxin (q. v.).

RUBAZONIC ACID C₂₀H₁,N₅O₂. Formed by oxidation of oxy-amido-phenyl-methyl-pyrazole (Knorr, A. 238, 137). Got also by boiling pyrazole-blue with NH,Aq. Prepared from the phenyl-hydrazide of oxy-phenyl-methyl-pyrazole by reduction with zinc dust and HOAc, followed by oxidation with FeCl, (Buchka a. Sprague, B. 22, 2551). Insol. water and dilute acids, v. sol. ether and benzene. Its solutions in alkalis are deep violet, but on boiling become yellow.

RUBERYTHRIC ACID C₁₈H₂₀O₁₄ i.e. C₁₄H₆O₂(OH).O.C₁₂H₁₄O₃(OH), Rubianic acid. [260°]. Obtained from madder-root by extracting with boiling absolute alcohol (Rochleder, A. 80, 321; 82, 205; Schunck, A. 66, 176; Liebermann a. Bergami, B. 20, 2241). Lemon-yellow needles, v. sol. hot water, v. sl. sol. cloohol, insol. ether. Its alcoholic solution is yellow. Alkalis form blood-red solutions. It does not ferment with yeast. Boiling dilute acids split it up into alizarin and sugar. Ac2O and NaOAc yield allizarin and sugar. Ac₂U and NaUAC yield $C_{2a}H_{2a}Ac_{a}O_{14}$, crystallising in yellow needles $[230^{\circ}] \cdot C_{2a}H_{2}KO_{14}$.—BaA'₂aq. **RUBIAN** $C_{2a}H_{34}O_{15}$. A glucoside in madder root, split up by acids, alkalis, or the madder-

ferment (erythrozym) into glucose, alizarin, and other bodies (Schunck, P. M. [4] 12, 200, 270; J. pr. 59, 465). Amorphous resin, v. sol. water, m. sol. alcohol, insol. ether. Its solutions are very bitter. Yields ruberythric acid on treatment with baryta. It is probably a mixture of ruberythric acid and other bodies.

RUBIANIC ACID v. RUBERYTHRIG ACID. RUBIDINE. A general name for homologues of pyridine of the formula OHH, N, e.g. DI-METHYL-ISOBUTYL-PYRIDINE.

Bubidine C, H, N. (280°). S.G. 22 1.017. Occurs in coal tar (Thenius, Rep. Chim. app. 4, 181). Liquid, sl. sol. water, miscible with alcohol and ether. Its salts redden in the air. Bleaching-powder gives a red colour. Colours acidified fir-wood red. — B'₂H₂PtCl₄: reddish

crystalline powder.
RUBIDIUM. Rb. At. w. 85.2. Mol. w. unknown. Melts at c. 38.5° (Bunsen, A. 125, 367). S.G. c. 1.52 (B., I.c.). Refraction-equivalent 12.1 (Gladstone, Pr. 18, 49); 11.6 (Kannonikoff, J. R. 1884 [1] 119). Chief lines in emission-spectrum are two in the red, Rb, and Rb,, 7800 and 6297; and two in the violet, Rb, and Rb, 4216 and 4206 (Kirchoff a. Bunsen, P. 113, 337; Lecoq de Boisbaudran, Spectres lumineux [1874] 46; v. also B. A. 1884. 438). Beketoff (J. R. 1888. 363) gives $[Rb^2, O] = 94,900$.

Occurrence.-Never free. Salts are widely distributed, but in very small quantities, along with salts of Cs, and frequently also salts of Li K, and Na. Many lepidolites contain Rb salts amounting to c. 24 p.c. Rb (K. a. B., P. 113, 337; 119, 1; Grandeau, A. Ch. [3] 67, 155; Allen, Am. S. [2] 34, 367). Traces of Rb salts have been found in specimens of orthoclase (Erdmann, J. pr. 86, 377, 448; Laspeyres, A. 134, 349; petalite (Grandeau, l.c.); micas (Schrötter, J. pr. 85, 458); basalt (Engelbach, A. 135, 126); carnallite (Erdmann, l.c.); in alum obtained on the island of Volcano (Cossa, Acc. dei Lincci, 11, 9); saltpetre (Dieulafait, C. R. 98, 1545). Small quantities of Rb salts, varying from c. .0002 to c. .03 g. RbCl per litre, occur in mineral springs (v. Bunsen, A. 122, 347: Grandeau, A. Ch. [3] 67, 155; Schrötter, J. pr. 85, 458; Redtenbacher, J. pr. 85, 458; Böttger, J. pr. 89, 378). Traces of Rb salts have been found in sea water (Sonstadt, C. N. 22, 25, 44); in fumaroles giving out boric acid (Hofmann, J. C. T. 1863. 354); in coffee, tea, cocoa, and tobacco (Grandeau, l.c.); in the ashes of beetroot (G., l.c.; Lefèvre, C. R. 55, 430); in the ashes of various plants (von Than, A. Suppl. 2, 81); in normal human urine (Schiaparelli a. Peroni, G. 10, 390). According to Lockyer a well-marked Rb line occurs in the solar spectrum (Pr. 27, 279).

Historical.-In 1860 Bunsen applied the method of spectroscopic analysis, then being worked out by him along with Kirchoff, to the examination of the residue obtained by evaporating very large quantities of the water from a mineral spring at Dürkheim. Two red lines appeared which were not known to belong to any element. By further investigation Bunsen separated the chloride of the element, and on electrolysing the molten chloride he obtained metallic globules, which rose to the surface and took fire. By strongly heating an intimate mixture of the carbonate of the new element with finely divided charcoal and distilling into a re-ceiver under rock-oil, Bunsen obtained the metal in some quantity. The name rubidium was given because of the characteristic lines in the red part of the spectrum (ruber = dark red) (v. Bunsen, A. 113, 337; 122, 347).

Formation. -1. By distilling the mixture of Rb.CO. and C obtained by carbonising Rb.H tartrate (Bunsen, l.c.; Setterberg, A.211, 100).-2. By distilling a mixture of RbOH and Al (Beke-

toff. J. R. 1888, 363).-8. By passing a strong electric current through molten RbCl, the positive electrode being graphite, and the negative an iron wire, globules of Rb rise to the surface, and there take fire. If the negative electrode is surrounded with H (v. Lithium, vol. iii. p. 148), a smalt-blue substance is formed, which dissolves in water with formation of RbOH and H; this blue solid is probably a lower chloride than RbCl, perhaps Rb,Cl (Bunsen, l.c.).

Preparation .- The saline residues from the manufacture of lithium compounds from Saxon lepidolite (at Struve's works in Leipzig) were found by Bunsen (l.c.), Heintz (J. pr. 87, 310), and Erdmann (J. pr. 86, 294) to be rich in Rb salts. The specimen examined by Bunsen contained 19.75 p.c. RbCl. Cossa (B. 11, 811) recommended the natural alum from the island of Volcano as a good raw material for preparing

Rb salts.

1. Bunsen's method (A. 122, 351) for separating Rb is based on the different solubilities in water of the platinochlorides of K. Rb. and Cs: these solubilities at 17° are in the ratio of 15:2:1. One kilo. of the saline residue from the preparation of Li compounds from Saxon lepidolite is dissolved in 2.5 kilos, water, and ppd., when cold, by 30 g. Pt in aqua regia. After settling the liquid is drawn off, and the pp. is boiled 25 times in succession with small quantities of water (1.5 kilos, in all), each portion being poured into the liquid which was drawn off from the pp. by the PtCl4. The 4 kilos. of liquid and washings are evaporated to 2.5 kilos. While this evaporation is proceeding, the washed platinochloride pp. is dried at 100°, heated nearly to redness in a stream of H until a mixture of Pt with RbCl, and perhaps a little CsCl, remains (if the solid melts reduction is incomplete); and the RbCl is dissolved out in hot water. The Pt which remains is dissolved in aqua regia, and added to the liquid which has been evaporated. The pp. is washed with small quantities of water as before, dried, and reduced in H, the supernatant liquid and washings being evaporated. The reduced Pt is dissolved and added to the liquid, and so on. These processes are repeated seven or eight times. From 1 kilo. material Bunsen obtained .125 kilo. RbCl, containing 3-4 p.c. KCl and a little CsCl. To separate KCl, the approximately pure RbCl is dissolved in water (36 g. in 1 litre), heated to boiling, and a boiling solution of PtCl, (30 g. Pt in aqua regia, diluted to 1 litre) is added; the pp. is washed repeatedly with water at 40°-50°, then dried, and reduced in H; the RbCl is dissolved in water, and the Pt in aqua regia, and these processes are repeated until the RbCl shows no trace of the red lines of K in the spectroscope. Finally, Bunsen separated CaCl by transforming the chlorides into carbonates, and treating the powdered salts with boiling absolute alcohol until the insoluble RbCl ceased to show the blue lines of Cs in the spectroscope (RbCl is insoluble, while CsCl dissolves, in absolute alcohol). This process has been modified by Heintz (J. pr. 87, 310), Grandeau (A. Ch. [8] 67, 155), Piccard (J. pr. 86, 449), Böttger (J. pr. 89, 878), Schrötter (J. pr. 85, 458), de Boisbaudran (Bl. [2] 17, 551), and others.

2. Redtenbacher's method (J. pr. 95, 148) is

based on the different solubilities of the alums of K, Rb, and Cs; the solubilities in water, at 17°, are as 22:4:1. The method has been modi-17°, are as 22'4:1. The method has been mounded by Stolba (J. pr. 99, 49), Godefiroy (A. 181, 176), Petersen (D. P. J. 224, 176), Cossa (B. 11, 811), Setterberg (A. 211, 100), Robinson a. Hutchins (C. N. 49, 253). The mother-liquor from which Li₂CO₃ has been separated by Schrötter's method (vol. iii. p. 149) is evaporated with 18°CO Ac with addition of Al (SO). with H₂SO₄Aq, with addition of Al₂(SO₄)₃, whereby Rb and Cs alums are obtained mixed with K alum. Or lepidolite may be decomposed by heating with H,SO, and CaF, the residue boiled with five or six volumes water, KOH added equal to 5 p.c. of the quantity of lepidolite used, the whole boiled with water, and filtered hot, when the alums crystallise out on cooling (Stolba, I.c.). The alums are dissolved in half their weight of boiling water, half as much cold water is added, and after stirring the whole is let cool to 45°, when almost all the Rb and Cs alums separate, leaving much K alum in solution. The solution in water, and cooling, are repeated, tomperature being allowed to fall to 40°; the alum which separates is dissolved in water equal to half the weight of the original quantity of mixed alums, boiled for some time, and allowed to cool to 60° while being stirred. The crystals which separate are almost pure Cs alum; the mother-liquor, when evaporated, yields almost pure Rb alum.

To prepare the metal, RbCl or Rb alum can be transformed into RbOII, and Rb prepared therefrom; or the RbOH may be dissolved in the proper quantity of tartaric acid to form RbH tartrate, which may then be charred, and Rb obtained from the mixture of Rb₂CO₂ and C

so formed.

To prepare RbOH, the RbCl is converted into Rb₂SO₄ by H₂SO₄Aq, the Rb₂SO₄ is dissolved in water, boiled, BaOAq is added, the liquid being kept boiling. BaSO, is removed by decantation, and the liquid is evaporated to dryness in a silver dish as quickly as possible. RbOH is obtained from Rb alum by dissolving in hot water, ppg. Al₂O₃ by slight excess of NH,Aq, filtering hot, evaporating to dryness in a Pt dish, strongly heating till (NH4)2SO4 is removed, and then proceeding to decompose the Rb₂SO₄ by BaOAq as already described. RbOH is mixed with Al clippings in the ratio 2RbOH:Al (=1 part Al to 7.5 parts RbOH), and the mixture is heated to full redness in a furnace, in an iron cylinder, connected by an iron tube with a glass receiver. The Rb distils over, and appears like Hg in the receiver. As H is given off, the Rb is surrounded by a non-oxidising atmosphere (ARbOH + 2Al = Rb,O.Al,O. + 2Rb + 2H.). From 28 to 33 p.c. of the Rb in RbOH is obtained (Beketoff, J. R. 1888. 363; abstracts in C. J. 58, 108, and B. 21, Ref. 424). For a description of the method of preparing Rb from Rb₂CO₃ and C v. Bunsen (A. 125, 367) and Setterberg (A. 211, 100). An explosive compound similar to the compound of K and CO (this vol. p. 300) is liable to be formed.

For a method of separating Rb from Cs and K, based on the formation of double compounds of RbCl with SbCl₂, and with SnCl₄, v. Muthmann (B. 26, 1019 [1893]).

Properties .- A very lustrous, white metal,

with an extremely faint tinge of yellow. Soft as wax, even at -10° ; melts very easily (c. 38.5°). Lighter than water. Bunsen (A. 125. 367) made one determination of S.G., which gave 1.52, but the result is not final. Heated in absence of O, the metal distils below redness, forming a blue vapour. Rb dissolves in liquid NH₃ (Seeley, C. N. 23, 169). When exposed to air Rb is at once covered with a greyish-blue film, which is supposed to be a suboxide: much heat is produced, and the metal soon takes fire. Decomposes cold water very rapidly, with evolution of H, which takes fire. Rb is the most positive element next to Cs. It closely resembles K in its chemical relations (v. Alkalis, METALS of the, vol. i. p. 114). The at. w. of Rb has been determined (1) by determining Cl in RbCl by Bunsen (P. 113, 339; 115, 584 [1861]), Piccard (J. pr. 86, 454 [1862]), and Godeffroy (A. 181, 180 [1975]). (2) 189 [1875]); (2) by determining V.D. of RbCl and RbI at c. 1200° (Scott, Pr. E. 14, 410). The S.H. of Rb has not been determined; but from observations of the molecular heats of RbCl and Rb₂CO₃, and comparisons of these with those of the corresponding salts of metals that have normal atomic heats, it is probable that the atomic heat of Rb is c. 6.4, and, therefore, that the S.H. is c. 075. The atom of Rb is monovalent in the gaseous molecules RbCl and RbI.

Reactions and Combinations.—1. Rapidly oxidises in air; much heat is produced, and the metal ignites. Beketoff (J. R. 1888, 363) gives [Rb²,0] = 94,900.—2. Decomposes cold water, with rapid evolution of H and production of RbOHAq; Beketoff (Le.) gives [Rb,H²OAq] = 96,400, with formation of RbOHAq and H.—3. Burns in vapour of chlorine, bromine, iodine, sulphur, and arsenie, forming compounds with

those elements (Bunsen, l.c.).

Detection and Estimation. — Phosphomolybdic acid gives a yellow pp. insol. acids (Debray, Bl. [2] 5, 404). Silicotungstic acid (SiW₁,0₂,H₃,xH₄,0) ppts. Rb salts, but not salts of K (Godeffroy, B. 9, 1365). As Cs salts are ppd. by SbCl₃ in conc. HClAq, added to solutions containing conc. HCl (as 6CsCl.SbCl₃), while Rb salts give no pp., Rb can be separated from Cs salts by addition of HClAq and SbCl₃ in HClAq (G., B. 8, 9). Rb is best detected by the spectroscope. The most characteristic lines are in the blue-violet, Rb₂(λ = 4206), and Rb₃(λ = 4216): '0002 mgm RbCl can be detected (Bunsen, l.c.). Rb is determined in the form of RbCl. For the separation of Rb from K, and estimation of the Rb, v. Bunsen (l.c.). Bunsen determined RbCl in presence of CsCl by finding the sum of the two chlorides, then estimating the total Cl, and calculating the quantity of each salt.

Rubidium, amalgam of. When conc. RbClAq is electrolysed, using Hg as negative electrode, a solid, white, lustrous, crystalline amalgam is formed. Decomposes cold water rapidly; becomes oxidised superficially in air, and then deliquesces with formation of RbOH. Is electropositive to K amalgam (Bunsen, A. 122, 847).

347). Rubidium, bromide of. RbBr. Formula probably molecular, from analogy of RbCl and RbI. Formed by burning Rb in Br. Also by saturating HBrAq with Rb₂CO₂, and evaporating.

White, lustrous, regular octahedra. S. 98 at 5°, | 104'8 at 16° (Reissig, A. 127, 38). Melts at c. 683° (Carnelley, C. J. 33, 279). Combines with IBr, to form RbBr.IBr; and with Br to form RbBr.Br; (Wells a. Wheeler, Am. S. [3] 43, 475).

Rubidium, chloride of, RbCl. Mol. w.

20-57. V.D. at 1200°-1500° 69-7 (Scott, Pr. E. 14, 410). Melts at c. 710° (Carnelley, C. J. 33, 279). By burning Rb in Cl. Also by saturating HClAq with Rb.CO₃, evaporating, and crystal-lising from water. Also by reducing Rb.PtCl₆ in H, and dissolving out RbCl in water (cf. Preparation, p. 411). White, lustrous, cubical crystals; unchanged in air; decrepitates when heated, and then melts, and volatilises at a very high temperature. S. 76.38 at 1°, 82.89 at 7°; sol. alcohol (Bunsen, l.c.). Molten RbCl is a good conductor of electricity (Hampe, Chem. Zeitung, 1887. No. 54). Double compounds: RbCl combines with many metallic chlorides; some at any rate of the products, e.g. the platingand platini chlorides Rb2PtCl, and Rb2PtCl6, are best regarded as Rb salts of acids containing metals and Cl. The following compounds have been prepared: M=RbCl. - 6M.SbCl3 (1); 3M.2SbCl₃ (6); 6M.BiCl₃ (1); 2M.CdCl₂, M.CdCl₂,αH₂O (1); 2M.CrCl₃,aq (2); 2M.CuCl₂ (1); M.GuGl₂æH₂O(1); 2M.GrOl₂aq (2); 2M.GuGl₂(1); M.AuGl₃ (3); 3M.FeGl₃aq (1); 2M.FeGl₃aq (2); 2M.HgGl₂ 2aq. HgGl₂ 2aq. M.2HgGl₃ M.2HgGl₄ M.4HgGl₂(1); 2M.NiGl₂ (1); 2M.PtGl₄ (4); 2M.PtGl₄ (5); 3M.TiGl₃ (2); 2M.SnGl₄ (1); 2M.ZnGl₂ (1). Reference to the above (1) Galacters B. 2

References to above.—(1) Godefiroy, B. 8, 9; (2) Neumann, A. 244, 329; (3) Rosenbladt, B. 19, 2535; (4) Nilson, Bl. [2] 27, 210; (5) Bunsen, A. 122, 347; (6) Muthmann, B. 26, 1010, 145.

1019, 1425.

RbCl also combines with IBr to form RbCl.IBr; with ICl, to form RbCl.ICl; with BrCl, to form RbCl.BrCl; and with Br to form

RbCl.Br₂ (Wells a. Wheeler, Am. S. [3] 43, 475).
Rubidium, cyanide of. Setterberg (A. 211, 100) probably obtained a cyanide of Rb by passing dry HCN into an alcoholic solution of RbOH. Reissig (A. 127, 33) failed to obtain the sult free from products of decomposition.

Rubidium, ferrocyanide of; v. vol. ii. p. 335. Rubidium, fluoride of, RbF. Formula probably molecular, from analogy of RbCl and RbI. S.G. 3.202 at 16.5° (Clarke, Am. S. [3] 13, 293). Melts at c. 753° (Carnelley, C. J. 33, 279). Forms a double compound with uranyl fluoride, 4RbF.UO₂F₂-6aq (Ditte, C. R.

91, 166). Rubidium, hydroxide of, RbOH. A white, brittle solid, with slight greyish tinge; very alkaline and caustic; easily sol. water, with production of much heat; sol. alcohol. Formed by decomposing HO by Rb; also by boiling Rb, SO, Aq till air is driven out, adding BaOAq gradually, keeping the liquid boiling till BaSO, ceases to be formed, decanting from BaSO,, which separates out rapidly, and evaporating in a silver dish. Melts below redness; is not decomposed by heating. When molten attacks Pt. Beketoff (J. R. 1888, 363) gives [Rb,O,H] = 164,800; [Rb²O,H²O] = 69,900.

Rubidium, iodide of, RbI. Mol. w. 211.53. V.D. 110.8 at 1200°-1500° (Scott, Pr. E. 14, 410). Melts at c. 642° (Carnelley, C. J. 33, 279). Lustrous, white, regular octahedra; unchanged

in air. S. 187.5 at 6.9°, 152 at 17.4°. Formed by saturating HIAq with Rb, CO,, evaporating, and crystallising from water. Also by heating Rb in I vapour (Reissig, A. 127, 33). RbF combines with I to form RbI.I. (Wells a. Wheeler. Am. S. [3] 43, 475).

Rubidium, oxides of. No oxide of Rb has been isolated. Rb burns in air, possibly with formation of an oxide and peroxide similar to K2O and K2O4. The greyish-blue film which is formed on the surface of the metal when exposed to the air is perhaps a suboxide. According to Beketoff (J. R. 1888, 363), the thermal value of [Rb2,O] is 94,900.

Rubidium, salts of. The principal salts formed by replacing H of oxyacids by Rb are borate, carbonates, chlorate and perchlorate, chromate and dichromate, molybdate, nitrate, oxalate, silicotungstate, sulphate, and thio-sulphate (v. Carbonates, Nitrates, &c.).

Rubidium, silicofluoride of. Rb,SiF, White, regular crystals. S.G. 3°338 at 20°, S.c. 16 at 20°, 1°35 at 100°. By ppg. hot Rb alum solution by CuSiF₆ (Stolba, J. pr. 102, 1). M. M. P. M.

RUBIJERVINE v. JERVINE.

RUE OIL. The essential oil (c. 229°) obtained by distilling Ruta graveolens contains methyl ennyl ketone C11H22O (224°), a ketone $C_{12}H_{24}O$ (232°), and a small quantity of terpene (Gerhardt, C. R. 26, 225, 361; Cahours, C. R. (Gernardt, C. A. 26, 282, 507, Calcatal), 26, 262; Greville Williams, T. 1858 [1] 99; A. 107, 374; Hallwachs, A. 113, 108; Harbordt, A. 123, 293). By boiling oil of rue with nitric acid (S.G. 1:2) an acid (C.H., N.Q. may be obtained (Chiozza, A. 85, 225; Alexejeff, Z. 1865, 736). This acid is a heavy oil, forming KA' and NaA', crystallising from alcohol in greenishyellow tables (Limpach, A. 190, 298).

RUFICOCCIN v. CARMINIC ACID.
RUFIGALLIC ACID v. HEXA-OXY-ANTHRA-

OUINONE. RUFIN C21H20O8. A product of the action of heat on phlorizin (Mulder, Rev. Scientif. 3, 50; Stas, A. 50, 198). Dark-red resin, sol. alcohol, nearly insol. ether and water. Its alkaline solutions are red. Ac₂O forms C₂₁H₁₉AcO₈ (Schiff,

A. 156, 5). RUFIOPINE is TETRA-OXY-ANTHRAQUINONE. RUFOL v. DI-OXY-ANTHRACENE.

RUTHENIUM -

RUTHENAMMINES

AMMONIUM COMPOUNDS, p. 418.
RUTHENATES v. RUTHENIUM, SALTS OF
OXYACIDS OF, p. 417.
RUTHENITES v. RUTHENIUM, SALTS OF

OXYACIDS OF, p. 417. RUTHENIUM. At. w. 101.4. Mol. w. unknown. Melts at highest temperature attainable by O-H flame, which is above 2000° (Deville a. Debray, A. Ch. [3] 56, 385). S.G. 12-26 at 0° (crystallised) (D. a. D., C. R. 83, 928); older determinations varied from 8-6 to 11-4. Joly (C. R. 116, 430) gives S.G. of Ru melted in an electric furnace as 12.63 at 0° referred to water at 4°. S.H. 0611 from 0° to 100° (Bunsen, P. 141, 1). C.E. at 40° (linear) .00000963 (Fizeau, C. R. 68. 1125).

Occurrence.-In many platinum ores; Ru is a constant ingredient of osmiridium (vol. iii. p. 47), the quantity varying from 8 to 6 p.c. (v. Claus, A. 56, 257; 59, 234; Gibbs, Am. S. [2] 29, 427; 81, 68; 84, 841). Wöhler found Ru₂S, in laurite, a rare mineral occurring in Borneo and

in Oregon (J. pr. 98, 226).

In 1828 Osann (P. 13, 283; 14, 329; cf. 64, 197) thought he had discovered three new metals in the portion of a Pt ore insol. in aqua regia; to these metals he gave the names polin, pluranium, and ruthenium (from Ruthenia = Russia). In 1845 Claus (A. 56, 257; 59, 234; cf. 63, 359) examined the substance called ruthenium oxide by Osann, and found it to consist chiefly of SiO₂, TiO₂, Fe₂O₃, and ZrO₂; from this material Claus isolated a new metal, to which he assigned Osann's name, ruthenium.

Formation. — 1. By reducing Ru₂O₃ by heating in H or C.—2. By strongly heating (NH₄),RuCl₃, (NH₄)₂RuCl₃, Ru(NH₄,NH₂Cl)₂, decided by heating RuSn₂in Ru(NH₂NH₂Cl)₂.—3. By heating RuSn₂in

a graphite boat in a stream of HCl.

Preparation. - Deville a. Debray (C. R. 82, 926) prepared pure Ru by heating the ordinary metal in a stream of O till every trace of Os was removed as OsO, (vol. iii. p. 646), fusing with KOH and KNO, dissolving in water, saturating with Cl, and distilling off RuO, into KOHAq, by heating in a stream of Cl on a water-bath, ppg. Ru₂O₃ by adding alcohol to the solution of KRuO,, heating the pp. in coal-gas till reduced to Ru, melting in a graphite crucible with 5 to 6 parts pure tin, treating with boiling HClAq, washing and drying the crystalline RuSn₂ which remained, and heating this strongly in a graphite boat in a stream of HCl .- 2. Osm-iridium is mixed with 2 parts KNO, and 1 part KOH, and the mixture is heated to redness in a large silver crucible, embedded in MgO in an carthenware crucible; the molten portion is poured off, and the residue is heated with more KNO, and KOH. The fused mass is lixiviated with water; the orange solution, which contains KOH and K salts of HNO2, HNO3, H₂OsO4, and H₂RuO4, is neutralised by HNO3Aq, when a black pp. forms containing OsO2.xH2O and Ru,O,xH,O. This pp. is filtered off, the filtrate being set aside, and is washed and boiled with HClAq and HNO, Aq in a retort connected with a receiver which is kept very cold; the boiling is continued till a drop of the distillate, when brought alternately into the oxidising and reducing parts of the Bunsen flame, ceases to give a bright flash in the former, i.e. until OsO. ceases to distil off. The residue, which contains RuCl₂ and RuCl₃, is dissolved in a little water, excess of NH Cl is added to the hot conc. solution, the liquid is poured off from (NH,) RuCl, evaporated and mixed with more NH4Cl, when (NH4)2RuCl ppts. Excess of NH,Cl is removed from the pps. by washing with alcohol. By strongly heating the pps. Ru is obtained. The solution filtered from the pp. of OsO2.xH2O and Ru2O3.xH2O contains OsO4 and RuO,; it is made strongly acid by HClAq, OsO, is distilled off, the solution is evaporated till most of the KNO, crystallises out, the mother-liquor is evaporated to dryness, the residue is dissolved in water, and Ru₂S₃ is ppd. by adding (NH₄)₂SAq and then acidifying; after washing and drying, the Ru₂S₃ is roasted, and the Ru₂O₄ so formed is reduced by heating in H, or by strongly heating in a graphite crucible; or the Ru,O, may be dissolved in HClAq, and NH,-Ru chlorides obtained from this solution and decomposed by heat (Claus, J. pr. 85, 129; Carey Lea, Am. S. [2] 38, 83).

For other methods of separating Ru from osm-iridium v. Deville a. Debray (A. Ch. [3] 56, 886; C. R. 83, 927; Fremy, A. Ch. [3] 44, 385; Gibbs, Am. S. [2] 34, 343; 37, 61). Debray obtained ruthenium in crystals by dissolving the spongy metal in molten lead, heating strongly, and, after cooling, dissolving out the lead (with which Ru does not alloy) in HNO₂Aq (C. R. 90,

1195).

Properties .- A white, lustrous, hard, heavy, brittle metal. As obtained by heating the double ammonium chlorides, Ru forms a white spongy mass; the metal formed by reducing the oxide by H appears in white porous fragments, which can be powdered; after fusion in an electric furnace Ru appears greyish (Joly, C. R. 116, 430). Next to Os, Ru is the most infusible metal; small pieces can be melted at the highest temperature of the O-H flame (D. a. D., A. Ch. [3] 56, 385); a little RuO₄ is formed and then decomposed to RuO₂ (D. a. D., C. R. 80, 457). Insoluble in all acids if in compact pieces; very finely divided Ru dissolves slightly and slowly in boiling aqua regia. Not attacked by molten KHSO,; oxidised to K.RuO, by fusion with KOH, KNO, or KClO, Ru dissolves in molten Zn or Pb; treatment with HNO Ag leaves the Ru undissolved. Small quantities of Ru when alloyed with Pt metals soluble in acids go into solution, with the Pt metals, in these acids. Finely divided Ru combines with O, when heated in O or in air.

Ru is closely related to Rh and Pd, and less closely, but very distinctly, to Os, Ir, and Pt;

v. Noble metals, vol. iii. p. 628.

The atomic weight of Ru has been determined (1) by determining the ratio of Ru to KCl in K,RuCl₃ (Claus, P. 65, 218 [1845]; (2) by analyses of the salts M,Ru(NO)Cl₃, where M=K, Na, and NH₄ (Joly, C. R. 107, 994; 108, 946 [1889]; (3) by determining V.D. of RuO₄ (Debray a. Joly, C. R. 106, 328); (4) by measuring S.H. of Ru (Bunsen, P. 141, 1). Claus's determinations gave values from 102-2 to 104-8 for the at. wt.

The only compound of Ru whose mol. weight is known in the gaseous state is RuO₄; the valency of the atom of Ru cannot be determined

from this datum.

Reactions and Combinations.—1. Finely divided Ru, when heated to redness in air or in oxygen, rapidly absorbs 18.6 p.c. O (Claus, J. pr. 42, 364); after 10 hours, c. 23 p.c. O has combined (D. a. D., C. R. 87, 441); the product is a mixture of RuO₂ and Ru (Claus failed to obtain a lower oxide than RuO₂ in this way). Crystals of RuO₄ are obtained by heating the metal in a tube in a rapid stream of O; according to Debray and Joly (C. R. 106, 1494), RuO₄ is formed and then decomposed (v. RUPHENIUM TETROXIDE, p. 417).—2. Heated in chlorine, a small portion is changed to a chloride; mixed with sodium chloride and heated in chlorine, Na_RuO₄ is formed (Claus, l.c.).—3. Spongy Ru is said to form HOlAq when placed in chlorine vater; and to produce chlorides in solutions of hypochlorites, O being given off (Schönbein, J. pr. 98, 76).—4. Very finely divided Ru dissolves slightly when kept in boiling aqua regia for some time, RuOl₂ being formed,—5. M₂RuO₂

soluble in water. is formed by fusing Ru with caustic alkalis, alkali chlorates, or alkali nitrates. Alkaline earth nitrates or chlorates also form ruthenates (v. RUTHENATES, p. 417).

Detection.—A few mgms. of the substance to

be tested are heated, in a spoon of Pt, with excess of KNO, until the whole melts and ceases to give off gas; when cold, the mass is dissolved in water, when a strongly coloured orange-yellow solution is obtained; a little HNO3Aq is added to this solution, followed by HClAq, and warming till the voluminous black pp., produced by HNO, Aq, dissolves to an orange-yellow solution; H,S is passed into this liquid, until it appears black from the presence of suspended Ru sulphide (or oxysulphide); on filtering, an azure-blue liquid is obtained, probably containing RuCl₂ (Bunsen, A. 146, 265). For estimation v. Deville a. Debray (C. R. 83, 927).

Ruthenium, alloys of. An alloy with iridium was obtained by Deville a. Debray (A. Ch. [3]. 56, 385). A crystalline alloy with tin, RuSn, is formed by melting Ru with 10 to 15 parts Sn, and when cold treating with HClAq. The tin is removed, and crystalline Ru remains, by heating, in a graphite boat, in HCl gas (D. a. D., l.c.; v. also C. R. 83, 927). Ru alloys with zinc; much heat is produced (D. a. D., l.c.). Ru dissolves in molten lead, but separates out again on cooling (Debray, C. R. 90, 1195).

Ruthenium, ammonio-salts of; v. RUTHE-

NIUM-AMMONIUM COMPOUNDS, p. 418.

Ruthenium, chlorides of. Two chlorides,
RuCl₂ and RuCl₃, are obtained by heating finely divided Ru in a stream of Cl. No other chloride has been isolated; the existence of double compounds of RuCl, with alkali chlorides is doubtful. The molecular weights of the chlorides are not known.

RUTHENIUM DICHLORIDE RuCl₂. (Ruthenous oride. Ruthenoso-chloride.) Prepared by chloride. Ruthenoso-chloride.) heating very finely divided Ru in a stream of Cl. Action begins at c. 360° (Joly, C. R. 114, 291) with formation of RuCl, which is removed by subliming, and the temperature is kept at dull redness for an hour or two; the residue is powdered, and again heated in Cl; and this treatment is repeated several times (Claus, A. 59, 234). A black crystalline mass; insoluble water, acids, or alkali solutions. The azureblue liquid formed by the action of reducers, such as Zn or H2S, on solutions of RuCl., was thought by Claus (i.c.) to contain RuCl,

RUTHENIUM TRICHLORIDE RuCls. (Rutheno-, or ruthenoso-ruthenic, chloride. Sesquichloride of ruthenium.) Obtained, as a brown, crystalline, very hygroscopic solid, by dissolving Ru(OH), (Claus, A. 59, 234), or RuO, (Joly, C. R. 107, 994), in HClAq, and evaporating to dryness. Joly (C. R. 114, 291) obtained RuCl, by heating finely divided Ru at 360° to 440° in a mixture of CO and Cl, the Cl being in excess. Claus says that RuCl, is sol. water, with partial decomposition to an insol. oxychloride; and that, on heating, the solution decomposes with separation of a black powder (partly oxychloride, partly RuO.H.), the colouring power of which is so great that 1 mgm. suffices to make 500 c.c. water appear quite black. Joly (C. R. 114, 291) says that RuCl, prepared by heating Ru in Cl and CO. is insol, cold water, acid solutions, CCl., CS,

CHCl, Et,O, or PCl, it is decomposed slowly by hot water; slowly dissolved by digesting with 50 times its weight of absolute alcohol, in a sealed tube. Solution in alcohol is purple-violet; slowly decomposes in moist air, more rapidly at 60°, giving RuCl. OH (v. RUTHENIUM HYDROXYchioring, p. 416). Rull, absorbs NH, to form 2Rull, 7NH; another compound containing NH,, viz. Rull, (OH), 7NH, 3H,O, is formed by throwing RuCl, in small successive quantities into cold saturated NH, Aq and then heating to 40° (Joly, C. R. 115, 1299).

Double salts. Chlor-ruthenites, RuCl₁.2MCl, or M_2 RuCl₃; $M=NH_4$, K, Na(Claus, A. 59, 234; 63, 359). Formed by evaporating RuO,H, in HClAq nearly to dryness, dissolving in water, and adding conc. solution of the alkali chloride; also by heating a mixture of Ru with KCl or NaCl in Cl (Joly, C. R. 107, 994). The potassium salt, which seems to be the most definite, is a brownish-violet, crystalline powder, scarcely sol. cold water, somewhat sol. boiling water, insol. alcohol of 80 p.c.

Joly (C. R. 108, 854) obtained ruthenium nitrosochloride RuCl, NO.H.O, by heating RuCl, with a large excess of HNO, Aq, and evaporating at 120°. Heated in vacuo, or in CO₂, at 440°, gives off NO, and leaves a mixture of RuCl₃ and RuO₂. Solution of the nitroso-chloride is not ppd. by alkalis in the cold; but on boiling with enough alkali to combine with 3Cl, a brown gelatinous pp. of nitroso-oxide, Ru₂O₂,2NO.2H₂O₃ is obtained. For compounds of RuCl₂ with NO and alkali chlorides, v. Nitrosochlor-ruthenates, infra.

RUTHENIUM TETRACREORIDE RuCl. (Ruthenichloride. Ruthenic chloride.) Claus (4. 59, 234) supposed that a solution of RuO, H, in HClAq contained this chloride; he also described various alkali chlor-ruthenates, M.RuCl. obtained by adding alkali chlorides to the supposed solution of RuCl. Joly, however (C. R. 107, 994), has shown that Claus' salts contain NO; and he asserts that the compound used by C. and supposed to be RuO, H, itself contained NO. Joly failed to obtain either RuCl, or the salts M.RuCl_a. The compounds described by C. as M.RuCl_a, but shown by J. to be M.Ru(NO)Cl_b. may be called nitrosochlor-ruthenates.

Nitrosochlor-ruthenates, $M_Ru(NO)Cl_*(RuCl_*,NO.2MCl)$. M = Am, K, Na. These salts were obtained by Joly (C. R. 107, 994) by heating RuCl, in HNO, Aq for some time and adding alkali chlorides, also by adding alkali nitrites to warm solutions of RuCl, in HClAq. According to Joly, the salts described by Claus as M.RuCl, are in reality nitrosochlorruthenates. These salts yield NO when heated with CaCO₃. Solutions of these salts are not ppd. by alkalis in the cold; on boiling with alkali sufficient to combine with 3Cl, a pp. of Ru₂O₃(NO)₂.2aq is slowly formed (J., C. R. 108, 854). The group NO evidently forms part of the acidic radicle of the salts (cf. RUTHENIUM-AMMONIUM COMPOUNDS. p. 418).

Potassium nitrosochlor-ruthenate,

K,Ru(NO)Cl,. Prepared by fusing Ru with KOH and KNO, dissolving in HClAq, and evaporating somewhat till excess of KCl and KNO, crystallise out; by evaporating the mother-liquor a mixture of K.RuCl, and K.Ru(NO)Cl, is obtained, from which water dissolves the latter salt. Purified by crystallisation from water, wherein the salt is fairly soluble. Black, orthorhombic prisms; transparent when in thin crystals. Solution in water is violet-red.

Ruthenium, cyanide of, and derivatives; v. vol. ii. p. 346.

Ruthenium, hydroxides of; v. Ruthenium, oxides and hydrated oxides of, in/ra.

Ruthenium, hydroxychloride of, Ru(OH)Cl₂. Described by Joly (C. R. 114, 291) as a solid, obtained by heating, in moist air to 60°, a solution of RuCl₃ in absolute alcohol. Very solwater; the deep indigo-blue solution slowly denosits RuO H.

Ruthenium, iodide of, RuI₃. This compound is formed, according to Claus (A. 59, 234), as a black pp. by adding KI to K_{*}RuCl_{*}Aq.

Ruthenium, nitrosochloride of, Ru.NO.Cl., v. under Ruthenium TRICILORIDE.

Ruthenium, nitrosopentoxide of,

Ru₂(NO)₂O₃.2H₂O, v. under Ruthenium pentoxide.

Rutenium, oxides and hydrated oxides of. Claus described four oxides of Ru: RuO, RuO, RuO, RuO, and RuO,; and the hydrated oxides Ru,O,3.3H₂O and RuO,2H₂O. According to Debray and Joly, RuO and Ru,O,3 have not been isolated, but the oxides Ru,O,3 and Ru,O, exist, besides RuO, and RuO,. According to Joly, Claus' RuO,2H₂O contains NO. Ru combines with O when melted in the O-H flame, with formation of RuO,; it is probable that RuO, is tormed, and then decomposed to RuO, + O.

RUTHENIUM MONOXIDE RuO. (Ruthenous oxide.) According to Claus (A. 59, 234), this oxide is formed, as a dark-grey, metal-like solid, by calcining RuCl₂ mixed with rather more than an equivalent of Na₂CO₃ in a stream of CO₂, and washing with water as long as anything dissolves. Debray and Joly (C. R. 106, 328, 1424) could not obtain this oxide.

RUTHENTIM SESQUIONIDE Ru₂O₃. (Ruthenocxide.) When Ru black is strongly heated in a Pt crucible, c. 18·5 p.c. O is rapidly taken up; O is then slowly absorbed till from 23 to 24 p.c. has combined, and a blue-black mass is formed. This blue-black solid is Ru₂O₃, according to Claus (A. 56, 257; 59, 231); according to D. a. J. (l.c.) it is a mixture of Ru and RuO₃.

HYDRATED RUTHENIUM SESQUIOXIDE
Ru₂O₃3H₂O or RuO₂H₂. (Black ruthenium hydroxide.) A black powder; prepared by ppg. solutions of RuCl₂ by alkali, or by alkali carbonate, phosphate, or borate (Claus, A. 59, 234). Also ppd.from an aqueous solution of Ru(Ol)Cl₂ (v. Hydroxychloride, supra). Even after washing for several days the pp. retains c. 1 p.c. alkali. Reduced, but incompletely, by H at ordinary temperature. Insol. KOHAq or NaOHAq, sl. sol. NH,Aq (Claus, l.c.); sol. in acids. The only salts of oxyacids derived from this oxide which have been prepared are Ru(NO₂)₃3KNO₂ and the corresponding Na salt (Claus, J. 1863. 697; Gibbs, Am. S. [2] 29, 427; 31, 63; 34, 341).

RUTHENTOM DIOXIDE RUO. (Ruthenic oxide.) Formed by strongly heating Ru sulphide, or Ru(SO.),, in air (Claus, A. 59, 234). Ru(SO.), is obtained by ppg. RuCl, solution by H.S., and oxidising the pp. by HNO. RuO. is also formed, as a crystalline sublimate, by roasting osm-

iridium containing Ru in a porcelain tube (Fremy, A. Ch. [3] 44, 385). Also obtained by strongly heating finely divided Ru for some time in a stream of O (D. a. D., A. Ch. [3] 56, 385; C. R. 83, 927; 87, 441). The whole of the Ru is not converted into RuO₂, but some metal remains unoxidised (D. a. J., C. R. 106, 1494). At a very high temperature RuO₄ is formed, and at a lower temperature this is resolved into RuO₂ and O (D. a. D., C. R. 80, 457; D. a. J., C. R. 106, 1424). D. a. J. (C. R. 106, 328) obtained RuO₂, partly amorphous and partly crystalline, by heating RuO₄ to 107°; also by heating RuO₄ to 440°.

Dark-violet, quadratic crystals; isomorphous with rutile (Fremy, l.c.; D. a. J., l.c.). S.G. 7.2 (D. a. D., A. Ch. [3] 56, 385). Insol. acids, sol. molten KOHAq. Easily reduced by H. The only salt of an oxyacid corresponding with RuO₂ which has been isolated is Ru(SO). (Claus. l.c.).

which has been isolated is Ru(SO₄)₂ (Claus, *l.c.*).

Hydrafed ruthentum disciple RuO₂.5H₄O or RuO₁H_{1.3}H₄O. The existence of this compound is doubiful. Claus (4.59, 234) gave this composition to the gelatinous, yellow-brown pp. formed by decomposing K₂RuCl₂Aq by Na₂CO₃; but Joly has shown that Claus' K₄RuCl₂ contains NO (cf. Ruthentum tetrachloride, p. 415). Claus also obtained hydrated RuO₂ by evaporating Ru(SO₄)₂Aq with KOHAq; but as the sulphate employed was obtained by oxidising Ru sulphide by HNO₃, it may have contained NO. Joly (C. R. 107, 994) gives the formula Ru₂O₃(NO)₂2H₂O to to the brown gelatinous pp. formed by boiling Ru(NO)Cl₃ or K₂Ru(NO)Cl₃ with KOHAq or K₂CO₃Aq. It seems probable that Claus' RuO₂.5H₃O is the same as the nitroso-compound obtained by Joly (cf. infra Hydrated nitroso-pentoxide).

RUTHENIUM PENTOXIDE Ru.O. (= RuO.,RuO.). When RuO. Ag stands for some time in a closed vessel, a black pp. settles down and a black crystalline crust forms on the sides of the vessel, while O is set free and escapes when the vessel is opened. The composition of the pp. and crystalline crust after drying at 100° is given by Debray a. Joly as Ru.O. (C. R. 106, 328). This oxide is also obtained by allowing a dilute solution of a ruthenate to stand for a long time, or by adding a dilute acid to such a solution. Ru.O. dissolves in HClAq, giving off Cl; heated to 360° Ru.O. is formed.

Hydrated nitroso-pentoxide Ru₂O₃(NO)₂:2H₂O. A black solid, formed by boiling Ru(NO)Cl₃ or K.Ru(NO)Cl₃ (v. Nitrosochloride, and Nitrosochlor-ruthenates, p. 415) with sufficient alkali or alkaline carbonate to combine with 3Cl, and drying the pp. at 150° (Joly, C. R. 103, 854). Slowly decomposes when heated to 360° in CO₂, giving Ru₁O₂; above 440° decomposes violently, giving off N oxides; reduced by H below 100°, giving off NH₂. Sol. in acids, forming nitrososalts.

RUTHENIUM NONOXIDE Ru_4O_9 (= $3\mathrm{Ru}O_2,\mathrm{Ru}O_3$). This composition was given by D. a. J. (C. R. 1005, 328) to the black, lustrous, crystalline crust obtained by heating $\mathrm{Ru}O_4\mathrm{Aq}$ to 100° . The same oxide is formed by heating Ru_2O_3 to 860° . Heated to 440° this oxide gives amorphous $\mathrm{Ru}O_2$ and O.

RUTHENIUM TRI-OXIDE RuO. (Ruthenic anhydride.) This oxide has not been isolated,

but salts derived from it are known. RuO, is the hypothetical anhydride of ruthenic acid (H_RuO,), which has not been isolated. For the salts corresponding with this oxide v. Ruthenates, under Ruthenium, salts of oxyacids of, infra.

RUTHENIUM HEFTOXIDE Ru₂O_r. (Per-ruthenic anhydride.) This oxide, the hypothetical anhydride of the non-isolated per-ruthenic acid (HRuO₄), has not been prepared. For the salts corresponding with this oxide v. Per-ruthenates, under RUTHENIUM, SALTS OF OXYACIDS OF, infra.

RUTHENIUM TETROXIDE RuO. (Sometimes called per-ruthenic acid.) and frequently ruthenic acid.) Mol. w. 165-24. V.D. 83-3 at 100° and 106 mm. pressure (Debray a. Joly, C. R. 106, 328).

Formation.—1. By passing Cl into a solution of the product of fusing Ru with KOH and KNO₃,—2. By the action of KClO₃ and HCl, not aqua regia, on K₂RuCl₃Aq (Claus, A. 59, 234).—3. By heating finely divided Ru in a stream of O to c. 1000°, and cooling rapidly by means of ice. If the temperature is allowed to fall slowly the RuO₄ formed decomposes explosively at c. 108° (Debray a. Joly, C. R. 106, 100).

Preparation.—A mixture of 1 part finely divided Ru, with 8 parts KOH and 1 part KNO, is heated to dull redness in a silver crucible till fused; the product, when cold, is dissolved in 16 parts water; the solution is placed in a tubulated retor; connected, by a long tube, with a very well cooled receiver (the connecting tube being also cooled), and a rapid stream of Cl is passed into the solution; a considerable amount of heat is produced, and RuO, passes over and solidifies in the receiver (Deville a. Debray, A. Ch. [5] 4, 537). To free the preparation from water D. a. J. (C. R. 106, 328) place it in a tube with fused CaCl₂, contract the tube in the middle, pump out the air, and seal off the tube. The RuO, slowly sublimes into the upper part, which is then separated from the rest. The RuO, is finally distilled in vacuo into tubes which have been very carefully cleansed from all traces of organic matter, and dried by heating to redness in a stream of H. RuO, may be obtained in well-formed crystals by subliming in vacuo at the ordinary temperature.

Properties .-- (D. a. J., C. R. 106, 328.) Golden yellow crystals, melting at 25.5° to an orange-red liquid, which solidifies slowly to a vitreous solid. Smell resembles that of ozone; the vapour causes coughing, but does not affect the eyes (Claus, J. pr. 80, 282). Sublimes at 3 to 4 mm. pressure on the slightest rise of temperature; the vapour is golden yellow. Decomposes at 106°-107° without boiling. The vapour-pressure of the crystals is almost nil at 0°, 20 mm. at 42°, and 182 mm. at 100.8°. May be distilled in water-vapour containing Cl or HClO. Gradually reduced to RuO₂ by sunlight (Joly, C. R. 113, 693). Dissolves in water, forming a golden-yellow solution, which gradually decomposes with ppn. of Ru₂O₃xH₂O. RuO₄ attacks Hg, and slowly acts on glass. RuO₄ does not form corrections of the contraction of the contractio responding salts, either by reacting with acids or alkalis. Moist RuO, is very easily reduced, e.g. by contact with paper.

Reactions.—1. Decomposed by heat; no ac-

tion below 106°; at 107° sudden decomposition occurs, with a smoky flame and formation of amorphous RuO2 on the walls of the vessel, and crystalline RuO, from the part that has melted (D. a. J., l.c.). According to D. a. J. (C. R. 106, 100), RuO₄ is formed when O is passed over spongy Ru at c. 1000°, and the product is rapidly cooled. If cooling is allowed to take place slowly the RuO, decomposes at c. 108° .-2. Dissolves in water; solution keeps unchanged for some time, but slowly deposits Ru,O,xH,O. Decomposition is more rapid at higher temperatures; at 100° Ru,O, xH,O is formed (D. a. J., l.c.).—3. Solution in water, or moist RuO, is quickly reduced by alcohol and several other organic compounds (Claus, J. pr. 80, 282) .-4. With solutions of alkalis forms ruthenates and per-ruthenates, with evolution of O. Alcoholic solution of potash ppts. Ru₂O₂.3H₂O₂.— 5. Heated with hydrochloric acid, Cl is given off and RuCl, formed in solution .- 6. Hydrogen sulphide gradually throws down a black pp. of an oxysulphide, from RuO, Aq (Claus, l.c.).

Ruthenium, oxyscids of. No oxyscid of Ru

Ruthenium, oxyacids of. No oxyacid of Ru has been isolated, but some salts of the hypothetical acids H₂RuO₄ and HRuO₄ are known (v. RUTHENIUM, SALTS OF OXYACIDS OF, infra).

Ruthenium, oxysulphide of. A current of H₂S passed into Ru₀/Aq slowly ppts. all the Ru as a black substance, which is said by Claus (J. pr. 80, 282) to be an oxysulphide, whose composition varies according to the quantity of H₂S passed in. The pp. suddenly glows when dried at 100°, and burns, giving off SO₂.

Ruthenium, saits of. Very few saits are known obtained by replacing the H of oxyacids by Ru. The double nitrites Ru(NO₂)₃.3MNO₃, where M = K or Na, are the only saits which have been prepared corresponding with Ru₂O₃; and Ru(SO₄)₂ is the only sait of RuO₂ which has been isolated; the double sulphite RuSO₃.K₂SO₃ corresponds with RuO.

Buthenium, salts of oxyacids of. A few salts of the hypothetical acid HRuO, and two salts of the hypothetical acid HRuO, have been isolated.

RUTHENATES, M¹₂RuO₄. Salts of hypothetical H₂RuO₄ (formerly called ruthenites). These salts are formed by heating Ru, or an oxide of Ru, with an oxide, hydroxide, nitrate, or chlorate of an alkali metal (Claus, A. 56, 257; 59, 234), or of an alkali metal (Claus, A. 56, 257; 59, 234), or of an alkaline earth metal (Deville a. Debray, A. Ch₂ [3] 56, 385). Ruthenates in solution are easily reduced by organic bodies, with ppn. of black Ru₂O₃.3H₂O; acids added to cone. solutions form per-ruthenates, M¹RuO₄.

Barium ruthenate BaRuO, aq. Obtained by adding RuO, to BaOAq. The solution is at first green, probably from formation of perruthenate; a black pp. is thrown down, which soon changes to the cinnabar-coloured crystalline Ba sait. This salt is also formed by adding BaCl,Aq to a solution of the K salt (Debray a. Joly, C. R. 106, 1494).

Potassium ruthenate K_RuO₄.aq (D. a. J., l.c.). 50 g. RuO₄, melted under water, are slowly added to 70 g. KOH in 500 c.c. water at 60°; temperature is kept at 60° until the evolution of O has ceased, when the solution is evaporated in vacuo; long, black, orthorhombic prisms, reflecting green light, are formed (for

crystalline measurements v. D. a. J. (l.c. p. 1497). After drying in vacuo, the crystals absorb moisture and CO₂ from the air. Unchanged at 106° in vacuo; loses H₂O at 200°, and may then be heated to 100° without decomposition. Very sol. water; solution is orange yellow; it soon decomposes in air, depositing Ru₂O₅.xH₂O, and probably forming KRuO Aq. Organic bodies dipped into the solution become black from deposition of Ru₂O₃,8H₂O. Acids hasten formation of KRuO₄Aq and Ru₂O₅; from conc. K₂RuO₄Aq acids ppt. KRuO₄, which decomposes to Ru₂O₅ and RuO, (D. a. D., C. R. 83, 927).

The magnesium, silver, and strontium salts are obtained by adding MgCl2Aq, AgNO3Aq, and SrCl2Aq respectively to K2RuO, Aq. The sodium salt has not been isolated; it cannot be separated

from excess of soda.

PER-RUTHENATES, MIRUO. Salts of hypothetical HRuO, (formerly called ruthenates). Obtained by the action of Cl on ruthenates, or of acids on conc. solutions of ruthenates. Alkalis produce ruthenates from solutions of per-ruthenates.

Potassium per - ruthenate KRuO. (Deville a. Debray, C. R. 83, 927). 50 g. RuO melted under water, are slowly added to 60 g. KOII in 250 c.c. water at 60°; O is evolved, and the solution becomes green; after O ceases to come off, the liquid is allowed to cool in a closed vessel; the cold (red) liquid, which contains K_RuO₄, is poured off, and the crystals of KRuO₄ that adhere to the sides of the vessel are dried in vacuo on an unglazed porcelain plate. Black, opaque, quadratic pyramids (for crystallographic measurements v. D. a. J., C. R. 106, 1496). Unchanged in air after drying in vacuo; decomposes suddenly at 440°, giving off O (? with formation of K₂RuO, and RuO₂). Cl reacts in the cold to form RuO, and KCl. Slightly sol. water; solution is blackish-green and soon decomposes, KOH being formed. Alkalis added to KRuO, Aq produce K, RuO, Aq, with evolution of O.

The sodium salt, NaRuO, aq, has been isolated; it forms black crystals. Addition of chlorides of alkaline earths to solution of KRuO, or NaRuO, ppts. M"RuO, not M"(RuO), and

the solutions contain RuO₄.

Ruthenium, sulphides of. No sulphide of Ru has been isolated with certainty. Claus could not obtain a sulphide by heating Ru with S in CO₂ (A. 56, 257; 59, 234). The pps. formed by H2S in solutions of Ru compounds vary in composition, and contain free S. By ppg. RuCl, solution by H2S, and heating the solid in CO, S and H₂O are given off, and a greyish-black metal-like substance remains, which is perhaps Ru, S, (C., l.c.). The pp. which H, S produces in RuO, Aq is probably an oxysulphide (q.v.). The mineral laurite, from Borneo and Oregon, contains Ru₂S₃ with Os sulphide (Wöhler, A. 139, 116; 191, 374). M. M. P. M.

RUTHENIUM-AMMONIUM COMPOUNDS. Ruthenammines. Ammoniacal ruthenium bases.) These compounds have not been obtained by treating Ru chlorides with NH,Aq. The starting-point for the compounds described by Claus was RuCl, 2NH, Cl. By treatment with NH, Aq, Claus obtained RuCl, 4NH, 3aq, and from this he prepared various salts RuX, 4NH,

where X = monovalent acidic radicle (N. Petersb. Acad. Bull. 1, 97; 2, 158). By evaporating a solution of the base Ru(OH), 4NH, in vacuo over H.SO., Claus obtained a new base, to which he gave the formula Ru(OH), 2NH, 4aq; he did not prepare any salts of this base. Joly (C. R. 107, 994) found that Claus' RuCl, 2NH, Cl is a nitroso-compound, and has the composition RuCl₃NO.2NH,Cl. Joly also showed (C. R. 108, 1300) that Claus' RuCl₂4NH₃ has the composition RuCl2-NO.OH.4NH3, and that the Rux, NO.OH.4NH,. Whether the base described by Claus as Ru(OH), 2NH, contains NO or not has not been determined; it is described here provisionally.

The nomenclature adopted in this article must be looked on as only provisional.

NITROSO-RUTHENI-DIAMMINES,

X.NO.Ru(NH₃.NH₃R)₂; R may or may not be the same as X. (Joly, C. R. 108, 1300; 111, 969.) Described by Claus as ammonium ruthenoso-di ammonium compounds, N2H4(NH4)2Ru.X2, or ruthenoso-diammines, Ru(NH, NH,X)2

Series I. Hydroxy-compounds,
OH.NO.Ru(NH₃,NH₂R)₂. The chloride, R = Cl,
was obtained (Joly, C. R. 108, 1300) by boiling
Ru(NO)Cl₃ (described under Rutherium Tri-CHLORIDE, p. 415) with excess of NH₂Aq, until the liquid became golden yellow, and deposited orange-yellow crystals of the salt. The bromids R = Br, and *iodide* R = I, were prepared similarly. The carbonate R = 1 CO3, nitrate R NO3, and sulphate $R = \frac{1}{2}SO_{\bullet}$, were prepared by the reaction of the chloride with Ag salts. By reacting on the chloride with moist Ag.O, Joly obtained a strongly alkaline liquid which probably contained the hydroxide, R=OH. The chloride

forms a double compound with PtCl.

Series II. Chloro - compounds,
Cl.NO.Ru(NH₂,NH₂R)₂ (Joly, C. R. 111, 969). The chloride, R = Cl, was obtained by dissolving the hydroxy-chloride in much HClAq, evaporating, and crystallising from boiling water; it combines with PtCl. The bromide and iodide, R=Br and I, were obtained similarly to the chloride.

Series III. Nitrato - compounds, NO3.NO.Ru(NH3.NH3R)2. The nitrate, R = NO3, was formed by the action of AgNO, Aq, or boilling HNO, Aq, on the chloro-chloride (J., l.c.). Series IV. Sulphato-compounds

Series IV. Sulphato-compounds, SO, 2[NO.Bu(NH, NH, R),]. Two sulphates, the normal salt where $R = \frac{1}{2}SO$, and the acid salt $2(SO, 2[NO.Bu(NH_2, NH_3, NG), SO])$. He SO, were obtained by the action of H_2SO_4Aq on the chlorochloride.

These compounds give off NH2 when heated in KOHAq, and separate Ru nitroso-hydroxide Ru(OH), NO, from which nitroso-salts are ob-

tained by the action of acids.

??Ruthenos-ammines, Ru(NH,X), or ruthenos-diammonium compounds, NH,(NH,)Ru.X, The only compound of this class which has been isolated is the hydroxide, Ru(NH, OH), 4aq, obtained by Claus (N. Petersb. Acad. Bull. 1, 97; 2, 158) by evaporating, over H₂SO, in vacuo, a solution of the base to which he gave the formula Ru(NH, NH, OH),. As the compound from which Claus obtained the supposed ruthenos-ammine hydroxide has been found

to contain NO, it is probable that the product of evaporation was also a nitroso- compound. M. M. P. M.

RUTIN C₀H₃₀O₃₃. [above 190°]. S. 58 at 100°. S. (boiling alcohol) 20. S. (ether) 29. Extracted by alcohol or HOAc from the leaves of the garden rue (Ruta graveolens) (Weiss, Pharm. Centr. 1842, 903; Bornträger, A. 53, 885; Förster, B. 15, 217). Occurs also in capers, the flower-buds of Capparis spinosa (Rochleder a. Hlasiwetz, A. 82, 197; 96, 123; Zwenger a. Dronke, A. 123, 145), in sattlower (Stein, J. pr. 58, 399; 88, 280), in rose leaves (Filhol, J. 1863, 594), and in the leaves of the buck-

wheat (Polygonum Fagopyrum (Schunck, C. J. 53, 262). Crystallises from water in pale-yellow needles (containing 3aq). Sol. alkalis, forming a yellow solution, from which it is reppd. by acids. FeCl, gives a dark-green colour. Lead acetate added to its alcoholic solution forms a yellow pp. Pb₃C₄₂H₄₄O₂₅. Does not reduce Fehling's solution. Decomposed by boiling dilute H.SO, into quercetin (1 mol.) and isodulcite (3 mols.).

RUTYL. A name sometimes used for decoyl

C10H19O or decyl C10H21.

RUTYLENE v. DECINENE.
RUTYLIDENE v. HENDECINENE.

 \mathbf{S}

SACCHARIC ACID C.H 10O, i.e. СО, Н.СН(ОН).СН(ОН).СН(ОН).СН(ОН).СО, Н. Mol. w. 210. Formed by the action of nitric acid (6 pts. of S.G. 1.15) on dextrose (glucose), and therefore on cane sugar and on milk sugar (Scheele, Opuscula, ii. 203; Trommsdorff, A. 8, 36; Guérin-Varry, A. Ch. [2] 49, 280; 52, 318; 65, 332; Erdmann, A. 21, 1; Hess, A. 26, 1; Thauloff, A. 27, 113; Liebig, A. 30, 313; 113, 1; Heintz, P. 61, 315; 105, 211; 106, 93: 111, 265, 291; A. 51, 185; Tollens, B. 21, 2149). Formed also by oxidation of dextrin, maltose, and dextrose by Br, and subsequent addition of ZnCO₃ (Herzfeld, A. 220, 352), and by the action of Br on glycuronic acid (Thierfelder, B. 19. 3148).

Preparation.-1. Dextrose (5 g.) is evaporated with HNO, (30 c.c. of S.G. 1.15) to a thick syrup. The syrup is dissolved in water (20 c.c.) and neutralised with K2CO3; HOAc is then added and the solution evaporated until the acid K salt crystallises out (Tollens, A. 249, 218) .-2. Starch (100 g.) is ground up with water (100 c.c.), poured into HNO, (500 c.c. of S.G. 1.15), and heated on the water-bath till red fumes begin to come off. The temperature is then lowered and kept at 65° until syrupy. The product is converted as above into the acid K salt (20 g.), which is dissolved in water, neutralised with ammenia, and ppd. by AgNO3. The Ag salt is then decomposed by HCl (Sohst a. Tol lens, A. 245, 4).

Properties. - Brittle deliquescent mass, v. sol. water and alcohol, v. sl. sol. ether. Dextrorotatory, [a]D varying from 8° to 38°. Reduces auric chloride and ammoniacal AgNO, (forming a mirror) but not Fehling's solution (Kiliani, B. 14, 2529).

Reactions .- 1. Oxidised by HNO, to dextrotartaric, racemic, and oxalic acids.—2. Potash at 250° yields acetic and oxalic acids. — 3. PCl, forms chloromuconic acid C.H.Cl.O. [260°] (Bell, B. 12, 1272).-4. Boiling dilute (30 p.s.) HClAq forms dehydromucic acid (S. a. T.; Schrötter, M. 9, 442).—5. HIAq and P at 150° forms some adipic acid (De la Motte, B. 12, 1572) .- 6. The ammonium salt decomposes at 1572).—6. The aminomian sais decomposes 160° into CO₂, NH₃, and pyrrole (Bella Lapper, B. 10, 1961). The ethylamine sait yields, in like manner, ethyl-pyrrole.—7. Phenyl-hydrasine sectate at 100° forms C₄H₄O₄(CO.N₃H₄Ph)₂, a

yellowish substance 210°], insol. water, alcohol. and ether; not decomposed by alcoholic potash

(Maquenne, Bl. [2] 48, 721).
Salts.—KHA": trimetric crystals; a:b:o
=1.763:1:2.234. S. 1.1 at 7°.—K₂A": crystalline crusts, v. sol. water.—(NH₂)HA". S. 1.22 BaA": minute crystals, v. sl. sol. water.—BaA"3aq: amorphous.—CaA"aq.—SrA"1\(\frac{1}{2} \) ag. BAA" 3aq: amorphous.—CaA" aq.—SrA 15aq.
—MgA" 3aq: crystallinq, m. sol. hot water.—
ZnA" aq. — CdA". — PbA". — Pb₂C₂H₂O₃.—
Pb₂C₁₂H₁O₄. — Pb₂C₁₂H₂O₃. — Pb₂C₄H₂O₄.

Pb₂Cl₄A".—Bi₂C₄H₄O₄ 2aq.—Ag₂A": white pp.

Ethyl ether Et₄A". Crystalline mass, v.
sol. water and alcohol.—(Et₄A")₂CaCl₄. Prisms,
y. col. water si sol. alcohol insol. ether.

v. sol. water, sl. sol. alcohol, insol. ether.

Tetra-acetyl derivative of the ethyl ether C₈H₄Ac₄Et₂O₈. [61°]. Monoclinic tables (from alcohol), insol. Aq, v. e. sol. hot alcohol.

Anhydride C.H.O. i.e.

 $CH(OH) < CH(OH) > CH.CH(OH).CO_2H.$

charolactone. [132°]. Formed by allowing syrupy saccharic acid to stand over H₂SO, for some days (Sohst a. Tollens, A. 245, 5). Thin plates (from water). Yields pyromucic acid on heating. Reduced in acid solution by treatment with sodium-amalgam to glycuronic acid CO,H.CH(OH).CH(OH).CH(OH).CH(OH).CHO (Fischer a. Piloty, B. 23, 937; 24, 521).

Di-acetyl derivative of the double anhydride C10H10On i.e. CH(OAc).CHO.CO

[188°]. CO.O ___CH - CH(OAc). from Ac,O, acid potassium saccharate, and H.SO. (Maquenne, Bl. [2] 48, 720; cf. Baltzer, Bl. [2] 10, 263; A. 149, 238). White places, v. sl. sol. alcohol and ether.

Amide C₆H₈O₆(NH₂)₂. Amorphous powder Isosaccharic acid C₀H₁₀O₃. [185°]. [a]_D = 46° at 20°. Formed by careful oxidation of glucosamine hydrochloride by dilute HNO₄ (S.G. 1-2) (Tiemann, B. 17, 246; 19, 1258, 1273). Trimetric crystals (from water). v. sol. water and alcohol, sl. sol. ether. Dextrorotatory. Converted by heat into CO, and pyromucic acid. Reduced by HI to adipic acid. Heated in a current of dry HCl it yields fuzfurane (aa')-dicarboxylic acid. PCl, forms C₄H₂ClO(CO₂H)₂, which yields Et₄A'' [40°].... KHA" ½aq: v. sol. water.—(NH.);A".—BaA".— CaA".—SrA".—PbA" 2aq.—CuA".—Ag,A". Ethyl ether Et,A". [73°]. (250°). [a]p

= +35.5°. Needles, v. sol. water. Yields a derivative C₄H₄(OAc)₄(CO₂Et)₂ tetra-acetyl [47°] v. sol. water and alcohol.

Amide of the anhudride $C_4H_1O(OH)_2(CONH_2)_2[226^\circ]$. [a]_D = 7·2°. Anilide of the anhydride. [231°]

Acetyl derivative C,H, (OAc), (CO2H)2 aq.

[101°]. Needles (from water).

Parasaccharic acid C.H.O. Formed, together with glycyrrhetin, by boiling glycyrrhizin with dilute H2SO4 (Habermann, C. C. 1880, 253). Hygroscopic mass, sol. water and alcohol. Its salts are amorphous.

Metasaccharic acid CaH10O8. The salt CaA" aq, got by boiling an aqueous solution of the dianhydride with CaCO₂, forms crystals, sl. sol. water. KA' and Ag.C₂H₂O₃, have also been prepared (Fischer, B. 23, Zi21). Solutions of metasaccharates turn deep red when exposed to

Dilactone CaHaOa i.e. CH(OH).CH.O.CO l- Mannosaccharic CO . O.CH-CH(OH) acid. [68°]. S. 5.5 at 15°. $[a]_D = -202^\circ$ (Fischer, B. 24, 541). Formed by oxidation of acid. [68°]. S. arabinose-carboxylic (mannonic) acid C₆II₁₂O, by digesting its lactone with HNO₃ (S.G. 12) for 24 hours at 50° (Kiliani, B. 20, 341, 2710; 21, 1422). Long colourless needles (containing 2aq), sl. sol. alcohol, insol. ether. Readily reduces Fehling's solution. Reduced by HI to n-adipic acid. Sodium-amalgam reduces it to mannite. Phenyl hydrazine hydrochloride and sodium acetate solution in the cold form CH(OH).CH(OH)

CO . O.CH.CH(OH).CO.N₂H₂Ph [192°] crystallising in minute plates (containing aq), v. e. sol. hot water. Phenyl hydrazine hydrochloride and boiling sodium acetate solution forms C₄H₄(OH)₄(ČO.N₂H₂Ph)₂, crystallising in minute

plates [213°], v. sl. sol. water. Di-acetyl derivative of the dilactone

ÇH(OAc).ÇH.O.ÇO

CO.O -- CH-CH(OAc) [155°]. Formed by adding a few drops of H2SO, to a mixture of the dilactone and Ac.O (Kiliani, B. 22, 524). Prisms, v. sol. hot HOAc.

Г190°]. C4H4(OH)4(CO.NH2)2 Amide Formed from the lactone and NH, Aq. Monoclinic tables.

Dextro-metasaccharic acid. d-Mannosaccharic acid C_eH₁₀O₈. Salts.—CaA": crystalline powder.—BaA": minute tables, m. sol. water.— '.-CdA": minute tables, v. sl. sol. water.

Lactone $C_6H_6O_6$. [180°-190°]. [a]_D = 202° at 23°. Formed by oxidation of mannose, of mannite, or of d-mannonic acid by HNO, (S.G. 1.2) at 50° (Fischer a. Wirthle, B. 24, 539; Easterfield, C. J. 59, 306). Long needles (from alcohol or water), v. sol. hot water. Readily reduces Fehling's solution. Turns yellow on boiling with potash. Phenyl-hydrazine acetate in the cold

forms CH(OH).CH(OH).CON₂H.Ph [191°], while at 100° it forms C4H4(OH)4(CO.N2H2Ph)2 [212°], almost insol. hot water.

Amide C₆H₁₂N₂O₆. [189°]. Formed from the lactone and NH₂Aq in the cold. Crystals.

Inactive metasaccharic acid C_aH₁₀O₃. i-Mannosaccharic acid. The salts of this acid greatly resemble those of the preceding acid.

Lactone C.H.O. [c. 190°]. Formed by mixing equal parts of the dextro- and levolactones in aqueous solution. Formed also by oxidising i-mannonic lactone (E. Fischer a. Stanley Smith, B. 23, 2622; 24, 544). The aqueous solution is inactive to light, and gradually becomes acid on standing. Phenyl-hydrazine acetate reacts, forming in the cold CH(OH).CH(OH) CO.O — CH.CH(OH).CON,H,Ph [190°-195°]

and at 100° C,H,(OH),(CON,H,Ph), [220°-225°]. Amide. [185°].

SACCHARIN. The lactone of saccharinic acid (v. infra). The name has also been applied to the imide of SULPHOBENZOIC ACID.

SACCHARINIC ACID C.H.,O. i.e.

CH. (OH).CH(OH).CH(OH).CMe(OH).CO.,H.

Formed by boiling an aqueous solution of dextrose, lævulose, or invert sugar with lime (Péligot, Bl. [2] 36, 226; C. R. 90, 1141; Scheibler, B. 13, 2212). On setting the acid free it changes, especially on heating, into the anhydride. The salts are v. e. sol. water.—KA': monoclinic tables.—NaA'. [α]_D = -17·2°.—CaA'₂ (dried at 100°). Formed by boiling the lactone with water and CaCO₃. Amorphous. $[a]_D = -5.7^{\circ}$. CuA', 4aq: blue nodules (Kiliani, B. 15, 2955).

Anhydride $C_bH_{10}O_s$. [161°]. $[a]_D = 94°$. S. 13 at 15°. Electrical conductivity: Walden, B. 24, 2028. H.C. 656,900. H.F. 252,100 (Stoh-

mann, J. pr. [2] 45, 313).

Preparation.—A cold solution of 1 kg. of invert sugar in 9 litres of water is treated with 100 g. of powdered lime and allowed to stand, agitating at intervals. After 14 days 400 g. more CaO2H2 is added, and the mixture again allowed to stand for one or two months, until it no longer reduces Fehling's solution. It is then saturated with CO, the remaining Ca precipitated with oxalic acid, and the filtrate evaporated nearly to a syrup. The saccharin which separates is recrystallised from hot water; the yield is 100 g. (Kiliani, B. 15, 2954).

Properties .- Prisms, with bitter taste, v. sol. hot water. Dextrorotatory. Converted by alkalis into lævorotatory salts of saccharinic acid. May be volatilised almost without decomposition. Can be extracted by ether, even from solutions containing Na₂CO₃. Does not ferment with yeast. Does not reduce Fehling's solution, even after long boiling with dilute H.SO. Not attacked by dilute HNO₂. Gonc. HNO₃ forms oxalic acid and saccharonic acid C₆H₁₀O₄. 1 g. reduces 4.6 g. of KMnO₄. Oxidised by moist Ag₂O to formic, acetic, and glycollic acids. Boiling HIAq reduces it to the lactone of γ-oxyisohexoic acid CH, CH(OH).CH, CHMe.CO, H, which is further reduced by HI at 200° to CHMePr.CO.H (Liebermann a. Scheibler, B. 16, 1821; Kiliani, A. 218, 371). I and KOH give iodoform. Potash-fusion forms formic and lactic acids (Hermann a. Tollens, B. 18, 1333). Boiling HClAq has no action. Phenyl-hydrazine forms C₄H₁₁O₅(N₂H₂Ph) [165°], crystallising from alcohol in needles, v. sol. water (Fischer a. Passmore, B. 22, 2733). Phenyl cyanate at 165° forms Cathan, Oa, crystallising in silky needles

[230°-240°], v. sol. hot aniline, sl. sol. alcohol | crystals (containing aq), v. al. sol. ether. Conc. (Tesmer, B. 18, 2607)

Isosaccharinic acid C.H,2O. i.e.

CH,(OH).CH(OH).CH2.C(OH)(CO2H).CH2OH? Formed by the action of lime on malt-extract at 20° or on milk-sugar (Cuisinier, Bl. [2] 38, 512). The free acid at once splits up into water and lactone. The Na salt is levorotatory. - CaA'2.

8. 1 in hot water. Crystalline powder. Lactone C.H. 100. Isosaccharin. $[a]_p = 63^\circ$ in a 10 p.c. aqueous solution; = 74° in HOAc. Electrical conductivity: Walden, B. 24, 2028. Prepared by allowing a solution of milksugar (1 kilo) in water (9 litres) mixed with slaked lime (450 g.) to stand for 6 weeks; filtering; saturating the filtrate with CO,; boiling, again filtering, and evaporating to 500 c.c. The calcium isosaccharinate (170 g.) which then crystallises is decomposed by oxalic acid (Kiliani, B. 18, 631). Large crystals, v. e. sol. water, alcohol, and ether. Dextrorotatory. Does not ferment with yeast or reduce Fehling's solution.

Reactions.—1. Reduced by HI and P to the lactone of oxy-hexoic acid, and finally to CHPrMc.CO₂H. -2. Oxidised by HNO₃ to dioxy-propane tricarboxylic acid C₃H₃(OH)₂(CO₂H)₃, which is split up by heat into CO₂ and αγ-di-oxyglutaric acid CH₂(CH(OH).CO₂H)₂ (Kiliani, B. 18, 2514). 3. Phenyl cyanate at 165° forms C_3 , H_{30} N₄O₅ [181°] a white amorphous powder (Tesmer, B. 18, 2609).

Anilide C, H, NO. [165°]. Formed by heating the lactone with aniline at 115° (Sorokin, Bl. [2] 47, 168; J. pr. [2] 37, 318). Needles, v. sol, water. Decomposed by acids and alkalis

into aniline and isosaccharin.

Metasaccharinic acid C₆H₁₂O₆ i.e. CH₂(OH).CH(OH).CH(OH).CH(OH).CH₂.CO₂H. Formed, together with isosaccharinic acid, by the action of lime on a cold solution of milk-sugar, its Ca salt being contained in the mother-liquor from which calcium isosaccharinate has crystallised (Kiliani, B. 16, 2625; 18, 642). The free acid splits up at once into water and lactone .-CaA', 2aq: crusts of minute prisms, v. sl. sol. cold water .- CuA', 2aq: groups of minute green plates.

Lactone C₀H₁₀O₃. Metasaccharin. [142°]. [a]_b = -48°. Large trimetric plates; a:b:c = -624:1: 899. V. sol. cold water and alcohol, v.

sl. sol. ether. Lævorotatory.

Reactions .- 1. Reduced by HI to the lactone of oxy-n-hexoic acid.—2. Oxidised by HNO3 to tri-oxy-adipic acid .- 3. Phenyl cyanate at 165° forms C₁₁H₁₀N₁O₂, a white amorphous powder [205°-210°] (Tesmer, B. 18, 2608).

SACCHAROLACTONE v. Anhydride of Sac-

CHARIC ACID.

SACCHARONIC ACID C.H,O, i.e.

CO,H.CH(OH).CH(OH).CMe(OH).CO,H.

Formed by heating saccharin (1 pt.) with HNO. (3 pts. of S.G. 1.375) at 35°, diluting, adding CaCO₃, filtering, evaporating, and extracting with ether (Kiliani, A. 218, 361). The product so obtained is the lactonic acid; the free acid at once splits up into water and lactone.-Na.A. Formed by boiling the anhydride with Na₂CO₃Aq. Crystalline. — (NH4)2A".—CaA": gummy.

Ag₂A": flocoulent pp.

Lactonic acid C₂H₂O₃. Saccharone.

[e]_p = -6°. Formed as above. Large trimetric

HIAq converts it into a dibasic acid C.H.O. [139] crystallising from water in small prisms. and finally to a-methyl-glutaric acid. Does not reduce Fehling's solution .- NaA' aq. Formed from saccharone (2 mols.) and Na₂CO₂Aq (1 mol.). Trimetric prisms with neutral reaction.—NH₁A': crystals. Its aqueous solution is ppd. by lead

subacetate, but not by lead acetate or AgNO₂.

SACCHARUMIC ACID C₁₁H₁₈O₁₁. A product of the action of baryta on dextrose (Reichardt, Vierteljahrschrift pr. Pharm, 19, 384, 503). Yellowish-brown powder with bitter taste, v. sol water and alcohol, sl. sol. ether. Its solution becomes dark on exposure to air or on addition of alkalis. — BaH,A''. — Ba,A'' 5aq: pp. Cu,A'' 3aq: greyish-brown pp. — l'b,A''.

Pb₂C₁H₁₂O₁₁.

SACCULMIC ACID C₁₁H₁₂O₁? together with sacculmin, by boiling cane-sugar (300 g.) with H₂SO₄ (15g.) and water (420 g.) (Stein, A. 30, 84; Sestini, G. 10, 121). The vield of the two bodies is about 10 p.c. of the sugar used. Glittering black mass, sl. sol. water and alcohol, insol. ether. The alcoholic solution is red, with reddish-brown reflex. Sol. KOHAq and reppd. by acids. AgNO, gives brown amorphous $C_{44}H_{30}AgO_{16}$. BaCl₂ ppts. brown $C_{22}H_{18}BaO_8$ aq. Chlorine passed into water in which sacculmic acid or sacculmin is suspended gives yellow flocculent di-chloro-oxysacculmide C, H, Cl,O,. Di-chloro-oxy-sacculmide boiled with KOHAq forms oxysacculmic acid C₁₁H₈O₈, which is sol. water, but insol. water containing H₂SO₄. CuSO₄ gives in its aqueous solution a brown pp. of C₁₁H₃₀CuO₂₁. Bromine and water form amorphous orange C₄₁H₂₈Br₆O₂₂ (Sestini, G. 12, 292).

Sacculmin C, H30015. Formed as above. Black amorphous mass, insol. KOHAq. Reacts with chlorine water in the same way as sacculmic acid. According to Conrad and Guthzeit (B. 18, 443; 19, 2844), sacculmin and sacculmic acid are mixtures of variable composition.

SAFFLOWER v. CARTHAMIN.

SAFFRANINE (PHENO-) C18H16N4O. Phenosaffranine. The hydrochloride may be represented as $C_0H_3(NH_2) < \frac{N}{NPhCl} > C_0H_3NH_2$ (Bernthsen, B. 20, 179, 2690; cf. Andresen, B. 19, 2215; Nietzki, B. 19, 3017, 3163; Witt, B. 19, 3121), or by $C_0H_1 < N_{NCl(C_0H_1NH_2)} > C_0H_1(NH_2)[\frac{2}{1}4]$ (Witt).

Formation.-1. Formed by gently warming phenylene-p-diamine (1 mol.) with aniline (2 mols.) and K₂Cr₂O₂ (Nietzki, B. 16, 466). A blue compound C₆H₄ N_{Cl(NHPh)} C₆H₄NH₂(?) is first formed, and changes at 100° into the red saffranine (Barbier a. Vignon, Bl. [2] 48, 838 772; C. R. 105, 939). The blue compound is reduced by zine and hydrochloric acid to $C_0H_4 < NH > C_0H_2$. NH_2 , which is exidised by air to amido-phenazine. According to Nietzki, however, the blue intermediate compound is the indamine C₆H₄(NH₂).N:C₆H₄:NH₂Cl and yields di-amido-diphenylamine on reduction.—2. From benzene-azo-aniline (amido-azo-benzene) treatment with nitro-benzene, Fe, and HClAq

Properties .- Golden plates. When freshly precipitated by baryta from the sulphate it is $C_{1s}H_{1s}N_1OH$, but after frequent recrystallisation from hot water it approximates to C18H14N4 (Nietzki a. Otto, B. 21, 1590). V. sol. hot water, sol. alcohol, almost insol. ether. Conc. H2SO4 gives a green colour, changing to blue and red on dilution. Conc. HClAq gives a blue colour. NaNO, added to a solution of saffranine hydrochloride forms the diazo- compound C18H15N3Cl2, which gives a blue solution and yields $C_{11}H_{11}N_1C_{12}AuCl_2$. This diazo-compound on boiling with alcohol forms $C_{14}H_{15}N_2$, the salts of which form red aqueous solutions and dye wool and silk a bluer shade than saffranine. The base $C_{18}H_{18}N_3$ is also got by adding H.SO, till the colour is violet, then adding excess of NaNO₂ and boiling: it yields B'HNO₃, B'H₂SO₄, and a violet acctyl derivative. Alcoholic potash forms NH, and saffranol. Zinc-dust and HCl give leuco-saffranine and, on long boiling, C₁₈H₁₉N₃O [130°], crystallising from water in long needles yielding C₁₈H₁₈AcN₂O [173°] and converted by nitrous ether into C₁₈H₁₈N₂O [117°], crystallising from alcohol in needles.

Salts. — (C₁₈H₁₅N₄Cl)₂PtCl₄. — C₁₈H₁₅N₄Cl. Flat needles with green lustre, sl. sol. cold, v. sol. hot water, insol. HClAq.-B'HNOs. Almost

insol. HNO3.

Di-acetyl derivative C18H14Ac2N4.-B'HCl. Got by heating saffranine hydrochloride with Ac2O and NaOAc (Nietzki, B. 16, 468). Lustrous brown plates, forming a violet solution

in alcoholic soda.-B'HI.

Di-methyl-saffranine. The chloride of this substance C₂₀H₁₉N₄Cl is formed, together with $N_2(C_pH_NMe_p)_2$ by the action of p-nitroso-dimethyl-aniline (1 mol.) on aniline (1 mol.) in alcoholic solution at 100° (Barbier a. Vignon, C. R. 105, 672). An isomeric (?) di-methylsaffranine got by oxidising a mixture of C_cH₁(NH₁)NMe₂ and aniline yields B'₂H₂PtCl_s and B'HNO₂ (Nietzki, B. 16, 869; 19, 3163). An isomeride is formed by heating benzenc-azo-xylidine with aniline at 150° (Menton, A. 263, 837). Crystalline, forming a rose-red aqueous solution. A tetramethyl-saffranine C22H22N4 is got by oxidising di-methyl-phenylene-green mixed with aniline acctate (Bindschedler, B. 16, 867). It yields B'HCl, v. e. sol. water and B'HNO, aq.

Ethyl-saffranine C₁₈H₁₃EtN₄. Formed by boiling p-phenylene-ethyl-diamine with aniline, K₂Cr₂O₇, and dilute HOAc (Schweizer, B. 19, 150). Formed also by oxidising phenylene-pdiamine, aniline, and ethyl-aniline with K2Cr2O, and dilute HOAc (S.). The hydrochloride forms bluish-green hygroscopic crystals, sol. water and alcohol, insol. ether. Its solutions exhibit olivegreen fluorescence.-B'2H2PtCls: dark lustrous

Di-ethyl-saffranine C22H24N4. Formed by oxidising a mixture of C₈H₄(NH₂)(NEt₂) (1 mol.) and aniline (2 mols.) with K₂Cr₂O₇ (Nietzki, B. 16, 470). Formed also by oxidising a mixture of phenylene-p-diamine, aniline, and di-ethyl-aniline with K₂Cr₂O₂ (N.). The alcoholic solution is fluorescent. The hydrochloride is sol. HClAq.

(B. a. V.). -3. By oxidising a mixture of NANO, added to its solution in HClAq gives a NH(O₂H₄,NH₄[1:4]), (1 mol.) and aniline (1 mol.) greenish-blue colour due to the diazo-chloride with K₂Or₂O₃ (B.). Which forms C₂₂H₂₂N₄Ol₂PtCl₄. — B'₂H₂PtCl₅: greenish-blue colour due to the diazo-chloride which forms C₂₂H₂₂N₃Cl₂PtCl₄. — B'₂H₂PtCl₄: green needles.

Acetyl derivative C₁₈H₁Et_ACN₄. The hydrochloride is ppd. as glittering brown needles on adding NaCl to its aqueous solution.

 $-\mathbf{B'_{2}H_{2}PtCl_{5}}$

Tetra-ethyl-saffranine $C_{26}H_{32}N_4$ or

C28H21N4.OH. Formed by oxidising a mixture of phenylene-di-ethyl-p-diamine, aniline, and di-ethyl-aniline with $K_c C r_c O_7$ (N.).— $B'_2 H_c P t C l_s$. Para-saffranine $C_{20} H_{18} N_s$. Prepared by dis-solving mauveine in dilute acetic acid and boil-

ing with PbO2. NaOH is added to slight excess, and the red filtrate boiled with some powdered zinc and CaCO, and then NaCl added. Commercial saffranine contains some parasaffranine (Perkin, C. J. 35, 728).

Properties.—Red-brown pp., dissolving in

water or alcohol. It is isomeric or identical with commercial saffranine, prepared from equal molecules of tolylene p-diamine, o-toluidine, and aniline. Salts.—B'HCl.—B'HNO3. These salts dye silk a shade more scarlet than saffranine.

Saffranine C21H20N4 or C21H21N4OH. Formed from o-toluidine by treatment with nitrous acid and oxidation of the product with K2Cr2O7 (Mène, C. N. 25, 215; Hofmann a. Geyger, B. 5, 526; Dale a. Schorlemmer, C. J. 35, 683). Obtained by heating toluene-azo-o-toluidine with o-toluidine hydrochloride at 150°-160° (Witt, B. 10, 873), and by adding K₂CrO₁ to a hot solution of tolylene-p-diamine hydrochloride (1 mol.) and o- or p-toluidine hydrochloride (2 mols.) (Witt, B. 12, 939; Bindschedler, B. 13; 207). The commercial saffranine (saffranine hydrochloride) can be purified by recrystallisation from water containing HCl, or by treatment with alcohol (Böttger, N. R. P. 23, 181). Reddish-brown crystals, v. sol. water and alcohol, insol. ether. Conc. IICl changes the colour of its solution through violet to blue. H2SO4 turns it blue and finally green. Decolourised by zinc and HClAq. Saffranine is also decolourised by glucose and NaOHAq on heating, and hence may be used as a test for sugar in urine (Crismer, C. C. 1888, 1510); the colour is restored by atmospheric oxidation. Commercial saffranine (.5 g.) is fatal when administered to dogs by subcutaneous injection (Weyl, B. 21, 2191).—B'HCl. Thin reddish crystals, sol. water and alcohol, insol. ether and NaClAq.—B'₂H₂PtCl₂. Yellowish-red crystalline powder, almost insol. water, alcohol, and ether. —*B'HBr: minute needles.—B'HNO₃. Slender reddish-brown needles, v. sl. sol. cold water. Sulphate: needles, m. sol. water.— B'CeII,N3O7: brownish-red insoluble needles.

Substances of the saffranine class are formed by heating NH(C₀H₁NH₂)₂ with (4,3,1)- and (4,2,1)- xylidine and with (5,4,2,1)-cumidine, but not with mesidine, (5,4,3,1)-cumidine, or (5,2,1)-, (6,2,1)-, (5,3,1)-, and (3,2,1)-xylidine (Nietzki, B. 19, 3163).

Saffranol C₁₈H₁₆N₂(OH)₂. Formed by boiling saffranine hydrochloride with alcoholic potash for 8 days (Nietzki a. Otto, B. 21, 1593). Ppd. as yellowish needles by adding HCl to its solution in alkalis. Nearly insol. water, alcohol, and HOAc. Conc. H₂SO₄ forms a brown solution. Yields a crystalline diacetyl derivative.

SAFFRON. The dried stigmas of Crocus sativus, used as a colouring matter. It contains erocin (q, v), erocose (q, v), picrocrocin (q, v), polychroite, and an oil $C_{10}H_{11}O$ (209°) miscible with alcohol and ether but decomposed by water (Quadrat, J. pr. 56, 68; Weiss, J. pr. 101, 65).

Polychroite C48H60O18. Dried saffron is washed with ether and extracted with water. The extract is mixed with alcohol and filtered, and the filtrate ppd. by ether. Orange deliquescent mass, v. sol. water, insol. alcohol. Yields glucose on boiling with dilute acids.

SAFROLE C10H10O2 i.e.

CH₂ CO.C.CH:CH O.C.CH:C.CH.CH:CH₂ . Shikimole. [8°]. (232°). S.G. 18 1 0956 (S.); 113 1 0963 (Gladstone, C. J. 59, 290). V.D. 81 (obs. and calc.), $\mu_{\rm D} = 1\text{-}539$ at 11° (d.), $R_{\infty} = 45\text{-}57$ (Brühl, B. 21, 477). H.C.v. 1,243,800. H.C.p. 1,244,700. H.F. 40,300 (Stohmann a. Langbein, J. pr. [2] 46, 533). The chief constituent of the essential oil of sassafras (Sassafras officinalis) (Grimaux a. Ruotte, A. 152, 88; J. Schiff, B. 17, 1935; Poleck, B. 17, 1940; 19, 1094; 22, 2861). Occurs also in the oil obtained from the leaves and fruit of *Illicium religiosum* (Eykman, R. T. C. 4, 36, 45; B. 22, 2757; 23, 864), and in the oil of the camphor tree, Cinnamomum camphora (Flückiger, Ph. [3] 17, 989). Monoclinic crystals, sol. alcohol and ether. Smells like oil of sassafras. Inactive to light. Oxidised by dilute KMnO4 to CO2, formic, oxalic, and piperonylic acids, and piperonal. potash converts it into isosafrole. Alcoholic react with hydroxylamine or BzCl. Does not combine with NaHSO₃. Brom C₁₀H₃Br₅O₂ [170°] S. (chloroform) 7. Bromine forms

Isosafrole C; H10O2 i.e.

 $CH_2 < {}_{O} > C_6H_3.CH:CH.CH_3.$ (247°). V.D. 80·3

(obs.); 81 (calc.). H.C.v. 1,233,600. H.C.p. 1,234,500. H.F. 50,500. Formed by boiling safraje (100 g.) with KOH (250 g.) in alcohol (500 c.c. of 94 p.c.) for 24 hours (Schiff; Ciamician a. Silber, B. 23, 1160). Liquid, even at -18°, miscible with alcohol, ether, HOAc, and benzene, insol. water and alkalis. Conc. H₂SO₄ forms an intensely red solution. Oxidised by K₂Cr₂O₇ and H.SO, to piperonal and acetic aldehyde. Alkaline KMnO, gives piperonylic acid. Bromine in CS₂ forms C₁₀Br₃H₉O₂ [110°], crystallising from ligroin in colourless needles. Sodium reduces it in alcohol solution to C₁₀H₁₂O₂

C_eH₃Pr COCH₂ (228°), a liquid miscible with

alcohol and ether. Isosafrole is converted by treatment with KOH and MeOH into a compound, apparently different from methyleugenol, but yielding isovanillic acid on oxidation, and [4:2:1] CsH3(CsH5)(OAc)2 on treatment with Ac O (Ciamician a. Silber, B. 25, 1470).

Nitrosite C₁₀H₃N₂O₄ i.e. CH₂O₂:C₆H₂,C — CMe ? (Angeli, B. 24, 3994; N.O.O.N

25, 1956). Mol. w. 224 (by Raoult's method). [124°]. Ac O forms a white modification [124°]. Alcoholic potash forms an isomeride [185°] which yields a mono-acetyl derivative [129°],

it to piperonylic acid. Reduced by tin and HClAq to C₁₀H₈N₂O₈ or CH₂O₈:C₆H₃.C.—CMe ? Mol. w. 197 (by Raoult's method). Zinc and HOAc yield C₁₀H₁₀O₂, probably represented by (CH₂O₂)C₆H₂,CH₂,CO.CH, [38°], which yields a phenyl-hydrazide C₁₀H₁₀O₂(N₂HPh) [37°]. Another product of the action of zinc and HOAo is C_mH₁₈N₂O₄ [180°]; and a third is O₁₀H₁₆N₂O₄ or CH₂O₂: O₄H₁.C_—CMe ? [159°], which

yields a di-acetyl derivative [138°].

SAGAPENUM. A gum resin imported from Egypt and Persia, consisting of yellow agglomerated granules, smelling like garlic and having an acrid bitter taste. Softens in the hand. Yields umbelliferone on distillation. HNO, forms styphnic acid. Potash-fusion forms resorcin (Brandes, N. Tr. 2, 2, 97; Pelletier, Bull. Pharm. 3, 481; Johnston, Tr. 1840, 361). After moistening with alcohol it dissolves in H₂SO₄, forming a brown liquid. Sagapenum is only partially soluble in alcohol and ether, but the ethereal extract is not clouded by addition of alcohol. FeCl, colours its solutions black (Hirschsohn, J. 1875, 859; Ar. Ph. [3] 10, 481; 11, 54, 152, 247, 312, 434; C. C. 1877, 182)

SAGE OIL. Obtained in the south of Europe by distilling sage (Salvia officinalis) with water, the plant being cut down in the autumn (M. M. P. Muir, C. J. 33, 292; 37, 678; cf. Rochleder, A. 44, 4; Herberger, R. P. 34, 138; Hlasiwetz, J. pr. 51, 355). Contains a terpene (156°), salviol (q. v.), C₁₀H₁₅O (c. 200°), a camphor CleHisO, probably a little cymene, and, especially when prepared from English plants, cedrene, C₁₅H₂₄ (c. 260°). The amount of salviol and of camphor is very small at first and increases with the age of the oil, being formed by oxida-tion of the terpenes. Pure salviol, pure sage terpene, and pure codrene do not resinify when singly exposed to heat and light; but a mixture

of these rapidly darkens.

SAGO. Balls of starch got from the pith of certain species of Sagus and Cycas by stirring with water, allowing to settle, and rubbing the deposit through sieves.

SALAMANDRINE C3, Hc0N2O5. An alkaloid obtained from the poisonous secretion of the cutaneous glands of the salamander (Salamandra maculata). Crystalline, v. sol. water and alcohol (Zalesky, Bl. [2] 6, 344). Alkaline in reaction. Poisonous.—B'H.Cl.: needles.

Featurn. Poisonous.—B In Dr.; needles.

SALICIN C₁₃H₁₀O, i.e.
C.H₁₁O, O.C.H₁CH_OH. Mol. w. 286. [201²]
(Schiff, B. 14, 304). S. 3·3 at 11° (Piria, A. 96, 378). [a]₀ = -62·6° (Tiemann, B. 18, 1600; cf. Hesse, A. 176, 116; Sorokin, J. pr. [2] 37, 331). Occurs in the bark of several species of willow and poplar, e.g. Salix helix, S. amygdalina, Populus tremula, P. graca (Leroux, A. Ch. [2] 43, 440; Bruconnot, A. Ch. [2] 44, 296; Pelouze a. Gay-Lussac, A. Ch. [2] 44, 220; 48, 111; Piria, A. Ch. [2] 65, 281; [3] 1 , 257; Bouchardat, C. R. 18, 299; 19, 602, 1179; 20, 610, 1635; Gerhardt, A. Ch. [3] 7, 215; Tischhauser, A. 7, 280). Occurs also in castoreum (Wöhler, A. 67, 360).

Formation. -1. By digesting an aqueous solution of helicin with sodium-amalgam (Lisenko, and a benzoyl derivative [146°]. KMnO, oxidises Z. 1864, 577) or with zinc and H.SO. (Michael, Am. 5, 172).-2. By boiling populin with lime-

water (Piria).

Preparation .- Willow bark (6 lbs.) is boiled with water; the filtrate evaporated (to 18 lbs.); mixed while hot with PbO (2 lbs.); digested for 24 hours and filtered; the filtrate evaporated to a syrup and left to crystallise (Duflos, A. 8, 200; of. Peschier, A. Ch. [2] 44, 418; Erdmann, B. J. **8**3, 1, 136).

Properties .- Trimetric tables;

a:b:c='927:1:2'494. Sol. water and alcohol, insol. ether. Lævorotatory. Tastes bitter. Neutral to litmus. Its solutions are not ppd. by lead acetate or subacetate, by gelatin, or by tannin. Cono. H.SO, gives a red colour. IClAq forms a crystalline body (Stenhouse, C. J. 17, 827). After injection of salicin, salicylic aldehyde and salicylic acid are found in the urino (Laveran a. Millon, A. Ch. [3] 13, 145; Ranke,

Reactions .- 1. Decomposed at 240° into saliretin and glucosan.-2. Split up by emulsin and saliva at 40° into glucose and saligenin (Piria; Städeler, J. pr. 72, 350).-3. Boiling dilute H.SO, forms glucose and saliretin. -4. Oxidised by chromic acid mixture to CO, formic acid, and salicylic aldehyde.—5. Cold dilute HNO₃ forms helicin. Hot conc. HNO₃ forms picric acid.—6. Potash-fusion forms salicylic acid.—7. Boiling NaOHAq forms saliretin.—8. HCl and KClO, give tetra-chloroquinone.

Metallic derivatives.—C₁₃H₁₂NaO,

Formed from salicin and NaOEt in alcohol (Perkin, C. N. 18, 110). Crystalline.—Pb₂C₁H₁,0. Got by adding NH₃Aq to a hot cone, solution of salicin, and then adding lead subacetate. Bulky white pp.

Acetyl derivative C13H11Ac,O2. Needles (from alcohol), nearly insol. water (Schiff, Z. [2]

Bensoyl derivative C₂₀H₂₂O₃ i.e. C₁₅H₁,B2O₃. Populin. [180°]. S. ·05 at 9° (Piria); ·04 at 15°; ·24 at 100° (Schiff); S. (alcohol) 1 at 16°. Occurs in the bark and course the arms (Darwher Heaville). (alconol) 1 at 10. General in the bank and leaves of the aspen (Populus tremula) (Braconot, A. Ch. [2] 44, 296; Piria, A. Ch. [3] 34, 278; 44, 366; A. 81, 245). Formed by heating salicin with Bz₂O (Schiff, A. 154, 5). Prepared by boiling the leaves of the aspen with water. ppg. with lead subacetate, removing lead from the filtrate by H.S. and evaporating to crystalthe filtrate by H.S. and evaporating to crystallisation. Light silky needles (containing 2aq).

Tastes sweet. Lavorotatory (Biot. a. Pasteur, C.R. 34, 607). Sl. sol. water and alcohol, nearly insol. ether. K.Cr.Q. and H.SQ. forms alicylic aldehyde. HNO₃ (S.G. 1.3) forms benzoylhelicin. Conc. H.SQ. forms a deep-red solution, the containing the cont whence water ppts. a red powder ('rutilin'). Boiling dilute acids split it up into glucose, benzoic acid, and saliretin. Alcoholic NH, at 100° forms benzamide, benzoic ether, and salicin. Populin is not hydrolysed by emulsin.

Di-benzoyl derivative C₁₃H₁₆Bz₂O₂. Formed, together with the mono- and tetrabenzoyl derivatives, by heating salicin with Bz₂O (Schiff). Flocculent mass, nearly insol. water, sl. sol. ether.

Tetra-bensoyl derivative C₁₃H₁₁Bz₁O₂.

Amorphous resin, not coloured by cold H₂SO₄.

Chlore-salicin C₁₃H₁₁ClO₇. Formed by passing Cl into water in which salicin is suspended

(Piria, A. Ch. [3] 14, 275). Long silky needlet (containing 2aq), sol. water and alcohol, insolether. Tastes bitter. Resolved by emulsin into glucose and chloro-saligenin. Yields a tetraacetyl derivative, crystallising from alcohol in prisms.

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Di-chloro-salicin $C_{13}H_{16}C_{12}O_7$. Formed by the action of Cl on chloro-salicin. Silky needles (containing aq), nearly insol. cold water, m. sol. alcohol. Gives no colour with FeCl, or H2SO4. Split up by emulsin into glucose and di-chloro-

saligenin. Tri-chloro-salicin C,3H,5Cl3O,. Formed by chlorinating the preceding body in presence of water and CaCo₃. Yellowish needles (containing aq) (from dilute alcohol), almost insol. cold water.

Bromo-salicin C15H17BrO7. [160°]. Formed by slowly adding Br to salicin (1 pt.) in water (20 pts.) (O. Schmidt, Z. [2] 1, 320). Four-sided prisms, v. sol. water and alcohol. Split up by

emulsin into glucose and bromosaligenin. The radicle o-oxy-benzoyl SALICYL.

[1:2]C_cH₄(OH).CO. The same name is sometimes applied to the radicle o-carboxyl-phenyl [1:2]CO_cH_cC_cH₄ and, rarely, to o-oxy-benzyl C_cH₄(OH).CH₂.

SALIGYLAMIC ACID. An old name for

o-Amido-Benzoic acid.

SALICYLAMIDE. The amide of o-Oxy-BENZOIC ACID.

SALICYLAMINE. A name for o-Oxy-BENZYL.

SALICYL-GLYCIDIC ACID v. OXY-PHENYL-GLYCIDIC ACID.

SALICYL-GLYCOLLIC ACID is o-CARBOXY-PHENOXY-ACETIC ACID.

SALICYLIC ACID v. o-OXY-BENZOIC ACID. Homosalicylic acid v. Oxy-TOLUIC ACID.

SALICYLIC ALDEHYDE v. o-OXY-BENZOIC ALDEHYDE.

SALICYL-LACTIC ACID v. DI-OXY-PHENYL-PROPIONIC ACID.

SALICYL-PHENOL v. DI-OXY-BENZOPHENONE. SALICYL-RESORCIN v. TRI-OXY-BENZOPHEN-

SALICYL-SULPHURIC ACID v. CARBOXY-PHENYL SULPHURIC ACID.

SALIGENIN v. o-OXY-BENZYL ALCOHOL. SALIGENOL. Another name for o-Oxy-BENZYL ALCOHOL.

SALIRETIN v. o-Oxy-BENZYL ALCOHOL.

SALOL v. Phenyl ether of o-Oxy-BENZOIC ACID.

SALT-FORMING OXIDES. Oxides which form salts, either by reacting with acids (or acidic oxides)—in which case the oxides are basic-or by reacting with basic oxides or hydroxides—in which case the oxides are acidic. For a table showing the compositions and general characters of the characteristic highest saltforming oxides of each group of elements, v. vol. M. M. P. M. iii. p. 661. M. M. P. M. SALTPETRE. A common name for potassium

nitrate; v. vol. iii. p. 514.

SALTS. The earliest use of the word salt seems to have been to designate the solid obtained by evaporating sea-water. The term was afterwards applied to solids which more or less resembled sea-salt, especially to those solid bodies which were easily soluble in water. The SALTS. 425

study of the compositions of salt-like substances led to the view that they were made up of two parts, one of which was electro-positive with regard to the other. When the compositions of acids had been generalised in the statement that acids are compounds of hydrogen with non-metallic, or negative, elements, the relation of salts to acids was indicated by calling salts metallic derivatives of acids. This conception of the composition of salts included the older view, inasmuch as the metallic derivative of an acid is necessarily a compound of a positive metal with a less positive non-metal, or with a (less positive) group of elements, which non-metal, or group of elements, was combined with hydrogen in the parent acid.

The most general conception of the composition of salts is that which formulates them as M.R., where M is the positive, or basic, or basylous part, and R is the negative, or acidic, or chlorous part of the salt. Both M and I may be either simple or complex. Common salt, NaCl, is the type of all salts as regards composition; the positive radicle, Na, may be replaced by other metals, or by groups of elements which are positive with regard to the other part of the compound; so the negative radicle Cl may be replaced by other non-metals, or by groups of elements which are negative with regard to the other part of the compound.

When an aqueous solution of a salt is electrolysed, the positive radicle is separated at the negative electrode, and the negative radicle at the positive electrode (secondary reactions may occur). An element may form part of the positive radicle of a salt, and the same element may form part of the negative radicle of another salt. Thus in the electrolysis of a ferric salt the iron travels to the cathode, but in the electrolysis of K, Fe(CN), the iron travels, with the cyanogen, to the anode. In the electrolysis of PtCl, the Pt is separated at the negative electrode, but in the electrolysis of Na,PtCl, the Rt is separated, with the Cl. at the positive electrode. We must then regard the radicles of, say. FeCl,, as Fe and 3Cl, the radicles of PtCl, as Pt and 4Cl, and the radicles of NaCl as Na and Cl; but we must look on the radicles of K₄Fc(CN), as 4K and Fe(CN), and the radicles of Na₂PtCl₅, not as 2Na, Pt, and 6Cl, but as 2Na and PtCl_s. Again, neither the salt K,Fe(CN)_s, nor the salt Na₂PtCl_s, in aqueous solution, gives the ordinary reactions of iron or platinum; but if these salts were composed of the radicles 4K, Fe, and 6CN, and 2Na, Pt, and 6Cl respectively, we should expect them to show the same qualitative reactions as solutions of FeCl, and PtCl. In contrast with these salts is the compound formed by evaporating a mixture of K2SO4Aq and CuSO4Aq. The salt thus produced, K.SO. CuSO. 6H.O. when dissolved in water, gives the ordinary reactions of sulphates, of K compounds, and of Cu compounds; moreover, on electrolysis the K and Cu appear at the cathode, and the group SO, is set free at the anode (where it reacts with H,O to give H,SO, and O).

But all these salts—NaCl, PtOl₄, FeCl₂, K_{*}Fe(CN)₈, Na,PtOl₂, and CuSO₄-K₈SO₄—are represented, as regards composition, by the general formula M_{*}R_{**}. This formula satisfactorily ax-

presses the composition of all salts; but it says nothing about the properties of these compounds. When solutions of two salts are mixed, a more or less complete interchange of positive radicles generally takes place. This capability of reacting as if they were composed of two parts—or, one may say, of reacting in a binary way—is characteristic of salts. Salts in solution are most probably dissociated into two parts, each of which carries an electric charge. Even if the whole of the salt is not dissociated, the portion which readily takes part in chemical changes is most probably dissociated binarily (cf. Electrical methods, p. 184).

Salts, then, may be regarded as compounds of the form M.Rv, which readily exchange M and R with other compounds of similar composition, and which in aqueous solutions are wholly or partially separated into their positive and negative radicles, each radicle carrying with it

an electric charge.

Salts are often classified as normal, acid, basic, and double salts.

An acid salt is one whose negative radicle contains hydrogen that can be eliminated by causing the salt to react with an alkali or basic oxide, while a normal salt contains no replaceable hydrogen. As an acid is described as a compound containing hydrogen, all or part of which is replaceable by metal when the acid interacts with a metal or a basic oxide, it is evident that an acid salt comes under the description of an acid, and, strictly speaking, is an acid. According to the meaning already given to the term 'salt,' the class of salts includes acids. It is, however, convenient to give a special name to the compounds of hydrogen with negative radicles. A basic salt contains a positive radicle or radicles which can be replaced by a negative radicle with formation of a normal salt. This positive radicle is sometimes the group OH, sometimes it is a group MzOy, where M is the metal of the salt. Thus Bi(OH),NO₃ and Pb(PbO)NO₃ are basic salts. When treated with nitric acid the former gives the normal salt Bi(NO₃)₃, and the latter the normal salt Pb(NO₃)₂. The basic salt is an intermediate stage between the base and the normal salt, just as the acid salt is an intermediate stage between the acid and the normal salt.

Basic salts are formed by fairly weak bases; the very strong bases, Na₂O, K₂O, CaO, &c., do not form basic salts.

Normal salts frequently combine with other normal salts to form double salts. Generally speaking, one of the components of a double salt is a salt of a strong base which forms acid salts but not basic salts, and the other component is a salt of a weaker base which readily forms basic salts but does not form acid salts. That component which is itself the salt of a strong base—e.g. K₂SO₄, NaCl, &c.—may be regarded as the more acidic or negative radicle of the double salt, while the component which is itself the salt of a weaker base-e.g. Al2(SO4)4, Zn_s(PO₄)₂, &c.—may be regarded as the more basic or positive radicle of the double salt. The double salt belongs to the type MzRy; both M and R are themselves salts. And just as many normal salts are formed by the direct union of their radicles-e.g. NaCl by combining Na and Cl. BaSO, by combining BaO and SO,—so double saits are formed by the union of a more positive with a less positive radicle, which is, in such cases, itself a sait.

The reactions of some double salts indicate that these salts are to be regarded as composed of the two simple salts which were brought together when the double salts were formed; the salt MgSO, K.SO, Gaq, for instance, gives, in solution, the reaction of sulphates, of Mg, and of K, and on electrolysis the Mg and K go to the negative electrode. On the other hand, the re-actions of some double salts indicate that these salts are not to be regarded as composed of the simple salts by the union of which the double salts were formed; the salt Cr2(C2O4)3.K2C2O4, for instance, does not give the reactions salt must be looked on as the potassium salt of the acid $H_2Cr_2(C_2O_4)$. If the salt $(NH_4)_2Cr_2(C_2O_4)_2H_2O$ is treated with NH_3Aq , a new salt is formed having the composition $Cr_2(C_2O_4)$. $(NH_4)_2C_2O_4$.4NH₃.xH₂O, and the reactions of this salt show that it is an oxalate, and therefore that it has a different constitution from that of the salt (NH₂), Cr₂(C₂O₂), from which it is obtained.

The salts of the haloid acids combine to form many double salts, e.g. PbI2.KI, BiCl3.3KCl, AuCl. KCl, &c. Most of these double haloids are generally regarded as double salts in the usual acceptation of the term; but several of them do not give the ordinary reactions of the less positive metal they contain, nor the reactions of the halogen which enters into their composition. For instance, PtCl, 2NaClAq reacts with two equivalents of AgNO₃ to give PtCl, 2AgCl; if PtCl, 2NaCl were a double salt, reacting in solution as if it were composed of the two radicles PtCl, and NaCl, it would interact with six equivalents of AgNO₃, and the products would be Pt(NO₃), NaNO₃, and AgCl. It is evident, then, that the Na-Pt chloride is the Na salt of the acid H₂PtCl_s, and that the constitu-tion of this salt is similar to that of the ordinary simple salts.

Remsen (Am. 11, No. 5 [1889]) proposes to regard all the so-called double haloids as simple salts similar to ordinary oxysalts. It seems to me that the constitutions of these salts cannot be determined by an examination of their composition only, but that the reactions of each salt must be examined. Some of the double haloids are undoubtedly simple salts, as some of the double oxysalts are certainly simple salts of metal-containing acids; but as some oxysalts containing two metals react so as to show that they are composed of two radicles, each of which is a simple salt, so some of the double haloids also give the ordinary reactions of both the metals, and also of the acidic radicle, which they contain, and must therefore be regarded as true

double salts. M. M. P. M. SALVIOL $C_{10}H_{18}O$. (200°). S.G. 12 938. $\mu_D=1^{\circ}462$ at 20°. R_{∞} 74°2. (M. M. P. Muir, C. J. 38, 292; 37, 683). A constituent of oil of Sace (q,v). It is a dextrorotatory liquid. On distillation some of it splits up into H_2O and $C_{10}H_{10}$.

Reactions.—1. Chromic acid mixture or cilute nitric soid produces acetic and oxalic

acids and camphor [174].—2. P₂O₂ produces polymerides of C₁₀H₁₆, a terpene (171°), an aromatic hydrocarbon (c. 130°), and a paraffinlike hydrocarbon (170°–180°). Cymene is not formed. Hence salviol is not C₁₀H₁₀O. However, according to Semmler (B. 25, 3350), salviol is identical with tanacetone.

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Constitution.—Refractive index appears to indicate absence of C:C groups.

SALYLIC ACID. A name given by Kolbe to a supposed isomeride of benzoic acid got from salicylic acid by successive treatment with PCl, and sodium-amalgam. It is identical with benzoic acid (Reichenbach a. Beilstein, A. 132, 309). The name is also applied by Städeler (A. Suppl. 7, 159) to two acids: (a) C₁, H₁, O₂ [101°] and (β) C₂, H₂₂O₃ [95°], obtained by allowing salicylic aldehyde to stand for 12 years under water. The (a)- acid forms small four-sided prisms, gives no colour with FeCl₃, and yields 'Ag, A''. The (β)- acid forms aggregates of needles, gives an intense violet colour with FeCl₃, and yields Ag₃A'''. Both acids are v. sol. alcohol and ether.

SAMARIUM. This name was given by Lecoq de Boisbaudran (C. R. 88, 322; 89, 212) to the metal of an earth which he separated from what was then known as didymia, occurring in samarskite. Delafontaine (C. R. 89, 632) obtained from didymia an earth which he called decipia, and when this had been removed by ppn. as sulphate, the new earth, samaria, remained in solution, and was obtained by fractionally ppg. by NH, Aq. Cleve (C. J. 43, 362) separated what he regarded as pure samaria from orthite; he prepared and described several salts of the new element. Cleve found the at. wt. of Sm to be 150, supposing the oxide to be Sm.O.; this number was confirmed by Bettendorff (A. 263, 164). It is still very doubtful whether samaria is a homogeneous substance; according to Crookes, it contains at least four different bodies (v. METALS, RARE, vol. iii. p. 244). Because of the great uncertainty attaching to the homogeneous nature of the so-called samaria it does not seem desirable to give an account of the bodies which have been described as compounds of Sm. The student is referred to the memoirs cited above, and also to the following:-L. de Boisbaudran, C. R. 114, 575; 116, 611 (spectrum and compounds of samaria); Marignae, Ar. Sc. [3] 3, 413 (spectrum, and compounds); Krüss a. Nilson, B. 20, 2134; 21, 2310 (spectrum); v. also, for spectrum, B. A. 1884. 438. The compounds of the supposed element are described by Cleve (l.c., and also Bl. [2] 43, 162) (cf. also Earths, vol. ii. p. 422). M. M. P. M. EARTHS, vol. ii. p. 422).

SANDAL WOOD. A dye wood furnished by Pterocarpus santalinus, which grows in tropical Asia. It dyes mordanted cotton red. It contains santalin (Meier, A. 72, 320). Yellow sandal wood (from Santalum album), yields by steam-distillation an oil containing santalol C₁₈H₁₀O, and santalal C₁₈H₂₀O (Chapoteaut, Bl. [2] 37, 303). After treatment with Na the oil yields a terpene C₁₈H₁₈, S.G. 919, $\mu_{\rm A}=1.487$ (Gladstone, C. J. [2] 10, 6). The crude oil heated in sealed tubes at 810° forms C₁₈H₂₀O (c. 840°), C₁₈H₂₀O (250°) and C₂₈H₂₀O (240°) whence P₂O₂ forms C₁₈H₁₄ (c. 177°).

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Santalol (310°) is converted by P₂O₃ into water and C₃₅H₂₄ (260°). HOAc at 150° forms the acetyl derivative C₁₅H₂₅OAc (298°), and a compound C₃₅H₄₆O (288°).

Santalal (300°) is converted by P2Os into

C18H22 (248°).

Sandal wood oil from Santalum Preissianum contains a crystalline solid [105°] (Ph. [3] 22, 828)

SANDARACH. A gum resin which exudes from Thuja articulata growing in Barbary, and from various species of Callitris growing in Australia and New Zealand (Johnston, J. pr. 17, 157; Maiden, Ph. [3] 20, 562). Transparent yellowish mass with vitreous fracture, resembling pine-resin in taste and smell. Sol. alcohol. Completely sol. ether. Its alcoholic solution is ppd. by Pb(OAc)₂. It appears to contain several resins (e.g. $C_{40}H_{62}O_6$, $C_{40}H_{62}O_6$, and $C_{40}H_{60}O_6$) differing in solubility in alcohol.

SANGUINARINE C₁,H₁₅NO₄ (E. Schmidt, Ar. Ph. [3] 26, 622). Prepared from the root of Sanguinaria canadensis (Dana, Annals of the Lyceum of New York, 2, 245; Probst, A. 29, 120; 31, 241; Schiel, A. 43, 233; Am. S. [2] 10, 220; Naschold, J. pr. 106, 385). According to Probst and Schiel it is identical with chelerythrine, but Naschold and Schmidt assign the formula C1: II 15 NO, to sanguinarine and C₁₈H₁₇NO₄ to chelerythrine. Prepared by exhausting the root with ether and ppg. the hydrochloride by HCl. Pearly grains, insol. water, sol. alcohol and ether. Poisonous.— Salts: B'HCl aq.—B'2H_PtCle (dried at 100°).— B'2H_PtCye. According to König (C. C. 1891, i. 321) sanguinarine has the formula CanH15NO4, crystallises with aq, melts at 211°, and forms the red sults B'HCl 5aq, B'HNO, aq, B'HAuCl, and B'2H2PtCl6.

SANTAL C. H.O. Obtained from sandal wood by extracting with very dilute KOH, ppg. with HCl, and extracting the pp. with ether (Weidel, Z. [2] 6, 83). It is accompanied by a scarlet crystalline powder C14H12O4? Santal crystallises from alcohol in colourless iridescent four-sided laminæ (containing 1 aq), insol. water, sl. sol. cold alcohol, sol. KOHAq, sl. sol. NH, Aq. FeCl, colours its alcoholic solution dark red. Potash-fusion yields protocatechuic

acid. **SANTALIN** $C_{15}H_{14}O_{4}$ (Meier, A. 72, 320); $C_{15}H_{16}O_{5}$ (Wegermann a. Hüffely, A. 74, 226); $C_{17}H_{16}O_{6}$ (Franchimont, B. 12, 14). [105°]. The colouring matter of sandal wood and of coliatur wood. Extracted by ether or alcohol, and purified by ppg. its alcoholic solution with Pb(OAc), and decomposing the pp. by dilute H.SO. Minute red prisms (M.) or amorphous (F.), without taste or smell, insol. water. Its alcoholic solution is blood-red. Sol. alkalis, forming violet solutions in which BaCl, ppts. Ba(Cl, H, O,), as a dark-violet amorphous pp. Pb(OAo), added to its alcoholic solution ppts. PbCl, H, O, (dried at 100°). On heating with HCl, santalin gives off McCl (1 mol.). Gives resorcin and HOAc on fusion with potash. KMnO, gives off an odour of yanilla.

BANTONIC ACID C15H20O4 i.e. C.H. CHMe.CH(OH).CH,.CO,.H (?) (Canpizzaro, B. 18, 2748). [171°] (Hvoslef, B. 6, 1471).

S. 56 at 17°. $[a]_n = -74°$ at 20° in chloroform (Nasini, B. 13, 2210; G. 13, 164). Formed by boiling santonin with baryta-water (Cannizzaro a. Sestini, G. 3, 241; Hesse, B. 6, 1280). Colourless trimetric plates (Strüver, G. 6, 849), m. sol. hot water, v. sol. ether, v. e. sol. alcohol. Acid (235°-245°) and C₁H₂I (144° at 3 mm.) (Cannizzaro a. Amato, B. 7, 1104). Boiling HIAq and P form (a)- and (β)-metasantonin. By boiling with HOAc and heating the residue it is converted into santonide and parasantonide. Sodium-amalgam yields hydrosantonic acid. Does not react with hydroxylamine. When its chloroform solution is heated with POCl. as long as HCl comes off, and a current of damp air passed through the product, there is formed PO(C₁₃H₁₈O₃Cl)₃ [98°] (Ĉannizzaro, G. 10, 459) Salts.—NaA'. Stellate groups of needles.

-BaA'2.—AgA': white pp.

Methyl ether MeA'.

(86°). Colourless needles (Cannizzaro, G. 6, 335). Ethyl ether Eth. [95°]. [a] = -45° at 26°. Trimetric crystals.

n-Propyl ether PrA'. (220° at 3 mm.). S.G. $\frac{20}{4}$ 1·125. $[a]_{D} = -40^{\circ}$ at 20°.

Isobutyl CH, PrA'. cther [a]D = -41°. Needles (Carnelutti a. Nasini, B. 13, 2208; G. 10, 530).

Allyl ether C,H,A'. [55°]. [a], = -40°. Acetyl derivative $C_{15}H_{18}AcO_4$. [140°] Got by boiling the acid for six hours with AcCl Got by boiling the acid for six nours with acid (Sestini, G. 5, 121). Prisms (from CHOL). It is accompanied by $C_{18}H_{20}O_7$ [128°].

Chloride $C_{11}H_{10}O_8$. [155°].

Bromide $C_{11}H_{10}O_8$. [145°].

Iodide $C_{11}H_{10}O_4$. [136°].

Hydrosantonic acid $C_{11}H_{10}O_4$. [170°].

Formed by reducing santonic acid with sodiumamalgam (Cannizzaro, G. 6, 341). Colourless trimetric crystals (from ether), less sol. alcohol than santonic acid. Dextrorotatory. Oxidised by Ag,O to metasantonic acid. HOAc at 150 'forms hydrosantonide C₁₅H₂₀O₃ [156°], which is reconverted into hydrosantonic acid by alcoholic potash (Cannizzaro a. Valente, G. 8, 309). AcCl converts hydrosantonic acid into acetyl-hydrosantonide C_{1.3}H_{1.9}AcO₂ [204°], which is converted by alcoholic NH₂ at 130° into hydrosantonamide C_{1.5}H_{2.0}S.NH₂ [190°]. BzCl forms benzoylhydrosantonide C_{1.5}H_{1.9}BzO₃ [157°].

Salts.-NaA' 3aq: trimetric crystals. -KA' 2aq : monoclinic crystals.

Santoninic acid C15H20O, i.e. ÇH:CH.ÇH.CHMe.ÇO CH:CH.CH.CHMe.CH.CH(OH).CH, CO2H (Cannizzaro, B. 18, 2746). Santonous acid. $a_1 = -26^{\circ}$ in alcohol at 22°. Formed by heating santonin with KOHAq (Hesse, B. 6, 1280). Trimetric tables, al. sol. cold water, m. sol. ether, v. e. sol. alcohol. Not turned yellow by light. Acid to litmus. Not coloured red by alcoholic

potash. At 120° it splits up into water and santonin; dilute H₂SO, acts in like manner. Salts.—NaA' 3½q. S. 33 in cold water, S. (90 p.c. alcohol) 25 (Lepage, J. 1876, 618). Stellate groups of needles. Lævorotatory; aj = -18° at 22°.—BaA'₂ aq.

Metasantonic acid C₁₃H₂₃O₄. [161°]. Formed

by heating silver hydrosantonate with water. Got also by distilling santonic acid at 45 mm.

by boiling santonide with KOHAq, and by the action of Na₂CO₂Aq on isosantonin. Trimetric crystals (from ether). Lesvorotatory. Its K and Na salts are very soluble.—AgA': pp., m. sol. water.

Methyl ether MeA'. [102°]. Chloride C₁₈H₁₉O₂Cl. [139°].

Parasantonic acid C15H20O4 [173°]. [a] = -99° in chloroform (Carnelutti a. Nasini G. 10, 534). Formed by boiling parasantonide with NaOHAq or HClAq. Trimetric crystals, m. sol. water and ether. Converted by AcCl, Ac₂O, or PCl, into parasantonide. Boiling HIAq and P form (a)- and (β)- metasantonin. The parasantonates are mostly v. sol. water.—BaA'2: slender needles (from water).

Methyl ether Me₂A'. [184°]. [a]_p = -109°

in chloroform at 27°.

Ethyl ether Eth'. [173°]. $[\alpha]_D = -100^\circ$ in chloroform at 20°.

n-Propyl ether PrA'. [113°]. [a] = -91°

at 26°. Colourless prisms.

Allyl ether C₃H₃A'. [149°]. [a]_D = -92°. Lævorotatory.

Photosantonic acid C15H22O5 i.e.

CH:CH.CH.CHMe.CO.H CH:CH.CH.CHMe.CH₂.CH(OH).CH₂.CO₂H [155°]. $[a]_p = -125^\circ$. Formed, as ethyl ether of the lactonic acid, by exposing a solution of santonin in 65 p.c. alcohol to direct sunlight (Sestini, Rep. ital. chim. pharm. 1865). Formed also by exposing an aqueous solution of sodium santonate to sunshine. Prepared by insolation of a 1 p.c. solution of santonin in diluted HOAc for one month (Cannizzaro a. Villavecchia, B. 18, 2750, 2859). Trimetric prisms (from alcohol). Gives off H₂O at 100°, forming the lactonic acid $C_{15}H_{20}O_4$, and then melts at 155°. V. sl. sol. water, v. sol. alcohol and ether. Lævorotatory

Salts. - (NH₄)₂A". Gaq. - BaA" aq: white amorphous pp.—CaH₂A"₂ 3aq: silky needles, sl. sol. cold water.—CaA" xaq.—Ag₂A": white pp.

Methyl ether of the lactonic acid. [57°]. Got by the action of sunshine on a solution of santonin in MeOH. Long prisms (from MeOH).

Ethyl ether of the (a)-lactonic acid $C_{11}H_{21}O_4$. [69°]. (305°). [a]_D = -118° in a 6 p.c. alcoholic solution at 14°. Got by exposing an alcoholic solution of santonin to sunlight (Sestini, J. 1876, 622). Formed also from Ag.C₁₈H₂₀O₅ and EtI (V.). Formed also by the action of alcohol and H₂SO₄ on photosantonic acid. Thin tables, almost insol. cold water, v. sol. alcohol and ether. Levorotatory. NaOH converts it into sodium photosantonate.

Ethyl ether of the (β)-lactonic acid C₁₁H₂₄O₄. [155°]. [a]_D = 77° in alcohol at 14°. Formed, together with the preceding, by insolation of a solution of santonin in absolute alcohol. Tables (from ether). Dextrorotatory.

Anhydrophotosantonic acid $C_{15}H_{20}O_4$ i.e. $C_{12}H_{18}(CO_2H)_2$. [133°]. [α]_D = +31°9. Obtained by saponification of its ether, which is formed by passing gaseous HCl into a solution of photosantonic acid in absolute alcohol (Villavecchia, B. 18, 2862). Crystalline solid. V. sol. alcohol and ether.—Bah": white amorphous solid, v. e. sol. water.

(180°-186°). ether Et,A": Di-ethyl $[a]_{p} = +20.4^{\circ}$. Colourless liquid.

Isophotosantonic acid $C_{15}H_{22}O_5$ i.e.

CH:CH.CH.CHMe.C(OH), CH:CH.CH.CHMe.CH.CH(OH).CH₂.CO₂H (?) [a]_p = 124° in a 3 p.c. alcoholic solution at 11°. Formed, together with photosantonic acid, by exposing a solution of santonin (1 kilo.) dissolved in HOAc (52 litres of S.G. 1.054) for several nionths to sunshine (Cannizzaro a. Fabris, B. 19, 2260). Thick trimetric crystals (from alcohol), sl. sol. water, m. sol. ether, v. sol. alcohol. Dextrorotatory. At 100° it gives an anhydride $C_{13}H_{20}O_4$. Sol. alkalis and hot Na₂CO₃Aq, forming orange-red solutions .- BaA'2 aq : white amorphous powder, v. e. sol. alcohol and water.

Acetyl derivative C₁₈H₂₁AcO₃.
[a]_D = 59°. Transparent needles. Dextro-

rotatory.

Di-acetyl derivative *C15H20Ac2O5. [c. 166°]. Crystals, v. sl. sol. alcohol and ether. Converted into C₁₈H₂₁AcO₈ by heating with absolute alcohol at 120°

Pyrophotosantonic acid C14H20O2 [94·5°]. Formed by heating photosantonic acid in a current of CO₂ or H₂ (Sestini a. Danesi, G. 12, 83). Got also by heating photosantonic acid with HI (Cannizzaro a. Fabris, B. 19, 2260). Crystals, sol. alcohol and ether. -BaA'2. Forms, on distillation, C13H20 (222°).

SANTONIDE $C_{1a}H_{18}O_{3}$. [127.5°]. [a]_D = 754° in chloroform at 20°; 666° in alcohol at 20°. S.V.S. 206. Formed by evaporating a solution of santonic acid in HOAc and heating the residue at 180° (Cannizzaro a. Valente; Carnelutti a. Nasini, G. 10, 528; 13, 149). Trimetric crystals. Dextrorotatory. M. sol. chloroform, v. sl. sol. alcohol. Not attacked by PCl. Boiling KOHAq forms metasantonic acid.

 $\begin{array}{cccc} \textbf{Parasantonide} & \textbf{C}_{15}\textbf{H}_{16}\textbf{O}_{3}. & [110^{\circ}]. & \textbf{S.G.} & ^{90}\\ \textbf{1} \cdot \textbf{202}. & [a]_{D} = 897^{\circ} \text{ at } 26^{\circ}. & \textbf{S.V.S.} & 206. & \textbf{Formed}\\ \textbf{by boiling santonic acid with HOAc, evaporating,} \end{array}$ and heating the residue at 260° (Cannizzaro, G. 8, 309; 10, 528). Trimetric crystals, v. sl. sol. alcohol, m. sol. Ac₂O. Not attacked by Ac₂O or PCl. Boiling KOHAq converts it into parasantonic acid.

Metasantonide. [138°]. $[a]_p = -223^\circ$ at 26°. S.V.S. 236. Prepared by heating santonin with conc. H_2SO_4 for some hours at 100° and $[a]_{D} = -223^{\circ}$ at ppg. by water (Cannizzaro a. Valente, Rend. Accad. Lincci, ii.; G. 10, 42). Crystals (from ether). Converted by Na₂CO₃Aq into metasartonic acid.

SANTONIN C15H18Os i.e. сн:сн.сн.снм**.**.со $CH:CH.CH.CHMe.CH.CH < CH_2 > CO$ or

ÇH₂.ÇMe.C.CH₂.ÇH.O -CO .CMe.C.CH₂.CH.CHMe CO (Cannizzaro). Mol. w. 246. [170°]. S.G. 12 1·247. [a]_p = -174° in alcohol of 90 v. p. c. (Hesse, A. 176, 125); = -172° in chloroform at 20°. S. 12 2 at 17·5°; •4 at 100°. S. (alcohol) 2·3 at 22·5°; 8 at 50°; 87 at 80°. S. (ether) 2·4 at 40°. S. (chloroform) 23 (Schlimpert, N. Br. Arch. 100, 151). Occurs in wormseed (semen contra, semen cinæ, or semen santonici), the undeveloped flower heads of Artemisia Vahliana and other species of Artemisia (Kahler, Brandes Archiv, 84, 818; 85,

216; Alms, ibid. 34, 319; 39, 190; H. Trommsdorff, A. 11, 190; Heldt, A. 68, 10, 40).

Preparation - From Artemisia maritima (Linn.) which contains 2 p.c. The seeds (5 pts.) are treated with lime (1 pt.) and water, and extracted with alcohol. The extract is freed from alcohol by evaporation and neutralised with HCl, when santonin crystallises out. In this process a lime- compound (C15H10O4)2Ca, is first formed, and atterwards decomposed by HCl, which forms santonic acid, $C_{13}H_{29}^{-}O_{4}$, whence santonin is formed by splitting off H_2O (Busch, $J.\ pr.$ [2] 35,

822).

Properties. — Flattened hexagonal prisms,
May be sublimed. which turn yellow in light. May be sublimed. Levorotatory, the specific rotation being but little affected by temperature or concentration of the solution (Hesse; Nasini, G. 13, 139). Nearly insol. cold water, v. sol. hot alcohol and Poisonous, exerting an anthelmintic ether. action, and producing temporary colour-blind-ness (Lavater, *Pharm. Viertelj.* 2, 110; Wells, *J. Ph.* [8] 15, 111; Martini, *C. R.* 47, 259; 50, 545). Reacts with hydroxylamine, forming an oxim (Cannizzaro, B. 18, 2746); santonin is best administered as oxim (Coppola, C. C. 1887, 1206, 1301). Not attacked by aqueous KMnO. Resinified by boiling conc. HClAq. KOH turns santonin crimson (especially in presence of alcohol) and forms $C_{1s}H_{1p}KO_4$. Accl has no action. Conc. H₂SO₄ containing FeCl₃ gives a violet colour (Lindo, C. N. 36, 222; Knapp, D. P. J. 268, 42).

Reactions .- 1. By treatment with 1 mol. of PCl, it gives a compound C15H1, ClO2[125° uncor.]. With 2 mols. of PCl₃ it gives a compound $C_{13}H_{13}Cl_{2}O$, [182° uncor.] (Pawlewski, B. 18, 2900). According to Klein (B. 26, 982) the compound is $C_{13}H_{13}Cl_{3}O_{2}$ —2. Reduced by HI and P to santonous acid C₁₅H₂₀O₃, -3. HNO₃ (S.G. 1·123) at 95° forms CO₂, succinic, oxalic, and acetic acids, and HCy (Wagner, B. 20, 1662).—4. Boiling baryta-water forms santonic acid.—5. Hot KOHAq forms santoniniò acid.—6. Potash-fusion forms formic and propionic acids (Banfi a. Chiozza, A. 91, 112).-7. An alcoholic solution exposed for some months to sunlight forms the ethyl ether of the lactonic acid of photosantonic acid (v. supra).-8. A solution in HOAc exposed to sunshine yields photo- and isophoto- santonic acids.—9. Forms santonol on distillation with zinc-dust. Distillation over red-hot zinc-dust gives di-methyl-naphthalene (Cannizzaro, G. 12, 415).—10. Cold conc. HClAq forms an isomeride C₁₃H₁₈O₂₁ [260°], sl. sol. hot alcohol, insol. water (Andreocci, B. 26, 1373). [a]_D = +112°. This body is not acted upon by hydroxylamine or phenyl-hydrazine, but yields an acetyl derivative C₁₃H₁₇AcO₃ [156°]. Like santonin it is insol. Na₂CO₃Aq, but sol. NaOHAq. It is reduced by zinc-dust and HOAc to $C_{13}H_{20}O_{3}$ [175°] [a]_D = -53.3° an acid isomeric with santonous acid, which when fused with potash yields propionic acid and di-methyl-(β)naphthol.-11. Br in glacial acetic acid forms C₁₅H₁₆O₂.HOAc,Br₂. Crystals (from alcohol), decomposing above 60°. On boiling with alcohol and aniline it yields bromo-santonin C15H17BrO3 [151°]. On boiling with KOHAq the acetate bromide yields santonin (Klein, B. 25, 3317).

Oxim C₁₈H₁₈O₂(NOH) aq. [209°] (Klein, B.

26, 411; cf. Gucci, G. 19, 867). Needles (from dilute alcohol). Ac.O yields Cl.H.,O.(NOAO) [166°] or [170°] (K.); [203°] (G.). The oxim prepared by alkaline hydroxylamine gives with HCl and FeCl, a violet-red colour [syn-oximic acid1.

Bensyl ether of the oxim [152°]. HIAq

forms benzyl iodide. Phenyl-hydrazide C15H18O2(N2HPh). [220°]. Pale-yellow needles (from alcohol), not decomposed by cold acids (Cristaldi, G. 17, 526; Grassi, C. C. 1887, 1163).

Chlorosantonin C₁₈H₁,ClO₃. Formed from santonin and chlorine-water (Heldt, A. 63, 34; Formed from Sestini, Bl. 5, 202). Crystalline. Turns yellow in light.

Di-chloro-santonin C13H16Cl2O3. Formed by passing Cl for a long time through water containing santonin in suspension (Sestini). Groups of small plates (from alcohol). Coloured orangered by alcoholic potash.

Tri-chloro-santonin C15H15Cl3O3. [213°]. Monoclinic prisms, not coloured by sunshine, m. sol. alcohol and ether.

(a). Metasantonin C₁₁H₁₁O₃, [161°]. (239°). S.V.S. 205. [a]_D=124° in chloroform at 20°. Formed, together with (β) metasantonin, by boiling santonic acid or parasantonide with HIAq and P (Cannizzaro, G. 4, 446, 452; 8, 318; 10, 401). Trimetric hemihedral plates (from ether). Dextrorotatory. Not affected by light. Yields C₁₃H₁,BrO₃ [212°] and C₁₃H₁₈Br₂O₃ [184°].

(β)-Metasantonin $C_{13}H_{18}O_3$. [136°]. S.V.S. 211. [α]_D = 124°. Formed as above. Monoclinic crystals. Yields $C_{13}H_{17}BrO_3$ [114°] and C₁₃H₁₆Br₂O₃ [186°].

Photosantonin. A name for the ethyl ether of the (a)-lactonic acid of photosantonic acid (v. supra).

SANTONOUS ACID $C_{13}H_{20}O_{3}$ i.e. $C_{10}H_{3}Me_{2}(OH).C_{2}H_{4}.CO_{2}H$? [179°]. [a]_D = 74° in alcohol at 20°. Formed by boiling santonin with HIAq and P (Cannizzaro a. Carnelutti, B. 12, 1574; G. 12, 393; 13, 385). White needles, v. e. sol. alcohol and ether, sl. sol. cold water, sol. Na CO Aq. May be distilled in vacuo. Distilled over powdered zinc in a current of hydrogen it yields di-methyl-naphthalene, dimethyl-naphthol, propylene, and a little xylene. On heating with Ba(OH)₂ above 360° it yields CO₂, CH₄, and di-methyl-naphthol C₁₂H₁₁OH [135°], which yields $C_{12}H_{11}OMe$ [68°]. Converted by heat into the anhydride of isosantonous acid, and, finally, into di-methyl-naphthol dihydride and propionic acid.

Salts .- NaA'. Needles, ppd. by adding ether to its alcoholic solution. V. sol. water .-

BaA'...—"AgA': white pp., quickly turning black.

Mathyl ether MeA'. [32°].

Ethyl ether EtA'. [117°]. [a]_b = 78° in chloroform or 67° in HOAc at 20°. White crystals, sol. alcohol and ether. Dextrorotatory. Converted by BzCl into C, H18BzEtO [78°]. Na added to its ethereal solution ppts. C₁₅H₁₈NaEtO₃, whence EtI produces C₁₅H₁₈Et₂O₃ [32°], which on saponification yields ethyl-santonous acid $O_{15}H_{19}EtO_3$ [116°], $[a]_b = +76^\circ$ in alcohol. Isosantonous acid $O_{15}H_{29}O_3$. [155°]. Formed by heating santonous acid, dissolving the re-

sulting anhydride in NaOHAq, and ppg. with

HClAq. Got also by heating santonous acid (1 pt.) with Ba(OH), (3 pts.) in a bath of molten lead (Cannizzaro a. Carnelutti, B. 12, 1574; G. 12, 400). Small plates, sl. sol. water, sol. alcohol and ether. Inactive to light. May be distilled in vacuo.

Ethyl ether EtA'. [125°]. Crystalline. BzCl at 100° yields C₁₅H₁₈BzEtO₃ [91°]. Na added to its ethereal solutions gives no pp., but on adding alcohol C₁₅H₁₅NaEtO₃ is thrown down as an amorphous powder, readily decomposed by water. The Na derivative is converted by EtI into C₁₅H₁₈Et₂O₃ [54°], whence alcoholic potash produces C₁₅H₁₉EtO₃ [143°], v. sol. alcohol and ether.

SAPONIFICATION. The conversion of the natural fats into soap (and glycerin) by boiling with alkalis. In a more general sense it is used to denote the resolution of compound ethers into acids and alcohols. In the widest sense it is used to denote the production of an acid from a neutral substance by hydrolysis.

SAPONIN $C_{32}H_{34}O_{19}$ (Rochleder, Z. [2] 3, 632); $C_{19}H_{39}O_{19}$ (Stütz, A. 218, 231); $C_{32}H_{32}O_{17}$ (Hesse, A. 261, 373). Struthiin. Githagin. Polygalin. Polygalic acid. Senegin. A glucoside occurring in the common soapwort (Saponaria officinalis) (Schrade, N. Journ. d. Chem. 8, 548), ogicinaus) (Schrade, N. Journ. d. Chem. 8, 548), in the Oriental soapwort (Gypsophila Struthium) (Bley, A. 4, 283; Bussy, A. 7, 168), in quillaja bark (O. Henry a. Boutron-Charland, J. Ph. 4, 249), in the cornockle (Agrostenna Githago) (Malapert, J. Ph. [3] 10, 339; Scharling, A. 74, 351; Christophsohn, Ar. Ph. [3] 6, 432, 461), in the root of Polygala Scriega (Bolley, A. 90, 211; 117), and in many other share. 91, 117), and in many other plants. White amorphous powder, insol. alcohol and ether, v. e. sol, water. The dilute aqueous solution froths like soap when shaken; the lather is prevented by addition of alcohol. Impure saponin produces sneezing. Saponin begins to turn black at 145° (Blyth), but does not melt or sublime when heated. Baryta forms amorphous $(O_{12}H_{20}O_{10})_2$ Ba $(OH)_2$. A solution of saponin is ppd. by lead acetate. Decomposed by boilting dilute acids into sapogenin and sugar $C_2H_{11}O_2$ $(I_{12}D=52^{\circ}$ at 25°) (Rochleder a. Schwarz, Sitz. W. 11, 339; Overbeck, N. Br. Arch. 77, 135; Schiaparelli; cf. Crawford, Pharm. Viertelj. 6, 361; Flückiger, Ph. [3] 8, 488).

Acetyl derivatives C₁₉H₂₂Ac₁O₁₀. [161°].—
C₁₉H₂₂Ac₂O₁₀. [99°].—C₁₂H₂₂Ac₂O₁₁. [137°].—
C₁₉H₂₂Ac₂O₁₂. [84°] (Stütz).—C²₂H₁₅Ac₂O₁₇.—
C₂₂H₁₄Ac₂O₁₇.—C₂₂H₁₆Ac₁₂O₁₇.—C₃₂H₄₆Ac₁₅O₂₀

Butyryl derivative $C_{19}H_{20}(C_1H_1O)_0O_{10}$ (Stütz); $C_{22}H_{43}(C_1H_1O)_1O_{17}$ (Hesse). [68°-72°]. According to Schiaparelli (G. 13, 422; Ph. [3] 14, 801), saponin obtained from soapwort has at 20°, yields amorphous $Ba_2H_2(C_{32}H_{32}O_{18})_3$, and is split up by boiling dilute H_2SO_4 into glucose and saponetin C40H86O13.

SAPOGENIN C₁₁H₂₂O₂. Formed by hydrolysis of saponin. Concentric groups of needles from alcohol), sol. ether, insol. water. From solution in dilute potash it is ppd. by cono. KOHAq as flocoulent potassium-saponin. Potash-fusion gives acetic and butyric acids and a crystalline compound [128°].

Oxysapogenin C, H22O, is obtained by the action of HClAq on a glucoside present in the alcoholic extract of Herniaria (Barth a. Herzig,

M. 10, 172).

SAPPANIN C₁₂H₁₀O₄. Formed, together with resorcin and a little pyrocatechin, by fusing extract of sapan wood with NaOH (Schreder, B. 5, 572). Crystallises from water in plates (containing 2aq), nearly insol. cold water, v. sol. alcohol and ether, insol. CHCl.. Neutral in reaction. FeCl, colours its aqueous solution red. NaOCl gives a grass-green colour. May be distilled. Pb(OAc), gives a yellowish pp. Reduces hot Fehling's solution and ammoniacal AgNO,. HNO, forms tri-nitro-resorcin (styphnic acid). Yields diphenyl on distillation with red-hot zincdust. AcCl gives $C_{12}H_cAo_4O_4$, crystallising from alcohol in prisms. Br and HOAc give $C_{12}H_bBr_bO_4$, crystallising from dilute alcohol in needles.

SAPRINE $C_3H_{16}N_{2}$. [From $\sigma\alpha\pi\rho\delta s$, putrid.] An alkaloid in putrefying flesh (Gautier, Bl. [2] 48, 13), v. Ptomaïnes.

SARCINE v. HYPOXANTHINE. SARCOLACTIC ACID v. LACTIC ACID. SARCOLEMMA v. MUSCLE.

SARCOSINE v. METHYL-AMIDO-ACETIC ACID. SARCOSINIC ACID C,H,NO2. [195°]. Occurs in a variety of shellac known as Sonora gum (Hertz, J. 1876, 912). White silky scales, v. sol. water, insol. alcohol and ether. Cannot

be sublimed. Converted by nitrous acid into lactic acid. Forms salts with acids and bases. It is a weaker acid than alanine.

SARCOSINURIC ACID v. vol. iii. p. 260. SARSAPARILLA v. PARILLIN.

SASSAFRAS OIL. Obtained by steam-distillation from the bark and wood of the root of Laurus sassafras of North America. Contains saffrole (q. v.) and a terpene C₁₀H₁₆ (156°). S.G. 9 ⋅835.

SATURATION, CAPACITY OF. When a base is added to an acid, a point is reached whereat the properties of the base are neutralised by those of the acid, and the properties of the acid are neutralised by those of the base. The compound that is produced—a salt—has neither the properties of the acid nor the properties of the base. The capacity of saturation of an acid is measured by the quantity of a base, taken in formula-weights, which must be added to the quantity of the acid expressed by its formula in order to form a normal salt. The capacity of saturation of a base is measured by the number of formula-weights of an acid which must be added to a formula-weight of the base in order to form a normal salt. The study of the capacities of saturation of acids and bases leads to the classification of acids as monobasic, dibasic, tribasic, &c., and of bases as mono-acid, di-acid, tri-acid, &c. (v. Acids, vol. i. p. 49; and Acids, Basicity of, vol. i. p. 51). The notion of equivalency also arises from the study of the capacities of saturation of acids and bases (v. vol. ii. p. 446).

When chlorine combines with potassium, one atom of the metal is saturated by one atom of the halogen; but three atoms of chlorine are required to saturate a single atom of bismuth or antimony. The notion of a definite capacity of saturation has been extended from the acids and

bases to the atoms of the elements. The development of this conception leads to the hypotheses of valency and atom-linking (3. CLASSIFICATION, vol. ii. pp. 213-215; Equivalency, vol. ii. p. 446; and FORMULE, vol. ii. p. 572). M. M. P. M.

SAVINE OIL. Oleum Sabinæ. The essential oil from Juniperus Sabina contains a sesquiterpene C₁₈H₂₄, which has a crystalline hydrochloride C₁₈H₂₄2HCl [118°] (Wallach, A. 238, 82).

SAVORY. Essence of savory (from Satureja montana) contains 40 p.c. carvacrol (232°) and two terpenes (174°) and (183°) (Haller, C. R. 94. 132). The oil from Satureja hortensis contains 20 p.c. cymene, 50 p.c. carvacrol, a terpene (179°). S.G. 15 .855, and a very small quantity of a phenol which differs from carvacrol in not being extracted by ether from its dilute alkaline solution, and yields a phosphate [69°] (Jahns, B. 15, 816).

SCAMMONY. A purgative gum-resin composed of the dried milky juice of Convolvulus scammonia and of other species of Convolvulus. It is purified by boiling with alcohol, neutralising the alkaline filtrate by dilute H2SO4, filtering, and evaporating (Perret, Bl. [2] 28, 522).

contains jalapin (q. v.).

SCANDIUM. Sc. At. w. 44. Mol. w. un-The oxide of a new element was isolated in 1879 by Nilson (B. 12, 554) from euxenite and gadolinite; the same oxide was obtained, about the same time, by Cleve, also from Scandinavian minerals (Bl. [2] 31, 486 [1879]). The name scandium was given to the metal of the new earth by Nilson to denote the locality of the minerals from which the oxide had been obtained. In his first memoir Nilson represented scandia as ScO_n and determined the at. w. of Sc to be c. 170; in his second memoir (B. 13, 1439) he adopted Cleve's correction, and formulated the oxide as Sc₂O₂, and gave the at. w. of the metal as 44. The element scandium has not yet been isolated.

Occurrence. — Sc₂O₃ is found, along with yttria, ytterbia, &c., in very small quantities in a few rare minerals-gadolinite, keilhauite, yttrotitanite, and euxenite. From 4 kilos. adolinite Cleve obtained 8 g. Sc₂O₃, and 1.2 g. Sc.O. from 3 kilos. yttrotitanite.

Preparation.—The metal has not been

isolated (v. Scandium oxide, infra).

Detection .- So salts give a very brilliant emission-spectrum, rich in rays. (B. 12, 555) gives the wave-lengths of the most characteristic lines as 6304, 6079, 6037 in the orange; 5526 in the yellow (very marked); 5031 in the green; 4415, 4400, 4374, 4325, 4326, 4314, and 4249 in the indigo (v. also B. A. 1884, 440).

Chemical relations .- Ten years before Nilson discovered So, Mendeléeff asserted that an element would be found in the group of which boron is the first member, and that this element would resemble B and Al. To this unknown element Mendeléeff gave the name ekaboron, and he stated the properties of the element and its compounds in detail. The properties of the compounds of scandium correspond with great closeness with those of Mendeléeff's ekaboron (p. tables in vol. i. p. 352; cf. vol. iii. p. 815).
The properties of ekaboron were arrived at by

comparing the properties of pairs of elements related to one another, as regards positions in the periodic arrangement, similarly to ekaboron and its atom-analogues. The relations expressed by the following scheme were specially studied by Mendeléeff:

Eb:Al = Ca:Mg = Ti:Si = V:P = Cr:S: Eb:B = Ca:Be = Ti:O = V:N = Cr:O = Mn:F.

These statements mean, the relations between the properties of Eb and Al are similar to the relations between the properties of Ca and Mg, &c. For a brief working out of similar relations in the case of eka-aluminium v. GALLIUM (vol. ii. pp. 598-9). Scandium is the second even-series member of Group III. It follows B. and is followed by Y, La, and Yb in the even series of this group. So resembles Al in many respects, but the difference between these elements is shown, among other ways, in the fact that the double sulphate of Sc and K-Sc2(SO4)3.8K2SO4-is not an alum (v. EARTHS, METALS OF THE ; vol. ii. p. 424).

Scandium, chloride of, ScCl_s(?). hygroscopic needles separate on evaporating a solution of the oxide in HClAq to a syrup; HCl is given off on heating, and an oxychloride remains as a white powder (Cleve, l.c.).

Scandium, oxide of, Sc.O. (Scandia.) Prepared by ppg. solutions of Sc salts by NH,Aq, washing the white, gelatinous, very bulky pp. of hydrated oxide, drying at 100°, and then heating strongly; also obtained by heating to redness Sc nitrate, sulphate, or oxalate. A white, light powder, resembling MgO; sol. in hot cono. H₂SO₄Aq or HNO₂Aq. S.G. 3·864 (Nilson a. Pettersson, B. 13, 1461). S.H. from 0° to 100° = 153 (N. a. P.).

Scandia is best obtained from euxenite. The finely-powdered mineral is fused with KHSO, the product is dissolved in cold water, and ppd. by NH₃Aq, the pp. is dissolved in HNO₃Aq, the solution is boiled for some time, filtered from any pp. which forms, and ppd. by oxalic acid; the ppd. oxalates are dried, heated strongly, washed with hot water to remove the K2CO3, dissolved in HNO3Aq, and the solution is evaporated to dryness and the residue heated till it melts; the fused nitrates are treated with water, when a pp. forms, consisting of oxide of Th with small quantities of oxides of Ce, U, and Fe; the filtered solution is evaporated to dryness, the nitrates are partly decomposed by heating, and then treated with water; the residue, which contains a basic nitrate of Sc, is evaporated with HNO, Aq, and the residue is again heated for some time, treated with water, and the insoluble evaporated with HNO, Aq, and so on. This process separates didymia, yttria, and terbia, the nitrates of which earths are not so readily decomposed by heat to basic nitrates as Sc nitrate is. By repeating this process 68 times Nilson (B. 13, 1442) obtained a nitrate solution which showed no absorption bands, and contained only salts of Sc and Yb. The solution of Se and Yb nitrates is evaporated with conc. H2SO4, saturated K2SO4Aq is added, the salt Sc₂(SO₄)₃.3K₂SO₄ which separates (Yb sulphate remains in solution) is dissolved in water, and ppd. by NH3Aq; the ppd. Sc2O3.xH2O is washed and dissolved in HNO, Aq, and Sc oxalate is ppd. by oxalic acid; the ppd. oxalate is washed,

A white salt, Barium selenate BaSeO₄. A white salt, obtained by decomposing an alkali selenate by BaCl2Aq, filtering, and washing. Insol. water and HNO, Aq; boiled with HClAq gives BaSeO,, which dissolves. S.G. 4.67 at 22° (Schafarik, J. 1863. 15; Michel, C. R. 106, 878).

Beryllium selenate BeSeO, 4aq. Rhombic

crystals (Topsöe, W. A. B. 66, 5).

Cadmium selenate CdSeO, 2aq. By dissolving CdO.xH2O in H2SeO4Aq, and crystallising; lustrous, rhombic plates; S.G. 3.632 (von Hauer, J. pr. 80, 214). Forms double salts with NH, and K (Topsöe, l.c.; von H., l.c.; von Gerichten, B. 6, 162).

Calcium selenate CaSeO₄, 2aq. Resembles CaSO₄; obtained by ppg. K₂SeO₄Aq by Ca(NO₂)Aq, dissolving in cold water, and ppg. by heating (von Hauer, l.c.). Also formed by fusing CaCl₂ with K₂SeO₄ and NaCl (Michel, C. R. 106, 878).

Chromium selenate. Not isolated. Double salts, which are alums, are known, of the composition Cr₂(SeO₄)₃.M₂SeO₄. 24aq (Wohlwill, A. 114, 162; Fabre, C. R. 105, 114; Pettersson, B. 6, 1466). Alums are also known of the com-

Cobalt selenate CoSeO, 7aq. Hydrated salts have been obtained with 6aq and 5aq (v. Mischerlich, P. 11, 327; Topsöe, W. A. B. 66, 5). Forms double salts with K2SeO4, and (NH4)2SeO4

(T., l.c.; von G., l.c.; von H., l.c.).

Copper selenate CuSeO, 5aq. Blue, transparent, lustrous crystals, isomorphous with the sulphate. By dissolving CuO2H2 in H2SeO4Aq (Mitscherlich, P. 11, 330). Forms double salts with selenates of NH, K (Topsöc, l.c.; von G., l.c.); also with Mg and Zn selenates (Wohlwill, l.c.).

Didymium selenate Di₂(SeO₄)₃ (Cleve, Bl. [2] 43, 362). Also with 5aq (C., l.c.); and with 6aq (Frerichs a. Smith, A. 191, 350). Forms double salts with NH, and K selenates (C., l.c.).

Iron selenate FeSeO. 7aq (Ferrous selenate). By evaporating, in H, a solution of Fe, or FeCO₃, in H₂SeO₄Aq; resembles FeSO₄. 7aq (Topsöe, *l.c.*). Obtained by Wohlwill (A. 114, 189) with 5aq. Forms a double salt with K_2SeO_4 (von G., l.c.).

Lanthanum selenate La₂(SeO₄)₃.12aq (F. a. B., l.c.).

Lead selenate PbSeO4. A white powder; by ppg. K₂SeO₄Aq by Pb(NO₂)₂Aq (Schafarik, J. 1863. 1*5*).

Magnesium selenate MgSeO, 6aq. White, monoclinic crystals; isomorphous with the sulphate; S.G. 1.928 (Topsöe, î.c.). Forms double salts with NH, and K selenates (T., l.c.; von G., l.c.).

Nickel selenate NiSeO, aq. By evaporating solution of NiCO, in H_2 SeO, Aq (Mitscherlich, l.c.; Wohlwill, l.c.). Forms double salts with selenates of NH, and K (von G., l.c.; von Hauer, J. pr. 80, 214).

Mercury selenates. 1. Mercuric selenate, HgSeO. By digesting HgO with H.SeO.Aq, or by adding excess of H.SeO.Aq to mercuric acetate, and evaporating; a yellowish-white solid. Decomposed by water, giving a basic salt HgSeO₄. 2HgO (Cameron a. Davy, Trans. I. 28, 187). 2. Mercurous selenate, Hg₂SeO₄; by ppg. HgNO, Aq by K, SeO, Aq (C. a. D., 1c.). With

NH.Aq forms (NHg.)2SeO. 2aq.

Potassium selenates. The normal salt. K2SeO4, is obtained by fusing Se, K2SeO2, or native lead selenide, with KNO, dissolving in hot water, allowing to cool partly, pouring off from excess of KNO, which separates, and colfrom excess of KNO, which separates, and collecting the crystals which separate from the mother-liquor. Equally sol. hot and cold water (Mitscherlich, P. 9, 623; 11, 327). Closely resembles K₂SO₄. The acid sall KHSeO₄ is obtained like, and closely resembles, KHSO₄ (M., l.c.). K₂SeO₄ forms many double salls; with MSO₄, M= Cd, Co, Cu, Fe, Mn, Hg, and Zn (von Gerichten, B. 6, 162); with Al₂(SeO₄); and Cr (SeO₄) the compounds being alums. and Cr₂(SeO₄)₃, the compounds being alums (von G., l.c.; Pettersson, B. 9,1559, 1676; Schröder, J. pr. [2] 22, 432; Fabre, C. R. 105, 114).

Silver selenate Ag, SeO, Similar to, and isomorphous with, Ag, SO, (Mitscherlich, Lc.).

Sodium selenate Na, SeO, Prepared like

K.ScO.; separates with 10aq when crystallised below 40° (M., l.c.).

Strontium selenate SrSeO,. Obtained by fusing SrCl₂ with NaCl and an alkali selenate: S.G. 4.23. Exactly resembles celestine in crystallographic and optical properties (Michel, C.R. 106, 878).

Thallium selenate Tl₂SeO₄. By dissolving Tl.CO, in H.SeO,Aq, and evaporating. Forms white, prismatic needles, isomorphous with K₂ScO₄; sl. sol. cold water; insol. alcohol or ether (Kuhlmann, Bl. 1864 [1] 330; Oettinger, Zeit. Chem. Pharm. 1864. 440). Forms double salts, which are alums, with Al. (SeO₄)₃ and with

Cr₂(SeO₄)₂ (Fabre, C. R. 105, 114). Zinc selenate ZnSeO₄, 7aq. Various hydrates are known (v. Mitscherlich, P. 11, 326; 12, 144; Topsöe, l.c.). Forms a double salt with Tl₂SeO₄ (Werther, Bl. 1865 [1] 60); also with K₂SO₄

(von Gerichten, B. 6, 162).

THIOSELENATES M12SeSO3. (Selenothiosulphates. Selenosulphates.) Solutions of the normal alkali sulphites dissolve Se, forming these salts. The acid has not been isolated. The salts correspond with the thiosulphates, S

being replaced by Se.

Potassium thioselenate K2SeSO3 aq. Formed by mixing K₂SeAq with SO₂Aq (Cloez, Bl. 3, 112; [2] 4, 419). Better prepared by digesting K2SO3Aq with excess of Se, filtering the cold liquid from Se, and concentrating without heat; crystals of K2SO4 mixed with K2SeS2O6 (v. infra) separate, and K2SeSO3 crystallises from the mother-liquor (Cloëz, l.c.; Rathke, J. pr. 95, 1). White, lustrous, six-sided tablets; deliquescent in moist air; effloresce over H₂SO₄. Decomposed rather easily by heat, giving K polyselenides; cold water separates Se, and forms K₂SeS₂O_g (v. infra); acids evolve SO₂ and separate Se; BaCl₂Aq ppts. BaSO₃ and Se from an aqueous solution of the salt; an ammoniacal solution of Ag,O forms Ag,Se and K,SO,Aq on heating

DITHIO - TRISELENATES MI SeS.O. (Selenotrithionates.) These salts may be regarded as derived from trithionates (M1,S3O,) by replacing S by Se; as the salts M2S2O, are called trithionates, so the salts M'2Se2O, might be called triselenates if they were isolated, and the salts MI_SSeO, may be called dithio-triselenates.

Potassium dithio-triselenate K_SeS_O_s. This salt is formed in the preparation of potassium thioselenate (v. supra); if KHSO_s is present in the K_2SO_s used considerable quantities of K_2SO_SO_s are produced (Rathke, J. pr. 95, 1). It is also obtained by mixing K_2SeSO_s with excess of K_2SO_s and conc. H_2SeO_3Aq. Forms lustrous, greenish-yellow, monoclinic prisms, isomorphous with K_2S_2O_s; stable in air; sol. water without change (Rathke, J. pr. [2] 1, 33). Acids evolve SO_2 and ppt. Se, on warming; ammoniacal solution of Ag_2O ppts. Ag_Se, forming also K_SO_4Aq and H_2SO_4Aq.

Dithio-triselenic acid, H.SeS₂O₆, is said to be present in the solution obtained by the action of excess of SO₂ on SeO₂Aq (Schulze, *J. pr.* [2] 32, 390). M. M. P. M.

SELENHYDRIC ACID H₂Se; v. Hydrogen SELENDE, vol. ii. p. 724.

SELENIC ACID H,SeO₄. Mol. w. not determined. S.G. 2.9508 at 15°; S.G. of superfused acid, 2.6083 at 15° (Cameron a. Macallan, Pr. 46, 18). Melts at 58°; the molten acid may be cooled below 5° without solidifying (C. a. M., l.c.). H.F. [SeO,3,Aq]=76,660; [ScO²Aq,O]=20,500 (Th. 2, 279).

Formation.—1. By passing Cl into H₂SeO₂Aq, and evaporating.—2. By fusing Se or SeO₂ with KNO₂, ppg. BaSeO₄ from solution of the fused mass, decomposing by K₂CO₃, filtering from BaCO₂, neutralising any K₂CO₃ present by HNO₃Aq, ppg. PbSeO₄, and decomposing this salt by H₂S (von Gerichten, A. 168, 214).—3. By heating Se with HNO₃Aq, boiling with HClAq (to reduce any H₂SeO₄ to H₂SeO₃), ppg. traces of H₂SO₄ by adding a little Ba(NO₃),Aq, filtering from BaSO₄, neutralising by Na₂CO₃, evaporating to dryness, heating to dull redness, boiling with HNO₃Aq, ppg. PbSeO₄ by addition of Pb(NO₃),Aq, and decomposing by H₂S (Fabian, A. Suppl. 1, 241).—4. By fusing SeO₂ with excess of KNO₃, boiling with HNO₃Aq, ppg. CaSeO₄ by addition of Ca(NO₃),Aq, decomposing the CaSeO₄ by addition of Ca(NO₃),Aq, decomposing the CaSeO₄ by addition of Ca(NO₃), Aq, decomposing the CaSeO₄ by addition of pure SeO₂ in water, digesting the ppd. Ag₂SeO₃ with water and a slight excess of Br, filtering from AgBr, and evaporating the filtrate, which contains H₂SeO₄ (Thomeen, B. 2, 598).—6. By oxidising H₂SeO₃Aq by K₂CrO₂Aq, PbO₂, or MnO₂ (Wohlwill, A. 114, 169, 176).

Preparation. - SeO2 is heated till sublimation begins; it is then dissolved in water, and BaOAq is added so long as a few drops, when filtered, continue to give a pp. with BaOAq; the filtered liquid is now free from H2SO, and H2SeO,, it is evaporated to dryness, and the residual SeO, is heated till it sublimes (Thomsen, B. 2, 598). The pure SeO₂ thus obtained is dissolved in water, excess of AgNO, Aq is added, the ppd. Ag₂SeO₃ is washed with water and shaken with water and Br-at first Br is added, and then BrAq till the liquid shows a faint orange colour; the liquid filtered from AgBr contains only H2SeO, it is evaporated and treated as described hereafter (T., l.c.). Another method consists in neutralising the solution of pure SeO, by K2CO, evaporating to dryness, fusing with a

little KNO₃ for some time, dissolving in water, slightly acidifying with HNO₃Aq, boiling for some time to decompose any nitrite present, allowing to cool, adding Pb(NO₃)₂Aq, washing the ppd. PbSeO₄, suspending this salt in water, and decomposing it by a rapid stream of H₂S; the filtered liquid is then evaporated (von Gerichten, A. 168, 214).

The solution of H. SeO, is concentrated by evaporation in an open dish on a water-bath so long as water passes off; an acid containing c. 83-84 p.c. H2SeO4 is thus obtained; this acid is placed in a small flask connected with a short wide tube containing solid KOII, which is connected with a large U tube also containing solid KOH; the U tube is connected with the receiver of an airpump, or with a vessel in connection with a good water-pump. The air is pumped out of the apparatus, and when a good vacuum is obtained the small flask is heated to 100° so long as acid distils over (this is known by the KOH effervescing slightly, as ordinary KOH contains K2CO3); the temperature is then raised to 180° (an oilbath being used to heat the flask), and heating at this temperature is continued so long as acid distils off; as soon as the potash ceases to be acted on the heating is stopped and the flask is at once cooled; a very good vacuum must be maintained throughout the process. H, SeO. crystallises as the flask is cooled. A small quantity of H2SeO4Aq should be evaporated thus at a time (Cameron a. Macallan, Pr. 46, 13).

Properties.—A white crystalline solid, crystallising in long hexagonal prisms, and melting at 58° to a colourless oily liquid. The liquid acid may be cooled below 5° without solidifying if it is not stirred; a crystal of H₂SeO₄ dropped into the liquid causes it to solidify at once, the temperature rising to 58°. The liquid acid is specifically lighter than the solid (v. data at beginning of article) (C. a. M., Le.). H₂SeO₄ is very hygroscopic; it mixes with water, with production of heat.

The following table is taken from Cameron and Macallan (l.c.):—

mu mucu	12022 (0.00)		
P.c. H ₂ SeO ₄	S.G. H.SeO.Aq at 15°	P.c. H ₂ SeO ₄	S.G. H ₂ SeO ₄ Aq at 15°
99.73	2.6083	90	2.3848
99.5	2.6051	89	2.3568
99.0	2.5975	88	2.3291
98.5	2.5863	87	2.8061
98.0	2.5767	86	2.2795
97.5	2 ·5695	85	2.2558
97	2.5601	84	2.2258
. 96	2.5388	83	2.1946
95	2.5163	82	2·1757
94	2.4925	81	2.1479
93	2.4596	80	2.1216
92	2.4322	79	2.0922
91	2.4081	73.5	1.9675
-			

Reactions.—1. With water much heat is produced, and hydrates are probably formed (v. infra, Hydrates of selenic acid). H.SeO. acts as a dehydrating agent, similarly to H.SO. (C. a. M., l.c.).—2. Heated in vacuo begins to decompose into O, H.O. and SeO. at c. 200°; the water formed dilutes the remaining acid, which then distils over. When dilute H.SeO.Aq is heated at ordinary pressure water distils off till temperature rises to 205°, when the acid has the

composition H₂SeO₄.H₂O; traces of H₂SeO₄ then distil over: at 260° white fumes of H,SeO, come off. When H2SeO, is strongly heated at the ordinary pressure, some of it is decomposed to SeO₂, O, and H₂O; the remaining acid is diluted by the water till a dilute acid distils off (C. a. M., l.c.).—3. Dilute H₂SeO₄Aq dissolves many metals, with evolution of H; warm conc. acid dissolves copper and gold, with partial reduction to H.SeO3.-4. Digestion with hydrochloric acid reduces H, SeO, Aq to H, SeO, Aq, with evolution of Cl; the acid is not reduced by sulphur dioxide nor by sulphuretted hydrogen .-5. Sulphur reacts with liquid H.SeO, at c. 60°, forming a deep-blue, very unstable substance (? SeSO₂) which decomposes to SO₂ and H₂SeO₃ (C. a. M., l.c.). -6. Selenion dissolves in H2SeO4, giving a green unstable substance—? Se₂O₃ (C. a. M., l.c.).—7. Tellurium dissolves in H₂SeO₄, forming a reddish body, probably TeSeO₃ (C. a. M.).—8. Heated with phosphoric anhydride, SeO2 is given off; but at a lower temperature crystals were obtained which C. a. M. think were SeO₃.

Hydrates of selenic acid. The monohydrate H₂SeO₄H₄O was obtained by C. a. M. (Lc.) by diluting H₂SeO₄ to 88.96 p.c., freezing at -23°, melting and re-crystallising by freezing several times. This hydrate forms long needles, melting at 25°, and remaining liquid even 50° below its melting-point; Pickering (priv. comm.) gives melting-point as 16·6°. S.G. of solid hydrate = 2·3257 at 15°; S.G. of superfused hydrate = 2·3557 at 15°. C. a. M. did not succeed in obtaining other hydrates as solids. For salts of H₂SeO₄ v. Selenates, p. 433.

M. M. P. M. **SELENIDES.** Se combines with most metals when heated with them. Se also combines with many non-metals, e.g. with B, Br, Cl, F, H, I, O, P, and S. Many metallic selenides are formed by heating the elements together (Uelsmann, A. 116, 122; Schneider, A. 97, 192; Little, A. 112, 211); also by the interaction of Se and metallic salts (Schneider, P. 127, 642; Potilitzin, B. 12, 697); sometimes by the interaction of Se and metallic sulphides at high temperatures (P., l.c.). For thermal data regarding the formation of many metallic selenides v. Fabre (C. R. 102, 1469; 103, 269, 345). Selenides of the alkali metals are sol. water; they are formed by saturating the hydroxides in water by H₂Se (Fabre, C. R. 102, 613), by reducing the selenites by C (Wöhler a. Dean, A. 97, 1), by reducing selenates by H at 200° (Fabre. C. R. 102, 1469), and by heating the elements together (Uelsmann, A. 116, 122). The selenides of metals other than the alkali metals are insol. M. M. P. M.

SELENION. Se. (Selenium.) At. w. 78·8. Mol. w. 157·6 (v. infra). M.P. 217° for crystalline variety (Hittorf, P. 84, 214; Draper a. Moss, C. R. 83, 1; v. Action of heat on selenion). Boils at 676°-683° (Carnelley a. Williams, C. J. 35, 563). S.G. c. 4·7 crystalline; c. 4·3 amorphous (for more details v. description of varieties of Se, infra). V.D. 111 at 860°, 92 at 1040°, 82 at 1420° (Deville a. Troost, C. R. 49, 239; 56, 891). S.H. crystalline - 20° to +7° = 0732, crystalline 20° to 98° = 0762, amorphous - 27° to +8° = 0746, amorphous 19° to 87° = 1036 (Regnault,

A. Oh. [3] 46, 257). C.E. vitreous at 40° = 0000368 (Fizeau, C. R. 68, 1125; cf. Spring, B. 14, 2580). For E.C. v. infra. $\mu_{\lambda} = 2.654$, $\mu_{\alpha} = 2.692$, $\mu_{\beta} = 2.98$ (v. Sirks, P. 143, 429). For emission and absorption spectra v. B. A. 1884. 440. H.C. [Se, 0] = 57,080; [Se, 0^3, Aq] = 76,660 (Th. 2, 274).

Historical.—In 1817 Berzelius (S. 23, 809) obtained a new element from the crystals formed in the leaden chamber of a sulphuric acid works at Gripsholm in Sweden; as the new element was found to resemble tellurium (discovered in 1798 by Klapstock), Berzelius gave it the name selenion (σελήνη = the moon). As Se is distinctly a non-metallic element, and as the termination um is characteristic of the names of metals, it seems altogether improper to use the name selenium rather than selenion.

Occurrence.—In small quantities uncombined with other elements; in combination with various metals, such as Bi, Cu, Pb, Hg, Ag, generally along with sulphur. Most selenion-containing metallic sulphides are very poor in Se; but certain selenides from the Argentine Republic contain from 29 to 48.5 p.c. Se, combined with Cu, Pb, and Ag. Minerals containing Se are fairly widely distributed, but occur only in small quantities (Stromeyer, S. 43, 452; MacIvor, C. N. 56, 251; Nordström, B. 12, 1723; Pisani, C. R. 88, 391; Hensler a. Klinger, B. 18, 2556; Stelzner, J. 1874. 1234). When sulphides which contain Se are roasted, the Se condenses in the flues. The deposits that form in sulphuric acid chambers often contain Se; and many specimens of the acid also contain this element. Commercial HClAq sometimes contains Se, derived from the H₂SO₄ used in making the HClAq Kemper, J. 1860. 84; Nilson, B. 7, 1719; Lamy, C. R. 74, 1285; Scheurer-Kestner, C. R. 74, 1286; Personne, C. R. 74, 1199; Drinkwater, An. 8, 63).

Formation.—1. By passing SQ, into H₂SeO₃Aq; H₂SeO₃Aq + 2SO₂ + H₂O

=2H₂SO₁+Se.—2. By allowing the solution of an alkali selenide to stand in air (Böttger, J. pp. 71, 512).—3. By adding acid to solution of a thio-selenate (Böttger, J. pp. 94, 439), or to KCNScAq (Oppenheim, J. pp. 71, 266).—4. By the action of such metals as Zn or Fe on H₂ScO₂Aq made strongly acid by HCl or H₂SO₂.
5. By heating (NH₄)₂ScO₃ or (NH₄)₂SeO₄.

Preparation .- 1. From the flue-dust formed in roasting sulphides containing Se. The flue-dust is washed with water, dried, and distilled; this method is applicable to dusts rich in Se. Dusts poorer in Se are washed, the heavier particles are lixiviated with dilute HClAq and then with water, dried, fused with pearlash and soda, and washed with water; the solution of alkali selenide thus obtained is allowed to stand in the air, and the Se which ppts. is washed, dried, and distilled (Böttger, J. pr. 71, 512). Or the washed dust is made into a thin paste with equal volumes of H2SO, and H2O, heated to boiling, with addition from time to time of a little HNO, or KClO, till the red colour of the liquid is destroyed, conc. HClAq is added equal to half the volume of the liquid, and the whole is evaporated to one-fourth its bulk, whereby Cl is evolved and H2SeO, is reduced to H2SeO,; SO, is passed into this solution, the ppd. Se is washed, dried, and distilled (Wöhler, G. A. 69, 264).—2. From the deposit in the leaden chambers of sulphuric acid works. The washed deposit is boiled with conc. Na, SO, Aq till it is black (from formation of PhS), and the liquid, which contains Na, SeO₂, is filtered into dil. HClAq, whereby Se is ppd. This process is repeated several times (Böttger, J. pr. 94, 439). Or the washed deposit is digested at 80°-100° with fairly conc. KCNAq until the red colour of the liquid has changed to grey, the liquid is filtered, the residue washed with boiling water till HClAq ceases to produce a reddish opalescence in the washings, and excess of HClAq is added to the filtrate and washings, whereby Se is ppd. (KCNAq+Se=KCNSeAq; KONSeAq+HClAq=KClAq+HCNAq+Se). The ppd. Se is dissolved in HNO, Aq, the solution is evaporated (slowly, to prevent loss of SeO₂) to dryness, the SeO₂ is sublimed in a tube of hard glass in a stream of dry dust-free air, the sublimate is dissolved in water, HClAq is added, and Se is ppd. by SO₂ (Oppenheim, J. pr. 71, 266). Se, as prepared by reducing cold H.SeO, Aq, is

a red amorphous powder; an amorphous vitreous variety is obtained by melting ppd. Se and cooling very rapidly by pouring on to a porcelain plate (Hittorf, P. 84, 214; Rammelsberg, P. 152, 151; Regnault, A. Ch. [3] 46, 257); a black crystalline variety of Se is prepared by allowing conc. K2SeAq or Na2SeAq to stand in air until a crust forms on the surface (H., l.c.; R., l.c.), also by crystallising any form of Se from Se₂Cl₂ (Rathke, A. 152, 181); a red crystalline variety is prepared by slowly and repeatedly heating a solution of Se in CS₂ in a sealed tube to somewhat under 100°, and allowing to cool (R., l.c.; Rathke, A. 152, 181), also by subliming amorphous Se (Bornträger, D. P. J. 242, 55); a grey metal-like variety is prepared by very slowly heating amorphous or red crystalline Se to 96°-97° (H., l.c., R., l.c.; Fabre, C. R. 103, 53). According to Schutze (J. pr. [2] 32, 390) a col-loidal soluble form of Se is obtained by reducing H₂SeO₃Aq by SO₂; no acid must be present. The colloidal Se remains in solution, colouring the liquid dark red. The solution is not changed by boiling but on adding an acid or a salt Se is ppd. in red flocks.

Properties.—Se exists in several, probably in five, forms.

I. Amorphous selenion; sol. in CS_x —

(i.) Red-powdery amorphous Seforms sealing-waxred flocks, or when dried at a low temperature a
dark-red powder; when formed by reduction of hot H_x SeO_xAq it appears as a black powder (Hittorf, P. S4, 214). S.G. at 20°=4°3 (Rammelsberg, P.152, 151; Schaffgotsch, P. 90, 66); 4°2 (Rathke, A. 152, 131). This variety is a non-conductor
of electricity (Hittorf, l.c.). It is sol. CS₂; S.
at b.p. of CS₂(46·6°)=1, at 0°=016 (Mitscherlich, J. 1855. 314); according to Rammelsberg
(l.c.) the solubility in CS₂ varies much. For
S.H. v. beginning of this article. Petersen
(Z. P. C. 8, 601) gives H.C. of this variety
[Se,0°]=57,250, and at. vol. 18·4; the change
from this form to any other form of Se is
attended with contraction and the production
of a small quantity of heat. For action of heat p. infra.

(ii.) Amorphous vitreous Se forms a black lustrous solid, appearing red in thin layers. S.G. 4-282 at 20° (Schaffgotsch, J. pr. 43, 308; 60, 312). Sol. in CS. No fixed melting-point; when heated it softens at 60°, and becomes gradually less viscous till at 250° it is quite liquid; if this liquid is rapidly cooled, the vitreous variety is re-formed (Hittorf, Lc.; Draper a. Moss, C. N. 33, 1). Heated very slowly to 96°-97° this variety changes to metallic Se, with production of heat (R., Lc.; Regnault, A. Ch. [3] 46, 257; Fabre, C. R. 103, 53).

A. Ch. [5] 40, 251; RADE, C. R. 105, 55).

II. Crystalline selenton; insol. in

CS₂—(i.) Black crystalline Se. Small, microscopic, glittering leaflets. S.G. 48 (R., L.);

476 to 478 at 15° (Mitscherlich, J. 1855. 314).

Insol. CS₂. H.C. [Se,O'] = 55,820; at. vol. = 16·5; change from amorphous Se to this form is accompanied by slight production of heat and
contraction (Petersen, Z. P. C. 8, 601).

(ii.) Red crystalline Se. Small, thin, transparent, lustrous crystals; in thicker layers appears black and opaque. S.G. 4·46 to 4·5 at 15° (R., l.c.; M., l.c.; Rathke, l.c.). Melts at 217° (H., l.c.; D. a. M., l.c.). Insol. incCs. Petersen (l.c.) gives H.C. [Se,O'] = 56,200; and at. vol. = 17·7. This variety is a conductor of electricity, the conductivity increasing with increase of temp. and also by exposure to light. (For details, v. infra.) When heated to c. 110° this variety becomes black. The crystals are monoclinic, ratio of axes = 1·62:1:1·6 (M., l.c.; Reguault, l.c.); isomorphous with monoclinic S (R., l.c.). For S.H. v. beginning of this article.

(iii.) Grey metallic Se. Lustrous, grey, metal-like, granular solid, resembling grey pigiron; somewhat malleable (Regnault, Lc.). Insol. in CS. S.G. 4.4 to 4.5 (R., Lc.). Melts at 217° (H., Lc.); on cooling, the vitreouts variety is chiefly formed, but if the cooling is stopped at 210° after a time there is a sudden rise to 217°, and the whole solidifies in the metallic form. All varieties of Se are sol. Se₂Cl₂ and SeEt..

Action of heat on selenion. Any one of the crystalline varieties of Se melts at 217°; when the molten Se is allowed to cool slowly it gradually becomes less soft, a thermometer placed in the cooling substance continuously falls and shows no point of rest (Hittorf, l.c.; Regnault, l.c.); the final product is crystalline Se, but if the cooling is caused to take place rapidly the amorphous vitreous variety is formed; if the cooling is stopped at 210°, and that temperature is maintained for some time. there is a sudden rise to 217° and the Se again solidifies in the crystalline (metallic) form.
When amorphous Se is heated it softens at c. 60°, and becomes gradually less viscous until at 250° it is quite liquid; if the heating is very gradual, there is a sudden evolution of heat at 96-97° (Riegnault, L.c., found temperature rise to 200°-230°), and the metallic variety is produced. Se boils at 676°-683°, forming a reddish. yellow vapour, the V.D. or which does not become constant until 600°-700° above the b.p.

Effects of light and heat on the electrical conductivity of crystalline selenion. Amorphous Se does not conduct electricity; but when heated rapidly it begins to conduct at 165°-175°, and conductivity increases until it attains a

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maximum at c. 217° (Draper a. Moss, C. N. 33, 1). Crystalline Se conducts, the conductivity increasing proportionally with increase of temperature to 217°, after which it decreases and reaches a minimum at 250° (Hittorf, P. 84, 214; D. a. M., l.c.). If Se is heated for a considerable time to 200° and is then allowed to cool, conductivity decreases as temperature rises and increases as temperature falls (W. Siemens, P. 159, 117). This observation seems to show that at c. 200° a variety of Se is formed which behaves like a metal, and that on cooling this form remains mixed with the ordinary crystal-line variety, so that the conductivity depends on the relative quantities of the two forms, and therefore on the temperature (cf. Kalischer, W. 31, 101). The electrical conductivity of crystalline Se increases enormously when the Se is exposed to light (Sale, Pr. 21, 283; Smith, B. 6, 204; Rosse, P. M. [4] 47, 161; Forssmann, W. 2, 513). Adams and Day (Pr. 24, 163) found that the resistance of Se varied directly as the square root of the intensity of the source of light; also that light caused an electric current in Se from the less to the more illuminated part (Pr. 25, 113; cf. Bidwell, C. N. 52, 191).

Se may be sublimed and distilled in vacuo, or in an indifferent gas (Schuller, J. 1884. 1550); heated in air it is burnt to SeO₂. Se dissolves in conc. H2SO, forming SeSO, and is ppd. again on adding water; Se is sol. in alkali solutions, forming alkali selenides; also in KCNAq, in alkaline sulphite solutions, in Se, Cl, Se, Br., and SeEt4; the amorphous varieties are

al. sol. CS₂

Se resembles S and Te in its chemical character; it is somewhat less negative than S and more negative than Te; it shows distinct analogies with Cr, Mo, W, and U (v. Oxygen GROUP OF ELEMENTS, vol. iii. p. 705; and CHRO-MIUM GROUP OF ELEMENTS, vol. ii. p. 168).

The atomic wt. of Se has been determined (1) by analysing SeCl, (Berzelius, P. 8, 21 [1818]); (1) by analysing SeU₁ (herrenus, P. 8, 21 [1613]);
(2) by analysing K₂SeO₁ (Mitscherlich a. Nitzsch, P. 9, 627 [1827]; (3) by oxidising Se to SeO₂, by reducing SeO₂ to Se, and by analysing BaSeO₃ (Sace, A. Ch. [3] 21, 119 [1847]); (4) by analysis of HgSe (Erdmann a. Marchand, J. pr. 55, 202 [1849]); (5) by converting Sc into SeCl, (Dumas, A. Ch. [3] 55, 186 [1859]; (6) by reducing SeO₂ to Se and by analysing Ag,SeO₃ (Pettersson a. Ekman, B. 9, 1210 [1876]; (7) by determining S.H. of Se (Regnault, A. Ch. [3] 46, 257); (8) by determining V.D. of, and analysing, SeH₂, SeO₂, Se₂Cl₂, SeCl₄, and SeBrCl₄.

The molecular wt. of Se has been found by determining the V.D. of Se at 860°, c. 1000°, and c. 1400°; the values at 1400° agree with the

formula Se₂.

The atom of Se is divalent in the gaseous molecule SeH₂, and tetravalent in the gaseous molecules SeCl₁ and SeBrCl₃.

Reactions and Combinations .- 1. Water and ozone produce H.SeO. (Mailfert, C. R. 94, 860, 1186). Water alone does not react at 160° (Cross a. Higgin, C. J. 35, 249).—2. Conc. sulphuric acid dissolves Se on warming, forming H₂SeO₂, and some H₂SeO₄, and giving off SO₂. Fuming sulphuric acid forms a greenish solution containing SeSO, (v. Thio-oxide, p. 441); on boiling H2SeO2 is formed and SO2 evolved

(Divers a. Shimosé, B. 18, 1209).-3. Hot coric. nitric acid oxidises Se to H.SeO, with evolution of NO. Hydrochloric acid does not react with Se.-4. Se dissolves in alkali solutions, forming alkali selenides; fusion with alkalis produces the same compounds .- 5. Fusion with nitre or potassium chlorate forms K.SeO. - 6. Potassium cyanide solution dissolves Se to KCNSeAq. 7. Solutions of alkali or alkaline earth sulphites dissolve Se, forming thioselenates (Rathke a. Zschiesche, J. pr. 92, 141; Uelsmann, A. 116, 123; v. also Thioselenares, p. 434).—8. Se vapour passed over heated lead fluoride forms Se fluoride (Knox, Pr. Irish Acad. 1841. 299).— 9. Se combines with oxygen to form SeO2, when heated in O or air .- 10. Se combines with chlorine, bromine, and iodine at the ordinary temperature.-11. Heated to low redness with hydrogen, H2Se is formed (Uelsmann, A. 116, 122).-12. Phosphorus combines at the ordinary temperature.-13. Se combines with arsenic and antimony, by heating the elements together .-14. Selenides of most metals are formed by heating Se with metals (v. Selenides, p. 436). Sometimes the combination is effected without heat, under the influence of light (v. Bidwell, P. M. [5] 20, 178; Moss, C. N. 33, 203).—15. Se dissolves in molten sulphur, but no definite compounds are formed in this way.-16. With sulphuric anhydride Se combines to form SeSO₃ (v. Thio-oxide, p. 441).

Selenion, acids of. Sclenhydric acid H.Se, vol. ii. p. 724; selenic acid H₂SeO₃, p. 435; selenicus acid H₂SeO₃, p. 445; Selenocyanhydric acid HCNSe, vol. ii. p. 348; also Selenocyanic acid, this vol. p. 443; salts of thioselenic acids, H2SeSO3 and H2SeS2O6, are known, p. 434; and salts of sclenosamic acids, Se(NH2)OM1 and 2SeO(NH.).OH.OMI, have been isolated, p. 446.

Selenion, antimonide of; v. vol. i. p. 283,

Antimony, Combinations of, No. 6.

Selenion, arsenides and arsenosulphides of; v. vol. i. p. 303, Arsento, Combinations of, No. 7.
Selenion, boride of. A yellow-grey solid is formed by strongly heating amorphous B in a stream of H.Se; the solid is decomposed by water with rapid evolution of H.Se (Sabatier, C. R. 112, 865). As S. gives the formula B₂S₃ to the boron sulphide formed by passing H.S. over B, it is probable that the Se compound has the composition B.Se.

Selenion, bromides of. Two compounds of Se and Br are known, Se, Br, and SeBr,; both are formed by the direct union of the elements. Both are decomposed by heat, but they are more stable towards heat than the corresponding S compounds (Evans a. Ramsay, $C. \hat{J}$. 45, 62). As the V.D. of neither has been determined, the formulæ are not necessarily molecular; but from the analogy of Se₂Cl₂ and SeCl₄, which formulæ represent the compositions of gaseous molecules of these chlorides, it is probable that the mol. wts. of the bromides correspond with the formulæ Se₂Br₂ and SeBr₄.

SELENIOUS BROMIDE Se₂Br₂. (Selenion monobromide.) Formula probably molecular, from analogy of Se,Cl. To 15.9 parts powdered Se covered with three times its weight of dry CS2, 16 parts Br are gradually added; after a time the CS, is distilled off; and Se, Br, remains as a thin oily liquid, having a dark reddish-brown colour (appearing black in a thickish layer), and an unpleasant smell resembling that of S₂Cl₂ (Serullas, A. Ch. [2] 35, 349; Schneider, P. 128, 327). A thin layer of Se₂Br₂ transmits rose-red light; the absorption spectrum has been examined by Gernez (C. R. 74, 1190). S.G. of Se₂Br₂ = 3·604 at 15°. Bris given off on heating, then a little SeBr₄, and at 225°-230° most of the Se₂Br₂ distils over, and finally some Se is obtained (Schneider, l.c.). Se₂Br₂ dissolves in all proportions in CS₃, less easily in CHCl₃, EtBr, and EtI. It sinks in water, and then decomposes to H₂Se₂Aq, HBrAq, and Se. Absolute alcohol forms SeBr₄ (which remains dissolved) and Se. Se₂Br₂ dissolves Se (c. 22 p.c.), on adding CS₂ the Se separates. Br is absorbed by Se₂Br₂, in CS₂ shaken with dry AgCN forms a little Se cyanide (Schneider, P. 129, 634).

Selenio Bromide SeBr. (Selenion tetra-bromide.) Formula probably molecular, from analogy of SeCl. To a solution of 1 part SeBr. in CS₂ 1½ parts Br are gradually added, the SeBr, which separates is allowed to stand in contact with the CS2 for some days, whereby it becomes crystalline, and the CS, is distilled off; the compound obstinately retains some CS₂. By heating to 75°-80° Br is given off, and the SeBr,, containing Se₂Br₂, sublimes in black, lustrous, six-sided leaflets, mixed with a little pure SeBr, in dark-orange crystals, and Se₂Br₂ remains (Schneider, P. 129, 450). SeBr, is also obtained by dissolving 1 part powdered Se in 10-12 parts Br, pressing the crystalline mass between filter-paper, and removing excess of Br by gently warming. SeBr, dissolves in CS2, CHCi, and EtBr; it dissolves with decomposition in alcohol, also in HClAq. SeBr, is very hygroscopic; in moist air it gives Br and Se,Br₂; in much water it forms H₂SeO₄Aq and HBrAq. Combines with SO₃ to form SeCl₄SO₃ (v. Selenion thio-oxychloride, p. 441). Forms compounds with KBr and NH₄Br, K₂SeBr₆ and $(NH_i)_2SeBr_6$ (v. Muthmann a. Schäfer, B. 26, 1008).

Selenion, bromochlorides of. Two compounds of Se, Br, and Cl were obtained by Evans and Ramsay (C. J. 45, 68) by the interactions of Se₂Cl₂ and Br, and Se₂Br₂ and Cl. The bromochlorides thus formed are SeBrCl₃ and SeBr₂Cl.

Selenion tribromochloride SeBr₃Cl.
Orange, hygroscopic crystals formed by adding 2·1 parts Br, in CS₂, to 1 part Se₂Cl₂, crystalsing from CS₂, and gently warming in a current of air to remove adhering CS₂ (Se₂Cl₂ + 3Br₂ = 2SeBr₃Cl). Decomposes when heated, giving off Br; as V.D. at 200° was c. half that calculated for SeBr₃Cl, dissociation is probably complete at that temperature.

Selenion Bromotrichloride SeBrCl₃. Mol. w. 264-66. V.D. at 179° and 754 mm. pressure = 131-5; dissociation begins at c. 190°-200°. Yellow-brown crystals; obtained by passing Cl into Se,Br₂ in CS₂, washing the pp. with CS₂, and drying in a current of warm air. Gives off Br when heated above c. 190°, and yields sublimate of SeBr₄.

Selenion, carbide of, v. Carbon selenide, vol. i. p. 693.

Selenion, chlorides of. Two chlorides are formed by passing Cl over heated Se; using an excess of Se the product is Se₂Cl₂, and with an excess of Cl the product is SeCl₄. Attempts to form SeCl₂, corresponding with SCl₂, have been unsuccessful.

SELENIOUS CHLORIDE Se₂Cl₂. (Selenion monochloride. Selenion selenochloride.) Mol. w. 228'34. V.D. 110 at 200°-250° (Evans a. Ramsay, C. J. 45, 62; Chabrié, Bl. [3] 2, 803). S.G. 2'906 at 17'5° (Divers a. Shimosé, C. J. 45, 198). Boiling begins at c. 145°, but no definite b.p. can be given (K. a. R., l.c.). H.F. [Se²,Cl²] = 22,150 (Th. 2, 405).

Formation.—1. By passing Cl over excess of heated Se.—2. By heating SeCl₄ with Se at 100° (Borzelius, P. 9, 225).—3. By passing HCl into a solution of Se in fuming H₂SO₄ (Divers a. Shimosé. C. J. 45, 194, 198).

Preparation.—HCl gas is passed into a solution of Se in furning H₂SO₄ till a deep-red liquid is deposited and the mother-liquor is yellowish-brown; the mother-liquor is then poured off, the red liquid is dissolved in fresh furning H₂SO₄ and HCl is passed in; this process is repeated again; finally, the red liquid is digested, in a closed vessel, with dry KCl (to remove H₂SO₄) and decanted (D. a. S., l.c.). The reactions are probably (1) 2SeSO₃+2HCl = SeSO₂·SeCl₂+H₂SO₄; (2) SeSO₃·SeCl₂+HCl = Se₂Cl₂+SO₂·Cl.OH (D.

a. S.).

Properties, Reactions, and Combinations.—
Se,Cl₂ is a heavy, deep-red liquid, smelling something like S.Cl₂; S.G. 2-906 at 17·5°; somewhat volatile at ordinary temperatures, giving off orange-coloured vapour at 100°, beginning to boil at c. 145°, but exhibiting no fixed b.p. (E. a. R., l.c.). V.D. determined at c. 200° gave results agreeing with Se,Cl₂ For absorption spectrum of vapour v. Gernez, C. R. 74, 1190. Se,Cl₂ is easily sol. CS₂, CHCl₃, C,H₆, and CCl₄. It is slowly decomposed by H.O. EtOH, and Et₄O; a solution in CS₂ shaken with water gives H₂SeO₂Aq, HClAq, and Se. Warm Se₂Cl₂ dissolves Se freely; on cooling the Se is partly ppd. in the metal-like form (Bathke, A. 152, 181). Se₂Cl₂ is decomposed by shaking with Hg or Ag (D. a. S., l.c.); with P it gives PCl₂ and Se (Baudrimont, A. Ch. [4] 2, 5). Se₂Cl₂ combines with PCl₃ to form a yellow substance (B., l.c.).

SELENIC CHLORIDE SeCl. (Selenion tetrachloride.) Mol. w. 220-28. V.D. at 180°=110 (Evans a. Ramsay, C. J. 45, 65). H.F. [Se,Cl'] = 46,160 (Th. 2, 405).

Formation.—1. By heating Se, or Se,Cl., in excess of Cl.—2. By heating SeO₂ with PCl₃ (v. Preparation).—3. By the action of SOCl₂ on SeOCl...

Preparation. To 13 parts PCl₃ in a long-necked flask 7 parts SeO₂ are added tittle by little, the reaction being allowed to cease after each addition before more SeO₂ is added (SeO₂+PCl₃=SeOCl₂+POCl₃); the mass becomes liquid and then suddenly solidifies (3SeOCl₂+2POCl₃=3SeCl₄+P₂O₃); excess of POCl₃ is now removed by heating the flask while a rapid stream of dry CO₂ is passed through it; a wide tube is then fitted by a cork into the neck of the flask, and the flask is placed in a tray containing hot sand (if the flask is

allowed to cool the condensing P2O2 may cause

it to crack) (Michaelis, J. Z. 6, 79).

Properties, Reactions, and Combinations.

A slightly yellow crystalline solid; volatilises when heated, without melting, in yellow vapours. Evans a. Ramsay (C. J. 45, 65) found V.D. at 180° to be 110, agreeing with the formula SeCl₄; dissociation to Se₂Cl₂ and Cl began at c. 210°, and at 350° c. 66 p.c. was decomposed. Clausnizer (B. 11, 2007) got the value 57 for V.D. at 218°, at which temperature E. a. R.'s value was c. 86; at 368° Chabrić (Bl. [3] 2, 803) obtained the number 57, which agrees fairly with phide; SO, has no action. NH₃Aq produces Se, N, and H at ordinary temperatures, and N selenide at a low temperature (Verneuil, Bl. [2] 38, 548). Dry NH, combines with SeCl, at -20°, forming a very unstable compound, probably SeCl, 4NH, (V., Lc.). With PCl, the compound SeCl, 2PCl, is formed (Baudrimont, A. Ch. [4] 2, 5).

Selenion, chlorobromides of, v. Selenion

BROMOCHLORIDES, p. 439.

Selenion, cyanide of; v. Cyanogen selenide,

vol. ii. p. 358.

Selenion, fluoride of. No definite compound of Se and F has been isolated. According to Knox (Pr. Irish Acad. 1841. 299) a fluoride of Se sublimes when Se vapour is passed over

molten PbF₂.

Selenion, haloid compounds of. Se comcompounds, Se, X, and SeX, (the fluorides have not been examined); the formulæ are probably molecular, as the V.D.s of Se,Cl, and SeCl, have been determined. The compounds Se₂X₂, where X = Cl or Br, are liquids at ordinary temperatures; the other compounds are solids. All the compounds are fairly easily decomposed by heat, but less easily than the corresponding S haloid compounds.

Selenion, hydride of; v. Hydrogen selenide,

vol. ii. p. 724.

Selenion, hydroxides of. The hydroxides of Se, SeO(OH)₂, and SeO₂(OH)₂ are acids; v. Selenious acid, p. 445, and Selenic acid, p. 435.

Selenion, iodides of. Two compounds of Se and I are known, Se2I2 and SeI4, corresponding

with the bromides and chlorides.

Selenious Iodide Se₂I₂. (Selenion mono-iodide.) Formula probably molecular, from analogy of Se.Cl. Formed by heating the elements together in the ratio Sc:I(1:1.61); also by heating Se, Br, and EtI at 100' in a sealed tube (Schneider, P. 129, 627). Crystalline, steel-grey, somewhat metal-like solid; melting to a dark-brown liquid at 68°-70°. Decomposed to Se and I by continued heating at 100°; also by solvents of I. Water forms H2SeO3Aq, HIAq, and Se.

Selenio iodide Sel. (Selenion tetra-iodide.) Formula probably molecular, from analogy of SeCl. Formed by heating together Se and I in the ratio Se:4I(1:6:44); also by mixing SeBr. and Etl in the ratio SeBr4:4Etl, the SeI4 separates after a little. Best prepared by adding

HIAq to conc. H.SeO.Aq as long as a pp. is produced; the pp. is washed, pressed, and dried over H₂SO₄ (Schneider, *l.c.*). A dark-grey solid, melting at 75°-80° to a blackish-brown liquid. Gives up all I when heated to c. 100°, or treated with solvents of I; slowly decomposed by water. Attempts to form an iodochloride of selenion were unsuccessful (v. Evans a. Ramsay. C. J. 45, 70).

Selenion, nitride of: v. Nitrogen selenide,

vol. iii. p. 570.

Selenion, oxides of. Only one oxide of Se has been isolated with certainty; this oxide is SeO₂. Berzelius thought that an oxide SeO was formed, along with SeO₂, by heating Se in air or O, by heating Se and SeO₂, and by the partial oxidation of Se sulphide by HNO₃. According to Chabrié (A. Ch. [6] 20, 202) Se takes up O approximately corresponding with that required to form SeO, when heated in air to 180°. Attempts to prepare SeO₃ have failed. By passing gaseous SeO₂ and O over hot spongy Pt, von Gerichten (A. 168, 214) obtained a white sublimate that dissolved in water with a hissing sound, forming H2SeO4, but Cameron a. Macallan (Pr. 46, 32) failed to confirm this result; C. a. M. (l.c.) did not get SeO₃ by passing O over hot Pt sponge mixed with Se, nor by the action of ozone on ScO2, nor by heating selenate of Sb, Bi, Fe, Pb, Hg, or Ag. By heating dry H₂SeO₄ with P₂O₅ in a closed flask they got a trace of a crystalline solid, analyses of which pointed to the composition SeO₃. A solution of Se in H₂SeO₄ perhaps contains Se₂O₄ (v. Selenic acid, Reactions, No. 6, p. 436).

SELENION DIOXIDE SeO₂. (Selenious oxide, Selenious anhydride.) Mol. w. not determined. S.G. 3.9538 at 15° (Cameron a. Macallan, Pr. 46, 27; Clausnizer, A. 196, 265). [Se,0²] = 57,250 from amorphous Se; 55,820 from black crystalline Se; 56,200 from red crystalline Se (Petersen, Z. P. C. 8, 601). Melts at 340° in a sealed tube; at ordinary pressure volatilises without melting, slowly at 250°, rapidly at 280° (Chabrié, A. Ch. [6] 20, 202; C. a. M., Le.). For absorption-spectrum of SeO₂ vapour v.

Gernez (C. R. 74, 803).

Preparation.—1. Se is placed in the lower part of a V-tube with one limb longer than the other, and the longer limb drawn to a fine opening; the shorter limb is connected with a gasholder, from which a stream of dry O is passed into the V-tube; the tube is heated till the Se burns; the SeO, condenses in the longer limb of the tube. -2. Se is dissolved in conc. HNO, Aq, the solution is evaporated to dryness, best in a retort (solidification occurs suddenly, with evolution of heat); the dry H2SeO3 is heated in the retort till sublimation begins, then let cool, and dissolved in water; the solution is ppd. by BaOAq; the solution, after filtering, is evaporated to dryness, and the residue is heated, when SeO2 sublimes; traces of H2SeO4 and H2SO4 are thus removed, excess of BaO remains in the residue (Thomsen, B. 2, 598; cf. Wohlwill, A. 114, 176; Fischer, P. 67, 412).

Properties and Reactions.-Long, white, lustrous, four-sided needles (for m.p. &c. v. beginning of this article). 1. Slowly withdraws water from moist air, forming H₂SeO₃; dissolves in water, forming same soid, with disappearance of

heat, $[SeO^2,Aq] = -920$ (Th. 2, 405).—2. Sl. sol. boiling acetic axhydride, crystallising un-changed; heated to 180°-200° oxidation of the Ac.O occurs (to CO₂, &c.) and Se separates (Hinsberg, A. 260, 40).—3. Dissolves in aqueous acetic acid, H₂SeO₃ separating on cooling (H., l.c.).—4. Dissolves in alcohol of 96 p.c., and is re-obtained on evaporation over H.SO. (H., l.c.). 5. Reacts with phosphoric chloride to give SeCl., P₂O₅, and POCl₂; heated with phosphoryl chlor-ide gives SeOCl₂ and P₂O₅ (Michaelis, J. Z. 6, 79).—6. Heated with sodium chloride yields SeOCl2 and Na2SeO3 (Cameron a. Macallan, Pr. 46, 35) .- 7. Heated with selenion tetrachloride in a closed tube produces SeOCl₂; with SeBr, probably forms SeOBr₂ (Schneider, P. 129, 450). 8. Decomposed by dry ammonia to H2O, Se, and N; when NH, is passed into SeO, in absolute alcohol, SeO(NH,).ONH, is formed (v. Selenos-AMIC ACIDS, SALTS OF, p. 446). -9. Heated with dry HCN and Ac.O. Se cyanide is probably formed (Hinsberg, A. 260, 40).—10. Hydriodic acid (Hinsberg, A. 200, 40).—10. Hydrions acta reduces SeO, to Se and H.O, even at 10°.—11. SeO₂ and sulphur dioxide do not react at any temperature (Schulze, J. pr. [2] 32, 390).— 12. The compounds K_SeBr, and (NH,) SeBr, are produced by dissolving SeO2 in hydrobromic acid and adding potassium or ammonium bromide (v. Muthmann a. Schäfer, B. 26, 1008)

Combinations .- 1. According to Ditte (A. Ch. [5] 10, 82), SeO, combines with dry hydrogen chloride to form two compounds, one of which, SeO2.2HCl, is liquid, and the other, SeO2.4HCl, is solid, at the ordinary temperature. hydrogen bromide SeO 4IIBr is formed, and when this is kept very cold and HBr is passed over it, D. says that SeO, 5HBr is produced. Hydrogen fluoride is said also to combine with SeO2, but the product has not been examined .- 2. With alkali halides the compounds MX.2SeO2.2H2O are formed (Muthmann a. Schäfer, B. 26, 1008).—3. Hinsberg (A. 260, 40) described a compound with alcohol, SeO_2 , C_2H_6O , obtained by evaporating SeO, in absolute alcohol over CaCl .. - 4. Large white crystals of the compound SeO, SO, are obtained by warming ScO, and pure sulphuric anhydride to 100°, distilling off excess of SO, at 60°-70°, and allowing to cool. At 100°

the compound gives up SO₃ (Weber, B. 19, 3185).
Selenion thio-oxide SeSO₃. (Selenion sulphoxide. Selcnion-sulphur trioxide.) Mol. w. not determined. Magnus (P. 10, 491) noticed that Se dissolved in fuming H₂SO, to produce a green solution; Weber (P. 156, 531) separated and analysed the green compound, and gave it the formula SeSO₃. Divers a. Shimosé (C. J. 45, 201) further examined this substance. Powdered Se is placed in liquid SO₃; heat is given off, and a dark-green liquid is formed; after a time the whole solidifies; after warming to 30°-40° for a few minutes the liquid part is drained off, and the adhering SO, is removed by the use of a Sprengel pump (for details v. D. a. S. on TeSO₃, C. J. 43, 324). SeSO₃ is a green solid, which may be heated to c. 35° without change; decomposition begins at c. 40°, and at c. 120° SO, and O are rapidly evolved and Se separates; by heating slowly in vacuo it changes to a yellow powder, which D. a. S. think to be a modification of the thio-oxide. SeSO, is sol. sone, H.SO,; on adding much water Se is ppd., and H₂SeO₂ and H₂SO₂ go into solution. HCl reacts with SeSO₂ in H₂SO₄ to form Se₂Cl₂ and SO₂Cl.OH (v. Selentous chioride, *Preparation*, p. 499). Schulz-Sellack (B. 4, 113) observed that the vapours of SO₂ react with Se to form a yellow powder.

Selenion, oyacids of, and their salts. The oxyacids of So are selenious acid H₂SeO₂ (v. p. 445) and selenic acid H₂SeO₂ (v. p. 435); salts of the thioselenic acids H₂SeSO₂ and H₂SeSO₃ have been isolated (v. p. 484); and salts of the selenosamic acids SeO(NH₂).OH and 2SeO(NH₂).(OH)₂ are known (v. p. 439).

Selenion, oxybromide of. By melting together SeO, and SeBr, Schneider (P. 129, 450) obtained needles which were probably SeOBr, corresponding with SeOCl₂ formed in a similar

Selenion, oxychlorides of. The oxychloride of Se, SeOCl₂, corresponds with sulphuryl chloride SOCl₂; an oxychloride containing Se and S, and corresponding with S₂O₂Cl₄, has also been isolated.

SELENYL CHLORIDE ScOCl₂. (Selenion oxychloride.) Mol. w. not determined.

Preparation.—1. Equivalent weights of SeCl, and SeO₂ are heated in a sealed tube to 150°, and the product is purified by repeated distillation (Weber, P. 118, 615).—2. SeO₂ and PCl₃ are brought together in the ratio SeO₂:PCl₃; SeOCl₂ and POCl₃ are produced, but the heat evolved suffices to cause a secondary reaction, which yields SeCl₄ and P₂O₃, so that very little SeOCl₂ can be obtained by this method (Michaelis, J. Z. 6, 79; cf. Selence chorded, Preparation, p. 439).—3. By distilling SeO₂ and NaCl in the ratio SeO₂:NaCl (Cameron a. Macallan, Pr. 46, 35).

Properties.—A yellowish liquid, fuming in the air, boiling at 179.5°, and solidifying below 0° to colourless crystals, which melt at 10° (M., l.c.).

Reactions and Combinations (M., l.c.).—
1. Water decomposes ScOCl., forming H.SeO.Aq and HClAq.—2. Ammonia produces SeO., Se, N, NH₄Cl.—3. Sulphuryl chloride produces SeOl, and SO₂.—4. Phosphoryl chloride forms SeCl₄ and P₂O₅ (v. Preparation of selenic chloride, p. 439).—5. With phosphorous chloride POCl₃, SeCl₄ and Sc₂Cl₂ are produced.—6. SeOCl₄ combines with stannic chloride to form SScOCl₂.SnCl₄; also with titanic chloride and antimonic chloride to form 2SeOCl₂.TiCl₄ and 2SeOCl₂.SbCl₅ (Weber, P. 125, 325).

Selenion, Thio-oxychloride or, SeSO₂Cl₄. (Pyrothioselenyl chloride. Selenion sulphooxytetrachloride.) Mol. w. not determined.

oxyletrachloride.) Mol. w. not determined.

Formation.—1. By the interaction of SO, and
SeCl. (H. Rose, P. 44, 315).—2. By dissolving
SeCl. in Nordhausen sulphuric acid (Clausnizer,
B. 11, 2007).—3. By heating SO₂Cl₂ and SeOCl₂
in a sealed tube to 170°-180° (C., l.c.).—4. By
the interaction of SO₂OH.Cl and SeO₂, SeOCl₂,
or SeCl₄ (C., l.c.).

Preparation.—SeCl, and SO, OH.Cl are warmed together in the ratio SeCl,:2(SO, OH.Cl) till the SeCl, is quite dissolved:

 $SeCl_1 + SO_2 OH.Cl = SO_2 Cl.OSeCl_1 + Cl.$ (Excess of $SO_2 OH.Cl$ is needed to hasten the reaction and to serve as a solvent.) The reddish solution solidifies on cooling; the white needles are separated by pressing between porous plates, and

dried over H,SO.

Properties and Reactions. - Small white needles; unchanged in vacuo or on gentle warming; deliquesces in moist air; melts at 165° and boils at 183°; V.D. at 209° = 48.5, $SeSO_3Cl_4 = 150$; dissociacalculated for tion has therefore occurred, perhaps thus: $2SeSO_3Cl_4 = 2SO_3 + Se_2Cl_2 + 3Cl_2(C., l.c.)$. Decomposed by water, at once, to H2SO, Aq, H2SeO3Aq, and HClAq.

Selenion, phosphides of; v. PHOSPHORUS

SELENIDES, p. 144.

Selenion, sulphides of. The only compound of Se and S that has been isolated is SeS. Divers a. Shimidzu (C. J. 47, 446) say that this is the only compound of the two elements that exists, but Rathke (B. 18, 1534) considers that others exist, although none but SeS has been obtained in a state of purity. Se and S may be melted together in all proportions, but no compound is produced (Bettendorff a. von Rath, P. 139, 329; Rathke, P. 141, 590). Isomorphous mixtures of the two elements crystallise from solutions of Se and S in Cs₂ (B. a. von R., l.c.). The pp. formed by passing H₂S into H₂SeO₃ contains Se and S in the ratio SeS., but it is a mixture of SeS with S (H. Rose, P. 107, 186; D. a. S., Lc.; Rathke, B. 18, 1534). The pp. containing Se and S in the ratio Se₂S obtained by passing H₂Se into H₂SO₃ is merely a mixture (D. a. S., l.c.).

SELENION MONOSULPHIDE SeS. Mol. w. not determined. Very dilute H₂SeO₃Aq, cooled to 0°-5°, is saturated with H.S, which is first passed through a flask filled with pieces of ice; the yellow pp. which forms is washed, dried in vacuo, moistened with CS2, and allowed to stand for some days till the mass becomes crvstalline, the CS, withdrawing S; CS, is added to the crystals, after a few minutes the CS, is decanted, and the residue is washed with CoH, and then with alcohol. SeS forms small, orangeyellow, lustrous tablets; S.G. 3.056 at 0°, 3.035 at 52°; S.H. 1274. On heating it melts, gives off S vapour, and then vapour of S and Se. Sol. CS., but not crystallisable therefrom by evaporation; insol. water and ether (Ditte, C. R. 73,

625, 660).

Selenion, sulphoxide of; v. Selenion thiooxide, under Selenion oxides, p. 441.

Selenion, sulphoxychloride of; v. Selenion thio-oxychloride, under Selenion oxychlorides,

Selenion, thio-oxide of; v. Selenion oxides,

Selenion, thio-oxychloride of; v. Selenion M. M. P. M. oxychlorides, p. 441. SELENIÓN, ORGANIC COMPOUNDS OF.

Methyl selenide or Selenion methide Me2Sc. Mol. w. 109. (58°). Formed by distilling a Solution of barium methyl sulphate with K₂Se (Wöhler a. Dean, A. 97, 5) or of KMeSO, with Na₂Se (C. L. Jackson, A. 179, 1). Heavy oil with nasty smell. Burns with bluish flame. with nasty smell. Burns with bluish mane.
PtCl, forms (Me₂Se)₂PtCl₄, crystallising from alcohol in yellow plates. Conc. HNO₃ forms (Me₂SeO)HNO₄ [91^o], whence HClAq produces Me₂SeCl₂ [60^o], while HBrAq gives Me₂SeBr₂ [82^o] and KlAq ppts. Me₂SeI.

Methylo-todids Me₂SeI.

Tri-methyl-pclenonium iodide. Yields (Me₂SeCl)₂PtCl₄,

crystallising from water in dark-red octahedra (Jackson, B. 7, 1277).

Di-methyl disclenide Me,Se₂. Formed from KMeSO, and K,Se₂ (W. a. D.; Rathke, A. 152, 211). Heavy reddish-yellow oil, with unpleasant odour, sol. HNO,Aq.

Methane selinic acid CH, SeO, H. [122°]. Formed by oxidising Me2Se2 with HNO3 (W. a. D.). Deliquescent crystals, v. sol. alcohol. Gives with HCl crystalline CH, SeO, Cl. -AgA': prisms.

Ethyl selenide Et₂Se. (108°). (Rathke; Pieverling, A. 185, 381). Oil, without unpleasant odour. HCl added to its solution in dilute HNO₃ ppts. Et₂SeCl₃, whence NH₃Aq forms (Et₂Se)₂OCl₂ (Joy, 4. 86, 35).

Ethyl iodide Et₂SeI. Crystalline. Con-

verted by moist Ag₂O into a strongly alkaline base which forms crystalline salts. - (Et, SeCl) ZnCl

thin plates.—(Ět₃SeCl)₂PtCl₄.

Di-ethyl diselenide Et, Se,. (186°). Liquid with disgusting odour. HCl added to its solution in dilute HNO, gives monoclinic crystals of C₂H₆SeO₂Cl.

Ethane selinic acid Et.SO.H. Yields with

HCl monoclinic crystals of C2HaSeO2Cl.

Ethyl selenhydrate EtSeII. mercaptan. Formed from KSeH and Ca(EtSO,)2 (Siemens, A. 61, 360). Heavy oil, boiling much below 100° and having an unpleasant odour. Reacts with HgO.

Ethyl selenite SeO(OEt)₂. (184°). S.G. 1º 1·49. Formed from Ag₂SeO₃ and EtI, and got also by heating SeOCl2 with NaOEt and dry ether at 180° (Michaelis, A. 241, 158). Thick liquid, miscible with water and alcohol. The chloride SeO(OEt)Cl [10°] (175°), formed from SeOCl, and alcohol, crystallises in needles.

Selenide of carbon CSc. Formed in small quantity by passing a mixture of CCl4 and H2Se through a red-hot tube (Rathke, A. 152, 199). Pungent yellow liquid. Converted by alcoholic potash into EtO.CSe2K, crystallising in yellow needles, v. sol. water and alcohol.

Se(CH₂.CO₂H)₂ Selenido - di - acetic acid Formed from ammonium chloro-acctate and alcoholic $(NH_4)_2$ Se (Ulrich, B. 8, 773). Monoclinic tables. — $\times (NH_4)_2$ A": insol. alcohol -- *CuA": bluish-green pp.

Amide.-Formed from ClCH2.CONH2 and alcoholic (NH₁)₂Se. Prisms, m. sol. cold water.

Di-phenyl selenide SePh₂. S.C. 22 1-450. V.D. 8-17 (calc. 8-09). Formed, together with selenophenol and Se₂Ph₃.C₆H₄Cl (240°-250° in vacuo), from SeCl, and benzene in presence of AlCl, (Chabrié, C. R. 109, 183; Bl. [2] 50, 133; [3] 2, 788). Oil. Boils at 227° under a few cm. pressure. Bromine forms Se(C_eH₄Br)₂ [112°], crystallising from alcohol in colourless hexagonal plates. H2O2, in presence of HCl and a current of air, forms Se(C₆H₄Cl).C₆H₄OH [145°] converted by HNO, into a crystalline product [188°]

Phenyl selenhydrate C.H.SeH. Selenophenol. [60°]. Formed from benzene, SeCl., and AlCl. (Chabrié, C. R. 109, 188; Bl. [3] 2, 788). Sol. alcohol, insol. water.

Tetra - methyl - di - amido - di - phenyl-selenide Se(C.H.NMe₂)₂. [124]. Formed from SeOCl, and di-methyl-aniline in ether (Godchaux, B. 24, 765). Yellowish needles, m. sol. cold alcohol

and ether.—B" H_2SO_4 . [55°]. Colourless needles, v. e. sol. water.—B" $2C_4H_2(NO_2)_3OH$. [135°]. Yellow plates.

Tetra ethyl di amido di phenyl selenide Se(C₈H,NEt₂)₂. [83°]. Formed from SeOCl₂ and PhNEt₂ in ether. Silky needles, v. e. sol. hot ether and alcohol.—B"H₂Cl₂. [73°].—B"2C₆H₂(NO₂)₈OH. [135°]. Yellow plates and needles.

Di-phenyl-selenone SeOPh₂. (230° at 65 mm.). S.G. 19°61 '48. Formed, together with the compound PhSeO(C₆H₄Cl) [94°], from SeOCl₇, benzene, and AlCl₈. Amber-yellow liquid. Not attacked by cold HNO₈. Bromine-water yields SeO(C₆H₆Rr)₂ [120°]. H₂O₂, HCl, and a current of air form SeO(C₆H₄Cl)₂ [159°].

Phenyl seleno-carbimide Ph.NC.Se. Formed by shaking Na₂Se with the chloride of phenyl-carbamine, PhNCCl₂, and ether for a day, filtering, distilling with steam, and drying the oil in vacuo over H₂SO₄ (Stolte, B. 19, 2350). Pale yellowish-red oil, v. sol. alcohol and ether.

Phenyl-seleno-urea NHPh.CSe.NH₂. [182°]. Formed by passing NH₃ into Ph.NC.Se dissolved in ether, and also by the action of H₂Se on phenyl-cyanamide in benzene (Stotte, B. 19, 1579, 2350). Crystals (from alcohol).

Di-phenyl-seleno-urea CSe(NHPh). [186°]. Formed from aniline and phenyl seleno-carbinide (Stolte, B. 19, 2351). Crystals (from alcohol), sl. sol. ether.

Selenaldine C₀H₁₃NSc₂. Formed by passing ScH₂ into an aqueous solution of aldehydeanmonia in absence of air (Wöhler a. Liebig, 4. 61, 11). Colourless crystals, with slight odour, sl. sol. water, v. sol. alcohol and ether. Its solutions are turned brown by air.

Amido-selenazole C₃H₁N₂Se i.e. Se. C(NH₂) N. Selenazylamine. [121°]. CH:CH

CH:CH

Formed by warming seleno-urea with di-chlorodi-ethyl oxide and aqueous NaOEt (G. Hofmanu,
A. 250, 308). White needles, v. sol. alcohol and
ether, m. sol. benzene and water. Decomposed
by prolonged boiling with water.—B'₂H₂PtCl₀:
orange-red pp.

Acetyl derivative C, H, AcN, Se. [c. 210°]. Needles.

Oxy-amido-selenazole Se .C(NH.2) N. Seleno-hydantoin. [190°]. Formed by boiling selenourea with chloro-acctic acid and alcohol (G. Hofmann, A. 250, 312). Thick crystals, m. sol. hot water and alcohol, insol. ether.—B'HCl: needles.

Di-oxy-selenazole Se.C(OH) N. [147°].

Formed by boiling oxy-amido-selenazole with NaOHAq (Hofmann). Prisms, v. sol. alcohol, m. sol. water.

Amido-methyl-selenazole Se.C(NH₂) N.
[80°]. Formed from seleno-urea and chloroacetone (G. Hofmann, A. 250, 305). Needles,
v. sol. alcohol and ether. Alkaline in reaction.
—B'HCl: prisms (from water).—B'₂H₂PtCl₂:

orange-red orystalline pp.

Acetyl derivative C,H,AoN,Se. [122°].

Needles (from benzene), al. sol. water.

Amido-methyl-selenazole carboxylic acid Sc.C(NH₂).

N. [195°]. Formed by heating seleno-urea with chloro-acetoacetic ether (G. Hofmann, A. 250, 309). Needles, m. sol. water, v. sol. alcohol and ether.—HA'HCl: plates, v. e. sol. water.

Acetyl derivative C,H,AcN,SeO₂. [220°]. Needles, almost insol. hot water.
Amido-phenyl-selenazole C,H,N,Se i.e.
Se C(NH.)

Se C(NH₂) N. [132°]. Formed from bromoacetophonone and seleno-urea (G. Hofmann, A. 250, 307). Needles or prisms, insol. water, sol. alcohol and acids.—B'HBr: yellowish plates, sl. sol. cold water.

Di-phenyl-selenazole C₁₅II₁₁NSe i.e.

Se .CPh N. [99°]. Formed from ω-bromoacetophenone and seleno-benzamide (G. Hotmann, A. 250, 31′). Plates, v. sol. alcohol and other. Its salts are decomposed by water.— B'₂H₂PtCl₆: pale-yellow pp.

Phenyl-methyl-selenazole C₁₀H₉NSe i.e. Se .CPh N. (283°) at 737 mm. Formed from PhCSe.NH₂ [126°] and chloro-acetone (G. Hofmann, A. 250, 316). Yellow oil.—B'₂H₂PtCl₆: pale-yellow needles.

Phenyl-methyl-selenazole carboxylic acid Se.CPh N. [207°]. Formed by saponifying its ether, which is got from scleno-benzamide and chloro-acetoacetic ether (Hofmann, A. 250, 318). Small needles (from benzene), m. sol. alcohol.—AgA'.

Ethyl ether Eth'. [1247]. Plates.

Seleno-benzoic acid. Amide C_aH₃.CSe.NH₄.

[1267] Formed by passing H₂Se into an alcoholic solution of benzonitrile made slightly alkaline with NH₃ (Dechend, B. 7, 1273; G. Hofmann, A. 250, 314). Golden needles (from water or ether). Reacts with a-chloro-ketones, forming selenazoles; e.g. X.CO.CHCl.X + CPh(SeH):NH

= H₂O + Se.CPh

NHCl.

Seleno-benzoic aldehyde v. Benzylidene selenide.

Selenocyanic acid HSeCN. The K salt is got by fusing K,FeCy_a (3 pts.) with Se (1 pt.) (Crookes, A. 78, 177; cf. Berzelius, S. J. 31, 60). The free acid is obtained, in solution, by decomposing the lead salt by H.S. It is decomposed by acids into Se and HCy. FeCl₂ does not give a red colour, but ppts. Se. Iodine added to a solution of KSeCN ppts. KC₂N₃Se₄. Air containing a little chlorine passed over a 10 p.c. solution of KSeCN forms a red crystalline pp. KSe₂C₃N₃ aq changing to yellow Se₂Cy₂, which separates from chloroform in yellow plates, and is decomposed by water into HCy, SeO₂, and Se₂ and yields in vacuo at 108° a crystalline sublimate of Se₂Cy₂, decomposed by hot water into HCy, SeO₃, and Se (Verneuil, C. R. 103, 144). Alcohol converts KSe₂C₃N₃ into Se and KSe₂O₃N₃ which forms brown crystals, sol. alcohol.

Salts.—KA'. Formed as above, and also by dissolving Se in aqueous KCy (Wöhler; Schiellerup, A. 109, 125; G. Hofmann, A. 250, 296). Very deliquescent needles, alkaline to litmus.—NH,A' (Oameron a. Davy, C. N. 44, 68).—KA'HgCl₂: white pp.—KA'HgBr₂.— KA'HgL₂.—KHg₂A'₂: prisms.—KHgA'₂.—Hg₂A'₂: olive-green pp.—HgA'₂: felt-like mass of yellowish crystals.—AgA'₂-HgCl₂.—PbA'₂: lemonyellow needles (from water).—K₂PtA'. Dark-red scales (Clarke, B. 11, 1325).—AgA'. Satiny crystals, blackened by light. Converted by ICy into volatile crystalline SeCy, (Linnemann, A. 120, 36).

Methyl ether MeA'. (158°). Yellow oil

(Stolte, B. 19, 1577).

Allyl ether C.H.A'. Oil.

Methylene ether CH.A'. [132°]. Formed from MeI and alcoholic KSeCN (Proskauer, B.

from Met and alconoloc KSeCN (Prostauer, B. 7, 1281). Rhombohedra (from alcohol). HNO, forms $\mathrm{GH}_2(\mathrm{SeO}_2\mathrm{H})_2$.

Ethylene ether $\mathrm{C}_2\mathrm{H}_4\mathrm{A}'_2$. [128°]. HNO, forms, on boiling, deliquescent $\mathrm{C}_2\mathrm{H}_4(\mathrm{SeO}_3\mathrm{H})_2$. which yields BaA'' , sol. hot water. KOH yields distribute the scheme of the scheme

diethylene tetraselenide [131°].

Propylene ether CH₂.CH(SeCN).CH₂(SeCN). [66°]. Formed by heating KSeCN with propylene bromide and alcohol (Hagelberg, B. 23, 1091). White crys-

Trimethylene ether CH2(SeCN).CH2.CH2(SeCN). [51°]. Converted by KOH into trimethylene diselenide [55°].

Benzyl ether v. vol. i. p. 502. Selenocyano-acetic acid CH₂(SeCN).CO₂H. [85°]. Formed from chloro-acetic acid and potassium selenocyanide (G. Hofmann, A. 250, 800). Yellowish needles (from ether and chloroform), v. e. sol. water and alcohol.—BaA',: amorphous.

Selenocyano-acetoacetic ether

CH₂.CO.CH(SeCN).CO₂Et. Formed from chloroacetoacetic ether and KSeCN (H.). Liquid.
Selenocyano-acetone CH₃, CO.CH₃, SeCN.

Formed from chloro-acetone and KSeCN (H.). Yellowish oil. Gives an oily phenyl-hydrazide and an oxim. Not more sol. alkalis than water.

Selenocyano-acetophenone

CaHa.CO.CH2SeCN. [85°]. Formed by boiling w bromo-acetophenone with alcohol and KSeCN (Hofmann). Ĉrystalline.

Selenocyano-ethyl-phthalimide

C.H.O.: N.CH2.CH2.SeCN. [125°]. Formed by heating bromo-ethyl-phthalimide with KSeCy and alcohol (Coblenz, B. 24, 2133). Crystalline mass. Converted by boiling dilute caustic potash into Solvered by bolling dutte causate potash into Se₂(C₂H₁,NH.CO.C₆H₁,CO₂H)₂ [119°], which forms yellowish crystals and is converted by HCl at 180° into Se₂(C₂H₁,NH₂)₂, which yields B"2HCl [188°] and B"2C₆H₂N₂O, [178°], both being crystalline.

 γ -Selenocyano-propyl-phthalimide C₂H₄O₂:N.CH₂.CH₂.CH₂.SeCN. [102°]. Formed by heating bromo-propyl-phthalimide with KSeCN and alcohol (Coblenz, B. 24, 2134). Converted by boiling dilute (10 p.c.) KOH into crystalline Se₂(C,H₂,NH.CO.C,H₂,CO₂H), [94°], whence HCl at 180° forms Se₂(C,H₂NH₂)₂, which yields B"2HCl [170°] and B"2C₂H₂N₂O₇ [165°].

ω-Selenocyano-o-toluic acid. Nitrile CH₂(SeCN).C₂H₃.CN. o-Cyano-benzyl seleno-cyanide. [121°]. Formed by warming the ni-trile CH₂Cl.C₃H₄.CN with KSeCN (Drory, B. 24, 2564). Long brownish needles (from alcohol) or prisms (from benzene). Converted by dilute

H.SO, into Se (CH, C, H, CN), [110°]. HCIAq at 100° forms Se and o cyano bensyl chloride.

Selenceyanuric acid H.Se,C,N, Formed from Cl₃Cy, and Na₂Se (Stolte, B. 19, 1578).

Methyl ether. [174°].

Seleno-phthalimidine C.H. CH. Se.
Formed from OH. (SeCN). C.H. CN and conc.
H.SO. (Drory, B. 24, 2566). Sol. alcohol.
Reactions.—1. NaOH forms the compound

Se₂(CH₂C₆H₄.CN)₂, crystallising in needles [110°], sol. alcohol and CS₂, and converted by HCl at 160° into Se and phthalide.-2. When steam is blown through a mixture of selenophthalimidine, alcohol, and KOH there is formed selenophthalide C_sH₄ CO Se, crystallising in broad plates [58°], insol. water, sol. alcohol.—3. Alcoholic potash and MeI form CH₂(SeMe).C₈H₄.CN (180°-200°).

Salts.—B'HCl: needles, slightly sol. water and alcohol.—B',H,PtOl,. Orange powder.—B'C₄H₄N₃O₅.—B'HBr. [264°]. Needles: sl. sol. water.—B'HI₂ (?) [223°]. Formed by heating CH₂(SeCy).C₅H₄,CN with HIAq at 100°. Darkviolet needles. Sulphate [145°-150°].

Piaselenole C_oH₄<N Se. [76°]. Formed

from o-phenylene-diamine and an aqueous solution of selenious acid (Hinsberg, \hat{B} . 22, 2897). Needles, v. sol. alcohol and ether, sl. sol. water. Its salts are yellow and decomposed by much water with separation of the base. Iodine forms a green periodide.

Amido-piaselenole C.H.(NH.):N.Se. [150°]. Formed by adding H.ScO, to a cool solution of tri-amido-benzene hydrochloride and NaOAc (Hinsberg, B. 22, 2898). Brownish-red needles, sl. sol. water, m. sol. alcohol. SnCl, separates Se. -B'HCl: reddish-brown needles, sl. sol.

Oxy-piaselenole. Ethyl derivative C_sH₃(OEt):N₂Se. [104°]. This is formed from $C_8H_3(OEt)(NH_2)_2$ and aqueous H_2SeO_3 . Needles torming a yellowish-red solution in H_2SO_4 .

Methyl-piaselenole CH .CH:C.N Se. [73°]. (267° uncor.). Formed from tolylene-diamine and aqueous SeO₂ at 80° (Hinsberg, B. 22, Needles, sl. sol. cold water. SnCl. yields tolylene-o-diamine and Se. Does not react with nitrous acid or with Ac₂O.—B'₂H₂PtCl₆.
Chloro-methyl-piaselenole C₆H₂ClMe:N₂Se.

[150°]. Formed by warming o-tolylene-diamine with SeO₂ and conc. HClAq (Hinsberg, B. 23, 1395). Small needles, volatile with steam.

Naphthopiaselenole C.H. CH:C.N Se.

[129°]. Formed from (aß)-naphthylene-diamine sulphate, aqueous NaOAc, and SeO2 (Hinsberg, B. 22, 866). Needles, sl. sol. water, m. sol. alcohol, v. sol. ether. Conc. H. SO, gives an intense yellow colour. SnCl₂ and HCl give Se and naphthylene-diamine.

Seleno-urea CSe(NH₂)₂. [c. 200°]. S. 11 at 19°. S. (alcohol) 3 at 18°. Formed by passing H.Se into a 2 p.c. solution of cyanamide in ether (Verneuil, C. R. 99, 1154; 100, 1296; Bl. [2] 43, 58, 583). White needles, v. sol. hot water, sl. sol. alcohol and ether. solutions are decomposed by light, especially in presence of an alkali, with separation of

selenium. In presence of air and HClAq it yields (CSeN2H4)2O2HCl, which forms brown orystals with violet reflex, converted by barytawater into Se, seleno-urea, and cyanamide. The compound (CSeN.H.), 02HBr may be formed in like manner. When the 'oxy-triselenourea' hydrochloride is allowed to stand in the acid liquid in which it is formed, it changes into yellow crystalline (CSeN₂H₄)₂Cl₂. H1Aq converts selenoures into (CSeN₂H₄)₂I₂. H₂SO₄ added to a saturated solution of selenourea forms scarlet crystals converted by heating with alcohol (100 pts.) and H₂SO₄ (4 pts.) at 50° into (CSeN₂H₄)₂OH₂SO₄, crystallising in pearly plates. Ethylene-\psi-seleno-urea C3H6N2Se i.e.

CH-Se C:NH. Formed by evaporating a solution of bromo-ethyl-amine hydrobromide (8 g.) with KSeCy (5 g.) to dryness on a water-bath (Baringer, B. 23, 1003). Unstable. Converted by bromine-water into ethylene-\u00fc-urea.-B'HBr. [170°]. Needles B'C₈H₂N₁O₇. [220°]. Needles. Needles. - B'2H2PtCls.

Propylene-ψ-selenourea C,H,N,Se. Obtained in like manner from β-bromo-propyl-amine. B'C,H,N,O, [110°].-B'2H,PtCl. Light-yellow

plates.

Trimethylene - ψ - selenourea C,H,N,Se. Formed from γ -bromo-propyl-amine and KSeCy.—B'HBr. [135°]. White crystals (from alcohol) soon turning red.—B'C₆H₃N₃O₇. [c. 53°]. Small concentric needles.

Seleno-isovaleric aldehyde $C_aH_{10}Se$. [57°].

Crystalline (Schröder, B. 4, 402).

nstalline (Schroder, D. 4, 202). Di-methyl-selenophene Se CMe:CH

Selenoxene. (154° uncor.). Formed by heating acetonyl-acetone with phosphorus pentaselenide P2Se, at 180°. Colourless mobile liquid of slight smell. With isatin and conc. H2SO, it gives a carmine-red colouration. By Laubenheimer's reaction a reddish-brown colour is produced. Benzoyl-formic acid also produces a reddish-brown colouration (Paal, B. 18, 2255).

SELENIOUS ACID H.SeO. Mol. w. not determined. This compound is the acid of the

anhydride SeO₂.

Preparation.—Se is dissolved in hot conc. HNO, Aq, the solution is evaporated to dryness, the residue is dissolved in water, BaOAq is added to ppt traces of H₂SeO₄, the filtrate is evaporated to dryness in a retort, and the residue is heated till SeO, sublimes (Thomsen, B. 2, 598); the pure SeO, thus obtained is dissolved in c. i its weight of hot water, on cooling large crystals of H.SeO, separate (Weber, P. 118, 479). To prevent formation of H.SeO, in the oxidation of Se, Divers a. Shimosé (C. J. 47, 439) recommend to dissolve Se in a large excess of conc. H2SO, instead of using HNO.

Properties .- Large white crystals, resembling nitre; effloresces in air; withdraws water from moist air; S.G. 3.0066 at 15.7° (Clausnizer, B. 11, 2009). Poisonous. The acid crystallises unchanged from solution in aqueous acetic acid, or in aqueous C_sH₆ (Chabrié, A. Ch. [6] 20, 202). H.F. [Se,O²,Aq] = 56,160 (Th. 2, 274). H,SeO₂ is a dibasic acid; this is shown by the existence of two salts M'HSeO, and M'2SeO, (v. SELENITES), and also by the heat of neutralisation, which is given by Thomsen (Th. 1, 172) as follows: this vol. p. 145.

 $[H^2SeO^3Aq, NaOHAq] = 14,770, [H^2SeO^3Aq]$ 2NaOHAq] = 27,020, [H*SeO*Aq, 4NaOHAq, = 27,480. As no derivative of H₁SeO₂ exists corresponding with C.H. SO.OH, and as only one ethyl selenite SeO(OEt), can be obtained, and as the compound SeO.Cl.OEt has been isolated, it appears that the acid is SeO(OH), and not SeO, OH.H (Michaelis a. Landmann, B. 13, 656; A. 241, 150).

Reactions.—1. Heat causes H.SeO, to decompose to SeO, and H.O.—2. Many oxidisable bodies remove O from H.SeO. For instance, sulphur dioxide passed into H.SeO. Aq ppts. Se; the reduction is complete only when the compounds interact in the ratio H.SeO,:280, (Schulze, J. pr. [2] 32, 390); the presence of HCl hastens the reaction (v. Michaelis, J. Z. 6, 88; Rathke, A. 152, 194). When SO2 and H.ScO, interact in other proportions than H₂SeO₃:2SO₂, thioselenic acids are formed (cf. p. 435). Hydrogen sulphide ppts. Se and S in the ratio Se:2S (Divers a. Shimidzu, C. J. 47, 441). Various metals, such as Cu, Fe, Ag, or Zn, also reduce H2SeO3Aq in presence of HCl, with ppn. of Se. H2SeO3Aq is partly reduced by exposure to air containing dust. M. M. P. M.

of selenious acid SELENITES. Salts of selenious acid (H,SeO₃), M₂ISeO₃, and MIHSeO₃. The alkali salts are formed by adding alkalis to H.SeO.Aq and evaporating; most of the other selenites are formed from the alkali salts by double de-

composition.

Selenites give selenides, or metallic oxide and Se, when heated with charcoal. Heated with NH,Cl, out of air, they give a sublimate of Se. Most selenites, except those of the alkalis, are insol. in water.

Many selenites combine with SeO2 to form acid salts; many basic selenites are also known.

Boulzoureano (Bl. [2] 48, 209) found that many selenites can be obtained in well-formed crystals by adding Na, SeO, Aq to solutions of metallic salts, and heating the pp. so formed with very dilute H2SeO2Aq in sealed tubes at 200°; also by dissolving metallic carbonates in dilute H_2SeO_3Aq , adding water, and heating in sealed tubes at 200°. The older investigations of selenites were by Berzelius (v. Lehrbuch) and Muspratt (C. J. 2, 52). Boulzoureano (l.c.; also A. Ch. [6] 18, 289) has made a more thorough investigation of these salts. Nilson (Bl. [2] 21 253; 23, 260, 353, 494) has also prepared and described many selenites.

It has been thought sufficient to give the names of the metals selenites of which have been analysed. Abstracts of B.'s papers will be found in C. J. 54, 220; 60, 262; and an abstract of Nilson's paper will be found in the 3rd Supp. of the first edition of this DICTIONARY, p. 1786. Al, Am, Sb, Ba, Be, Bi, Cd, Ca, Ce, Cr, Co, Cu, Ai, Aii, Se, La, Pb, Li, Mg, Mn, Hg (cf. Cameron B. Davy, *Trans. I*, 28, 146), Ni, K, Ag, Na, Sr, Tl, Th, U, Zn. M. M. P. M. Tl, Th, U, Zn.

SELENO-ANTIMONATES v. ANTIMONATES, vol. i. p. 286. SELENOCYANHYDRIC ACID v. vol. ii. p.

SELENOCYANIDES v. vol. ii. p. 848. SELENOMETAHYPOPHOSPHI**TE**S RIPSe and RII(PSe), v. DIPHOSPHORUS SELENIDE,

SELENOPYROPHOSPHATES R, P,Se, and | R, IP, Se, v. PHOSPHORIC SELENIDE, p. 145. SELENOPYROPHOSPHITES R, IP, Se,

R. 11P. Se. v. Phosphorous selenide, p. 145. SELENOSAMIC ACIDS, SALTS OF. Selenosamic acid SeO(NH2)OH has not been isolated, but the NH, salt of this acid, and also the NH, salt of diselenosamic acid, 2SeO(NH2).(OH)2, have been obtained.

Ammonium selenosamate SeO(NH2)ONH1 is formed by the action of dry NH, on SeO, dissolved in alcohol. It is a wine, conditioned deliquescent salt; very unstable, easily giving disclenosamate. Water solved in alcohol. It is a white, crystalline, off NH, and forming diselenosamate. partially converts this salt into (NH₄), SeO₃.

Ammonium diselenosamate 2SeO(NH₂).OH.ONH₄ is formed by boiling an alcoholic solution of the selenosamate, or by letting the solution stand over HoSO, in vacuo. It crystallises from alcohol in large, deliquescent prisms (v. Cameron a. Macallan, Pr. 44, 112). M. M. P. M.

SELENOTHIO-OXIDE SeSO3 v. Selenion thio-oxide, under Selenion oxides, p. 441.

SELENOTHIO-OXYCHLORIDE SeSO, Cl. v. SELENION THIO-OXYCHLORIDE, p. 441

SELENOTHIOSULPHATES M.ScSO. Thioselenates, under Selenates, p. 434.

SELENOTRITHIONATES M,SeS,O Dithiotriselenates, under Selenates, p. 434.

SELENOTRITHIONIC ACID H.SeS.O. Dithiotriselenic acid, under Selenates, p. 435.

SELENYL BROMIDE and CHLORIDE v. Selenion oxygnomide and Oxychloride, p.

SEMINOSE v. MANNOSE.

SENEGIN v. SAPONIN.

SENNA v. CATHARTIC ACID.

SENNITE is identical with PINITE, the methyl ether of dextrorotatory inosite.

SEPTYL. A name for HEPTYL.

SEQUOIENE $C_{13}H_{16}$. [105°]. (290°-300°). V.D. 5·66 (obs.). Occurs, together with $C_{10}H_{16}$ (155°), S.G. 16 ·852, [α]_D = 24°, and oily $C_{18}H_{20}O_3$ (229°), in the leaves of Sequoia gigantea (Lungo a. Steinkauler, B. 13, 1656). White plates with characteristic smell, volatile with steam; sol. alcohol, ether, benzene, and chloroform.

SERICIC ACID C₁₅H₃₀N₄O₇. Formed by the action of conc. baryta-water on silk (Champion, C. R. 72, 330). Deliquescent, translucent mass.

BAA',... PbA',: pp.
SERIN 0,H,NO, a-Amido-hydracrylic acid?
8.8 at 10°; 5 at 20°. Formed by boiling silk with dilute H.SO₄ (Crämer, J. pr. 96, 76; Barmann, B. 15, 1735; Melikoff, C. C. 1881, 354). Monoclinic crystals, insol. alcohol and ether. Converted by nitrous acid into glyceric acid.-CuA'₂.—HA'HCl: needles, v. e. sol. water.— HA'HNO₃: minute needles.

SERINE v. PROTEÏDS.

SERUM ALBUMEN v. PROTEÏDS. SERUM CASEIN v. PROTEÏDS. SERUM GLOBULIN v. PROTEÏDS.

SESAME OIL. S.G. 20 9191. $\mu_{\rm D} = 1.474$ at 20° (Long, Am. 10, 392). A fatty oil obtained from the seeds of Sesamum orientale. It contains glycerides of oleic and linoleic acids (Pohl, J. pr. 63, 400; Hazura a. Grüssner, M. 10, 247). Gives a raspberry-red colour on warming with HClAq and cane-sugar (Zipperer, Chem.

Zeit. 11, 1600). The oil contains 05 p.c. of sesamin C₁₈H₁₈O₃ [118]. S. (alcohol) ·27 at 20°; 8·07 at 78°. S.G. 1·305. H₂SO₄ containing HNO, colours sesamin green and afterwards bright red (Tocher, Ph. [3] 23, 700).

SEXTYL. Another name for HEXYL.

SHEA BUTTER, obtained in West Africa from the nuts of Bassia Parkii, contains ole in and stearin (Oudemans, J. pr. 89, 205).

SHELLAC v. LAC.

SHIKIMIC ACID C, H10O, i.e.

СH(OH)<СH(OH).СН СH₂.СH(OH) >С.СО₂H. [184°]. S.G. 14 1.599. $\mu_{\infty} = 1.303$ at 14°. $[a]_{D} = -186^{\circ}$ in a 7 p.c. solution. S. (ether) 015 at 23°; S. (alcohol) 2.25. Occurs in the fruit of *Illicium* religiosum (Japanese, shikimi) and Chinese star-anise (Eykman, R. T. C. 4, 49; 5, 299; B. 24, 1278). Crystalline powder composed of minute needles, sl. sol. alcohol and CHCla nearly insol. ether. Levorotatory. Yields poxy-benzoic acid when heated with HClAq. NH, A': crystals.

Dihyďride

 $CH(OH) < CH(OH) \cdot CH_2 > CH \cdot CO_2H$. [175°]. S.G. 2 1·47. $\mu_{00} = 1.324$ at 19°. $[a]_{D} = -18^{\circ}$. S. 14 in the cold. Formed by reducing the acid with sodium-amalgam in presence of HClAq. Monoclinic crystals. Converted by HCl into benzoic acid.

Dibromide

CH(OH).CHBr CBr.CO₂H. [c. 188°] $\mu_{\infty} = 1.295$. [a]₀ = -58° . Formed by adding Br to a cold solution of the acid. Tetrahedra. Converted by moist Ag₂O into C, H_BBrO, [235°], S. 6·3 at 17°, $[\alpha]_D = +22^\circ$, crystallising in hexagonal needles, sl. sol. other, converted by baryta into oxyshikimic acid [156°]

SHIKIMIPICRIN C,H,,O, (?). [200°]. S. 6.2 in the cold. Occurs in the fruit of Illicium religiosum (Eykman, R. T. C. 4, 53). Large

crystals, m. sol. alcohol, sl. sol. ether.

SHIKIMOLE v. SAFROLE. SIEGBURGITE. A fossil resin found near Siegburg. It contains styracin, metastyrene, and some free cinnamic acid (Klinger a. Pitschke, B. 17, 2742).

SIKIMINE. [175°]. A poisonous substance in the seeds of Illicium religiosum (Eykman,

Ph. [3] 11, 1046). Prisms, al. sol. water, ether, and CHCl₁, v. sol. alcohol and HOAc.

SILICA SiO₂. (Silicon dioxide. Silicic anhydride.) Mol. w. not known. S.G. quarts 2:647 to 2:652, tridymite 2:282 to 2:326, amorphous 2.20 at 15.6° (Schaffgotsch, P. 68, 147). S.H. quartz 1787 at ord temp., 305 at c. 400°, constant from 400° to over 1000° (Pionchon, C. R. 106, 1344). H.F. [Si,O'] = 219,240 from amorphous Si; 211,120 from crystalline Si (Troost a. Hautefeuille, C. R. 70, 252).

Occurrence.-Compounds of SiO2 are very widely distributed in large quantities; quartz, flint, chalcedony, jasper, opal, &c., are nearly pure SiO. Silica is the chief constituent of sandstones; felspar, agate, and a vast number of other minerals contain silica. Silica (or silicates) is also found in many plants.

Preparation.—(i) Amorphous silics.-1. Quartz is finely powdered, best by heating to SILICA.

redness and plunging into cold water, and heated with c. 6 times its weight of Na₂CO₃ in a Pt orucible till the whole fuses quietly; the cold mass is treated with water, the solution, when clear, is poured slowly into excess of fairly cone. HClAq, the liquid (after filtration, if necessary) is evaporated to dryness in a Pt dish, the residue is moistened with cone. HClAq, warmed, and allowed to stand for an hour or two; this treatment with acid is repeated two or three times; water is then added and, after warming and standing, the solution is filtered off, the residual SiO₂ is washed with hot water, dried, and heated to rodness.—2. SiF₄ (o. p. 459) is passed into water, the gelatinous SiO₂ which is ppd. is pressed between linen, thoroughly washed, dried, and heated to redness.

(ii.) Crystalline silica.—1. Moist ppd. SiO₂—e.g. the pp. got by passing SiF, into water-is dissolved in boiling NaOHAq, and the solution is heated in a sealed tube; crystals of tridymite (v. infra, Properties) separate below 180°, and crystals of quartz separate above 180° (Maschke, P. 145, 549) .- 2. Small tubes of hard glass are half-filled with solutions of dialysed silicic acid (v. Silica, hydrates of, infra) containing c. 10 p.c. SiO₂, closed by fusion, and heated to 250° for some months; small crystals of quartz are thus obtained (Kroustchoff, C. R. 104, 602).-3. Any hydrate of SiO2 yields crystalline silica by heating in a forge-fire (Fremy, A. Ch. [3] 38, 327).—4. Crystalline SiO₂ is formed by fusing silicates with microcosmic salt (G. Rose, J. pr. 101, 228), or with borax (G. Rose, B. 2, 388). For other methods of preparing crystalline silica v. Rammelsberg (B. 5, 1006), Hautefeuille (C. R. 86, 1133; 90, 830), Sénarmont (A. Ch. 42, 129), Friedel a. Sarasin (Bl. [2] 31, 481), and Daubrée (Ann. M. [5] 12,

Properties.—The mol. w. of silica is unknown, but there is reason to think it is a considerable multiple of that indicated by the formula SiO₂. By applying the cryoscopic method to an aqueous solution of colloidal silicio acid (v. Metasilicio acid, infra) Sabanéeff (J. R. 21, 515; Abstract in C. J. 58, 1215) obtained numbers pointing to silica being a very high polymeride of SiO₂. The great infusibility and non-volatility of silica, especially when this compound is compared with CO₂, make it probable that the molecular formula of silica is nSiO₂, where n has a large value (v. Mendelceff's Principles of Chemistry, vol. ii. p. 93).

Orystalline silica. SiO₂ crystallises as guartz in colourless, transparent, hexagonal, six-sided prisms having the axes-ratio 1:1·0999 (S.G. c. 2·65), and as tridymite in hexagonal forms with the axes-ratio 1:1·631 (S.G. c. 2·3). Crystalline SiO₂ is insol. or almost insol. in alkali solutions; it is attacked by HFAq slowly and without notable rise in temperature.

Amorphous silica is a white, loose, tasteless powder; S.G. 2.2. It dissolves in hot alkali solutions; after continued heating to a high temperature it is less sol. or nearly insol., owing to change into the crystalline form. Dissolves in HFAq, with intumescence and considerable rise of temperature.

Silica is fusible in the O-H flame to a

colourless glass; when fused it may be drawn into extremely fine threads. Cramer (Zeit. fitr angewand. Chem.) finds that quartz is volatile at a temperature whereat Pt boils (v. Abstract in C. J. 64, ii. 164). SiO, is insol. in acids, except in HFAq. It is slightly volatilised in steam (v. Jeffreys, A. 39, 255). Silica is insoluble in molten microcosmic salt (NaNH, HPO).

Reactions.-1. Fused with alkalis, alkali silicates are formed; with alkali carbonates CO, is evolved.—2. Decomposes most solid salts by fusion with them with formation of silicates (cf. Silicates, p. 448). According to Mills a. Meanwell (C. J. 39, 533) SiO₂ does not react with pure Na, SO, or K, SO, even at a very high temperature.—3. SiO, is decomposed by potassium at a red heat, forming K silicate and silicide; it is also reduced at red heat by calcium. strontium, and magnesium (Bunsen a. Matthiessen, A. 94, 111; Phipson, Pr. 13, 217; Parkinson, C. J. [2] 5, 128; Winkler, B. 23, 2642).—4. Heated with carbon and certain metals, SiO₂ is reduced, with formation of silicides of the metals; Ir, Pd, Pt, and Ru react in this way (Boussingault, C. It. 82, 591; cf. Warren, C. N. 60, 5). Au and Ag reduce SiO, only when strongly heated therewith in presence of Na₂SiF₈ and Na (W., l.c.).—5. Dry SiO₂ (prepared from SiF.) which has not been strongly heated reacts with molten metaphosphoric acid to form SiO, P,O, and SiO, 2P,O, 4H,O (Hautefeuille a. Margottet, C. R. 96, 1052; 104, 56; v. Silico-риозгнови охибея, p. 462).—6. Mixed with finely divided carbon and heated in hydrogen sulphide, SiS, is formed (v. Silicon sulphide, p. 462).-7. A mixture of SiO, and carbon heated in chlorins or hydrogen chloride gives SiCl, and CO (v. SILICON TETRACHLORIDE, p. 458); when bromine or hydrogen bromide is used, SiBr, is formed (v. Silicon tetrabromide, p. 457).—8. With hydrogen fluoride, SiF, is obtained (v. Silicon TETRAFLUORIDE, p. 459). -9. Heated to low redness in vapour of boron trichloride, SiCl, and B2O3 are formed (Troost a. Hautefeuille, A. Ch. [5] 7, 476).

SILICA, HYDRATES OF. (Silicic acids.) The hydrates of SiO₂ act as weak acids. The compositions of these hydrates are very uncertain. The silicates nSiO₂, mRO are derivable from hydrates of SiO₂, some of which have been isolated while others are hypothetical (v SILICATES, p. 448).

METABLICIC ACID H₂SiO₂ = SiO₂.H₂O. (Silica monohydrate.) Obtained by the action of moist air on Si(OEt)₁; Si(OEt)₁+3H₂O = SiO₂.H₂O + 4EtOH (Ebelmen, J. pr. 37, 359). Also by dialysing a mixture of Na silicate and excess of HClAq until the liquid in the dialyser is free from chlorides, concentrating by boiling in a flask, allowing to gelatinise, and drying the jolly-like mass over H₂SO₄ for two days (Graham, T. 1861. 183). SiO₂.H₂O is described by Graham as a transparent, glassy, lustrous solid; insol. water.

ORTHOSILICIO ACID H₄SiO₄ = SiO₂.2H₄O. (Silica dihydrate.) This hydrate of SiO₂ has not been isolated with certainty; it is supposed to exist in the solution obtained by dialysing a solution of K or Na silicate with excess of HClAq; but as the compositions of the silicates of K and Na are very doubtful, the argument

based on the supposition that these silicates are ortho- salts—and, therefore, will yield ortho- acid—is not very trustworthy. Various esters of the form Si(OX), exist where X is Me, Et, &c. The solution of SiO, xH₂O, when x is supposed to —2, obtained by dialysing K or Na silicate solution with excess of HClAq till the liquid in the dialyser is free from chlorides, is described by Graham (l.c.) as a clear liquid, which may be boiled in a flask till it contains c. 13 p.c. SiO, without separation of any solid. The liquid soon becomes opalescent on keeping, and after a time sets to a transparent, colourless jelly, which is insol. water, and, dried over H2SO4, gives SiO2H2O (v. METABLLICIC ACID, p. 447). The solution of SiO2xH2O is coagulated by a minute trace of an alkali or alkaline earth carbonate, also by CO,, but not by dil. H. SO, Aq, HNO, Aq, or H.C. H., O. Aq. The solution reddens litmus (cf. Doveri, A. 64, 256; Liebig, A. 94, 373; Karsten, P. 6, 357; Fuchs, A. 82, 119; Struckmann, A. 94, 341; Rose, P. 108, 20; Kühn, J. pr. 59, 1; Fremy, A. Ch. [8] 88, 314; Maschke, J. pr. 68, 234).

Trisilicic Dihydrate $3SiO_2H_2O = H_4Si_3O_8$.

By decomposing K or Na silicate solution by CO, or SiF, by H.O, and drying the gelatinous pp. so formed in vacuo, Fremy (l.c.) obtained a hydrate containing 16.2 to 16.8 p.c. water (3SiO₂.2H₂O requires 16.67 p.c. water). Several naturally occurring silicates may be regarded as derived from this hydrate (v. SILICATES,

infra).

DISILICIO MONOHYDRATE 2SiO₂.H₂O = H₂Si₂O₃. The gelatinous pp. formed by decomposing SiF₄. by water, after drying for six weeks in air at 20°-25°, was found by Merz (J. pr. 99, 1771) to contain from 13.1 to 13.5 p.c. water (the formula

given requires 13.05 p.c. water).

OTHER HYDRATES. By drying the gelatinous pps. obtained by decomposing SiF, by water, or by decomposing alkali silicate solutions by weak acids and washing (v. Kühn, J. pr. 59, 1), solids are obtained of varying and uncertain composition (v. Carnelley a. Walker, C. J. 53, 80); hydrates of fair definiteness agreeing approximately with the formulæ 3SiO₂H₂O = H₂Si₂O₃, 9SiO₂2H₂O = H₄Si₂O₃, and 6SiO₂H₂O = H₂Si₂O₃, have been obtained (Fuchs, A. 82, 119; Gotthave been obtained (Fuchs, A. 82, 119; Gottlieb, J. pr. [2] 6, 185; Merz, J. pr. 99, 1771). For methods of preparing gelatinous pps. of SiO, xHO v. Struckmann, A. 94, 337; Kuhlmann, A. 41, 231; Liebig, A. 94, 374; Guyton-Morveau, A. Ch. [2] 31, 246; Hautefeuille a. Margottet, C. R. 96, 1052. Concerning the absorption of water by SiO v. van Bemmelen R. sorption of water by SiO, v. van Bemmelen, B. 11, 2232; 13, 1466.

Thomsen (Th. 1, 215) has examined the thermal phenomena accompanying the interaction of NaOHAq and SiO2Aq; the SiO2Aq was prepared by adding exactly an equivalent of HCl in dilute solution to Na silicate solution of known composition. He gives the following

tables :-

m	[mNaOHAq,SiO*Aq]	· #	[NaOHAq.xSiO*Aq
ì	2652	1	1353
į	3241	Ī	2615
4	8555	ş	3548
ĭ	4316	I	4316
1	4731	흕	5332
· §	5230	2	648 3
•	5412	В	7956

There seems to be no fixed point of neutral-

Putting [NaOHAq,xSiO²Aq] = x.O isation.

where C and n are constants having the values C=13,410 and n=2.13, the calculated values agree very fairly with the observed so far as data go; if the formula is supposed to be accurate then the heat of neutralisation of SiO_2Aq , when SiO_2 is taken as $= \infty$ in the reaction NaOHAq + SiO2Aq, is = 13,410, which is about the thermal value of the interaction of an acid with one molecular weight of NaOH. affinity of SiO2Aq is almost nil. M. M. P. M.

SILICATES. Compounds of SiO, with basic radicles. The basic radicles of silicates are generally oxygen-containing groups; sometimes they contain negative elements other than O. Silica, like other feebly acidic oxides, combines with bases in many proportions, forming compounds which may be represented as normal salts, and also compounds of the type of basic and acidic salts. The general composition of silicates is given by the formula $nSiO_2mR$, where R = basic radicle. Most of the silicates occurring in rocks vary in composition between the limits SiO, 4MO and 2SiO, MO, where M = a mono- or di-valent metal, and the limits $SiO_2.2M_2O_3$ and $6SiO_2.M_2O_3$ where M=a trivalent metal. The metals most commonly found in these silicates are Al, K, Na, Ca, Mg, Fe, and Mn. A fair number of natural silicates contain Cl or F as part of the basic radicle. Few pure silicates occur in rocks: the siliceous minerals are generally mixtures of isomorphous silicates; hence it is not possible to deduce satisfactory formulæ for naturally occurring silicates solely from the results of analyses of minerals.

Mendeléeff (Principles of Chemistry, 2, 111) compares the siliceous minerals to alloys. Several silicates which occur as mineral species have been formed artificially; the study of the altera-tion-products of natural silicates, and the comparison of silicates with carbon compounds (v. e.g. Mendelceff, l.c., note p. 111) throw light on the constitution of these bodies.

The most important memoirs on the constitution and chemical relations of the silicates are to be found in Groth's Tabellarische Uebersicht der Mineralien nach ihren Krystallographischchemischen Beziehungen (3rd ed.), pp. 89 et seq., and in a series of papers by F. W. Clarke (Am. 10, 120; Am. S. [3] 38, 384; 40, 303; 43, 190), (v. also Clarke in U.S. Geological Survey Bulletins, No. 90 [1892]; also A. C. J. May 1893).

Groth and Clarke both look on the natural silicates as derived from a few fairly simple types. They are very stable compounds; most of them are formed at high temperatures, their number is not very great, and a few typical forms containing a small number of common metals are very widely distributed. Among the commoner silicates are SiO₂2MO, 2SiO₂8MO, SSiO_2MO, where M is very frequently an alkaline earth metal; 3SiO_2R_2O_3, 2SiO_2R_2O_3, 6SiO_2R_2O_3, M_2O, and 3SiO_2R_2O_3, 3MO, where R is Al or Fe, and M is K, Na, or an alkaline earth.

The consideration of the probable constitution of the typical silicates may be approached by seeking to derive these salts from the silicia acida nSiO₂·mH₂O. Metasilicic acid, SiO₂·H₂O, has been isolated; the formula may be written H₂SiO₂ or OSi(OH)₂. Orthosilicic acid, SiO₂·2H₂O = H₄SiO₄ = Si(OH)₄, also probably exists. A few other hydrates of silica have been isolated, but their compositions are not quite definitely established; 2SiO₂·H₂O = H₂Si₂O₃, and 3SiO₂·2H₂O = H₄Si₃O₃, seem to be fairly certain.

Silicates derivable from metasilicic acid O:Si(OH)₂. The typical empirical formule of normal salts of this class are SiO₂M₂O₃, SiO₂MO, 3SiO₂M₂O₃, 4SiO₂R₂O₃MO, and 4SiO₂R₂O₂MO. The atomic ratio of Si to O in these salts is 1:3; this ratio is maintained in the acid salts. Silicates of the forms SiO₂MO and SiO₂M₂O₃ may be represented as basic salts of this class; the atomic ratios of Si to O in these are 1:4 and 1:5. Examples of normal salts of this class are sodium silicate O:Si(ONa)₃, wollastonite O:Si(O₂A₃, and leacite (O:SiO₂)₄Al₂K₂. The basic salts may be regarded as derived from O:Si(OH)₂ by replacing each H by a monovalent basic radicle, such as AlO or ZnOH; for instance, siliceous calamine SiO₂2CnOH,O may be formulated O:Si(OZnOH)₂, and kyanite SiO₂Al₂O₃ is probably O:Si(OAl:O)₂. If only one H is replaced in O:Si(OH)₂ the product will be an acid salt of the metasilicate class; gyrolite, for instance, 3SiO₂2CaO.H₂O may be represented as

O:Si(OH)O.Ca.O.Si.O.Ca.O.(HO)Si:O.

Silicates derivable from hypothetical metadisilicic acid

$$2 \left(\frac{\text{O.Si(OH)}_2}{\text{O.Si.OH.}} - \frac{\text{HoH}}{\text{O}} = \frac{\text{Ho.Si.O.Si.OH.}}{\text{O}} \right)$$
 The

typical empirical formula of normal salts of this class are 2SiO₂M₂O, 2SiO₂MO, 6SiO₂R₂O₃, and 8SiO₂R₂O₂M₂O. The atomic ratio of Si to O in these salts is 2:5; this ratio is maintained in the acid salts. Silicates of the form 2SiO₂2MO.H₂O, wherein the atomic ratio of Si to O is 2:7, may be regarded as basic salts of this class. Petalite 8SiO₂Al₂O₃.Li₂O is probably an example of a normal salt of the metadisilicate class; thus

$$\begin{array}{c} \textbf{0:} \text{Si.0} \\ \overset{\bullet}{\textbf{0}} \\ \textbf{0:} \text{Si.0} \end{array} \hspace{-0.5cm} \text{Al} \begin{array}{c} \textbf{0-} \\ \overset{\bullet}{\textbf{0}} \\ \text{Li0.} \\ \text{Si.0} \end{array}$$

Picrosmine 2SiO₂.2MgO.H₄O may perhaps be a basic salt of this class, (HOMg)O.Si.O.Si.O(MgOH); but it may also be O O

regarded as an acid orthodisilicate (v. infra). One of the soluble glasses, 4SiO_xNa₂O.H₂O, may be written as an acid salt of this class, HO.Si.O.Si.ONa.

Silicates derivable from orthosilicic acid Si(OH),. The typical empirical formulæ of normal salts of this class are SiO.2M.O., SiO.2M.O., SiO.2M.O., and SSiO.2M.O., SiO.3M.O. The atomic ratio of Si to O in these salts is 1:4; this ratio is maintained in the acid salts. Salts of the forms SiO.4MO.2H.O and SiO.2M.O., atomic ratio of Si to O-1:8, may be formulated as basic orthovolume.

silicates. Olivine SiO..2MgO, and sirconits
SiO..ZrO. are likely normal salts of this class;
Mg<0>Si<0>Mg and Si(0,Zr). Xenolite
SSiO..2Al_O, is also a normal orthosilicate;

iO₂.2Al₂O₃, is also a normal orthosilicate; AlO₃:Si.OO₂:Si:O₂O.Si:O₃Al.

Al Al

Andalusite SiO₂.Al₂O₃ is probably partly a basic salt and partly a normal salt of this class; $Si(O_3Al).O.AlO$. Dioptase SiO₂.CuO.H.O may be formulated as an acid salt of the orthosilicate class; $Si(OII)_{x}O_2Cu$.

Silicates derivable from hypothetical orthodisilicic acid

2Si(OH),-H₂O= (HO),Si.O.Si(OH),. The typical empirical formulm of normal salts of this class are 2SiO₂M₂O, 2SiO₂MO, 2SiO₂MO, and 4SiO₂M₂O, 3M₂O. The atomic ratio of Si to O in the normal and acid salts is 2:7. Serpentine 2SiO₂:3MgO is probably a normal salt of this class, (MgO₂)Si.O. Si(O₂Mg). Okenits O.Mg.O

2SiO..CaO.2H.O seems to be an acid salt of this class, HO.Si.O.Si(OH), picrosmine O.Ca

2SiO_x2MgO.H₂O may also be an acid orthodisilicate, MgO_w(HO)Si.O.Si(OH).O_xMg; but it may be formulated as a basic metadlisilicate (v. stopra).

Silicates derivable from hypothetical orthotrisilicic acid. By removing 2H₂O from 3Si(OH), the acid

(HO)₃Si.O.Si.O.Si(OH)₃ would remain. Some (OH)₂

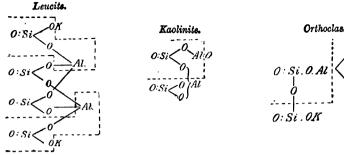
natural silicates may be looked on as salts of this hypothetical acid; mecrschaum, for instance, 3SiO,2MgO.2H₂O, may have the formula MgO₂(HO)Si.O.Si.O.Si(OH).O₂Mg. Groth (l.c.), (OII),

however, thinks it is not necessary to call in a hypothetical trisilicic acid to express the composition of silicates.

Some silicates which do not fit into any of the classes already mentioned may be looked on as derived from more than one of the acids simultaneously. Others may be represented as salts of hypothetical acids formed by climinating water from one or other of the acids that have been mentioned. Orthoclass, 65iO_Al_O_xK_O, may be taken as an example of a silicate derived, according to Groth (l.c.), from two acids, metasilicic and metadisilicic; thus

$$0.Si.< \stackrel{O}{\bigcirc} > Al.O.Si.O.Si.O.K.$$
 Groth urges that

this formula is in keeping with the facts (1) that felspars of the orthoclass class are derived from silicates, such as leucite, which are metasilicates, and (2) that orthoclass readily yields kaolinite 2SiO. Al.O., which may be a basic metadisilicate. Writing leucite as a metasilicate, and kaolinite as a basic metadisilicate, and kaolinite as a basic metadisilicate, it is seen that both contain the group O.SiCO. Al., a group which is represented as present in orthoclass also. Thus



The group common to the three silicates is indicated by the dotted lines. If HHO were removed from orthodisilicic acid the product

Again, $4\text{Si}(OH)_4 - 3HO\Pi = \text{Si}_4O_3(OH)_{10}$ $[(OH)_2\text{Si}.O.\text{Si}.O.\text{Si}.O.\text{Si}(OH)_3]$; if H_2O were $(\ddot{O}H)_2(\ddot{O}H)_2$ removed from this hypothetical orthotetrasilicic acid, there would result Si,O,(OH), O:Si.O.Si.O.Si.O.Si(OH)37; and from this ĊΗ нонононо might be derived the following acids:-[O:Si.O.Si.O.Si.O.Si:0] он онононон он and Si,O,(OH), ононон O:Si.O.Si.O.Si.O.Si:O Ö Si₂O₂(OH)₂

Some of the natural silicates may be represented as derived from one or other of these acids. Acids containing OH yield Cl derivatives wherein OH is replaced by Cl, generally by interaction with PCl. As Cl derivatives of some of the hypothetical silicic acids are known, the existence of these derivatives is an argument in favour of representing certain silicates as salts of acids which have not themselves been isolated. Thus, besides SiCl., which corresponds with orthosilicic acid Si(OH), and SiCl., SH, which is derived from the hypothetical orthothosilicic acid, there exists Si,OCl, corresponding with ortho-disilicic acid Si,O(OH), Si,O,Cl, corresponding with ortho-tetrasilicic acid Si,O,(OH), soli,O,Cl, corresponding with the acid Si,O,(OH), and Si,O,Cl, corresponding with the acid Si,O,(OH), to supra).

Clarke (l.c.), recognising the two main divisions of ortho silicates and meta-silicates, seeks to derive the various members of each class as

far as possible from the typical normal aluminium salts by substituting metals or basic groups, wholly or partially, for Al.

Orthosilicates. Clarke starts with normal Al orthosilicate, 3SiO_x2Al₂O₃=Al₄(SiO₄)₃, which forms the mineral species xenolite; allied to xenolite are fibrolite SiO_xAl₂O₃=Al₂SiO₄, topaz SiO_xAl₂O₅P₂=Al₂SiO₁P₂, muscovite 6SiO_x3Al₂O₃K₂O₂2H₂O = 2Al₃KH₂(SiO₄)₃, paragonite, corresponding with muscovite but containing Na in place of K, and eucryptite 2SiO_xAl₂O₃Li₂O = 2AlLiSiO₄. By trebling the formulæ given for fibrolite and topaz, using the simplest formula given for muscovite and paragonite, and trebling the simplest formula given for eucryptite, Clarke arrives at the following comparable formulæ for the six silicates:—

These silicates are represented as derived from normal Al orthosilicate by substituting either metals, metals and hydrogen, or basic groups, for Al. If such substitution is carried further a series of silicates may be obtained, for some of which Clarke suggests the following formulæ:—

$\begin{array}{l} Dumortierite.\\ \text{O.Si:}O_{3}\text{:}(AlO)_{3}\\ \text{O.Si:}O_{3}\text{:}(AlO)_{2}\\ \text{O.Si:}O_{3}\text{:}Al \end{array}$	$\begin{array}{c} \textit{Grossularite.} \\ \text{Al} \left\{ \begin{array}{c} \text{O.Si:O_s} \\ \text{O.Si:O_s} \end{array} \right\} \\ \text{O.Si:O_s:Al} \end{array}$
$\begin{array}{c} \textbf{Prehnite.} \\ \textbf{O.Si:} \textbf{O.si:} \textbf{O.si:} \textbf{CaH} \\ \textbf{O.Si:} \textbf{O.si:}$	$\begin{array}{c} \textbf{Natrolite.} \\ \textbf{O.Si:O_s:NaH,} \\ \textbf{O.Si:O_s:NaH,} \\ \textbf{O.Si:O_s:Al} \end{array}$

Fibrolite alters by hydration, giving westanite 4SiO, 3ALO, HLO = 2Al, HSi,O, kaolinite 2SiO, Al,O, 2HLO = Al, Si,H,O, and montmorillonite 4SiO, Al,O, 7H,O = 2AlSi,H,O, Clarke suggests the following formulæ for these products of alteration of fibrolite;—

If it is supposed that two groups Al(O.Si:O₃), combine with elimination of one of the O.Sio, groups (= SiO₂+2O), then there remains the

a number of silicates, especially iron and magnesian micas, may be derived. Thus-

$$\begin{array}{c|c} \textbf{Annite.} & \textbf{Sodalite.} \\ \textbf{O.Si:O_3:FeH} & \textbf{Al} \begin{cases} \textbf{O.Si:O_3:FeH} \\ \textbf{O.Si:O_3:FeH} \\ \textbf{O_2:Si:O_2:K_2} \\ \textbf{Al} \begin{cases} \textbf{O.Si:O_3:FeH} \\ \textbf{O.Si:O_3:FeH} \\ \textbf{O.Si:O_3:FeH} \\ \textbf{O.Si:O_3:FeH} \\ \textbf{Nosean.} \\ \end{array} \\ \textbf{Nosean.} \end{array}$$

Noscan. O.Si:Oa:Nas 0.Si:0,:Al Oz:Si:Oz:Nag Al O.Si:O.Al (SO.Na

Clarke (Am. 10, 126) suggests that ultramarine may be analogous to these silicates;

thus,
$$\begin{array}{c}
A1 \\
O.Si:O_3:Na_3\\
O.Si:O_2:Na_3\\
O.Si:O_2:Na_3\\
A1 \\
O.Si:O_3:A1\\
S.Na
\end{array}$$

The metasilicates are considered by Clarke (l.c.) in a way similar to that whereby he has elucidated the orthosilicates. The startingpoint is Al metasilicate, Al₂(SiO₃)₃. This salt is not itself known. The formula may be

Inasmuch as many metasilicates of the form AlM(SiO₃)₂, where M=Li, K, Na, H, may be simply derived from the first, but not from the second, formula given for Al2(SiO3)3, thus O:Si:O,:Al.O.Si:O OM, Clarke thinks that the first

formula may be taken to represent Al₂(SiO₃)₃. Several other metasilicates may be formulated as derived from the Al salt by substituting metals or basic groups for one of the AlSiO, groups; or many metasilicates containing divalent metals may bem ore simply derived from the normal form MuSiO,, by doubling this formula and then replacing one MII in the formula MIIMII(SiOa), by other metals or by basic groups.

The species albite and orthoclase, AlMSi,O, are looked on by Clarke as derived from the

Al salt of the acid H₄Si₂O₈ (-8SiO₂·2H₄O), which acid has probably been isolated, in the same way as many orthosilicates are derived by him from the normal Al salt Al, (SiO,) s. The triclinic felspars are generally thought to consist of mixtures ranging between the limits marked by albite AlNaSi3O8, and anorthite Al2Ca(SiO4)2; if these formulæ are trebled and written thus

Anorthite.

$$\begin{array}{l} \mathbf{A}\mathbf{l} \left\{ \begin{array}{l} \mathbf{O}.\mathbf{Si}:\mathbf{O}_3 = \mathbf{Ca}_2 = \mathbf{O}_3:\mathbf{Si}.\mathbf{O} \\ \mathbf{O}.\mathbf{Si}:\mathbf{O}_2:\mathbf{A}\mathbf{l} & \mathbf{Al}:\mathbf{O}_3:\mathbf{Si}.\mathbf{O} \\ \mathbf{O}.\mathbf{Si}:\mathbf{O}_3:\mathbf{A}\mathbf{l} & \mathbf{Al}:\mathbf{O}_2:\mathbf{Si}.\mathbf{O} \end{array} \right\} \mathbf{A}\mathbf{l} \\ \mathbf{A}\mathbf{l}bite. \end{array}$$

O.Si₃O,:Na₃ O.Si₃O,:Al both silicates repre-O.Si,O,:Al

sented by strictly comparable formulæ. also draws attention to the fact that the four silicates muscovite 6SiO₂.3Al₂O₃.K₂O.H₂O, garnet 3SiO2.Al2O3.3CaO, orthoclase AlKSi3O3, and tourmaline 4SiO2.Al2O3.2M2O3(or 6MO)B2O3, are very frequently associated in granite veins. By halving the formula for muscovite and writing it Al3KH2(SiO4)3, writing the formula for garnet Al2Ca3(SiO4)3, trebling the formula for orthoclase and writing it Al, K, (Si,O,), halving the formula for tourmaline and writing it AlR (BO2)(SiO4)29 where R is a metal or group equivalent to Al. very suggestive relationships are disclosed between the four silicates; thus

$$\begin{array}{lll} \textit{Muscovite.} & \textit{Garnet.} \\ \text{Al} \left\{ \begin{matrix} \text{O.Si:O}_s \text{iKH}_2 \\ \text{O.Si:O}_s \text{iAl} \\ \text{O.Si:O}_s \text{iAl} \end{matrix} \right. & \text{Al} \left\{ \begin{matrix} \text{O.Si:O}_s \\ \text{O.Si:O}_s \\ \text{O.Si:O}_s \text{iAl} \end{matrix} \right. \\ \textit{Tournaline.} & \textit{Orthoclase.} \\ \text{Al} \left\{ \begin{matrix} \text{B:O}_2 \\ \text{O.Si:O}_s \text{iR} \\ \text{O.Si:O}_s \text{iR} \end{matrix} \right. & \text{Al} \left\{ \begin{matrix} \text{O.Si}_s \text{O}_s \text{iA} \\ \text{O.Si}_s \text{O}_s \text{iAl} \\ \text{O.Si}_s \text{O}_s \text{iAl} \end{matrix} \right. \end{array} \right.$$

In Am. S. for November 1889 ([3] 38, 384), and A. C. J. May 1893, Clarke has applied the substitution method, as sketched above, to the mica group of silicates, and in the same journal for March 1892 (Am. S. [3] 43, 190) he has applied the same method to the chlorite group.

The micas all fall within the limits of composition indicated by the two formulæ Al₃Ri₃(SiO₄)₃ and AlR₀'(Si₂O₈)₃. The first formula is derived from Al₄(SiO₄)₃ by substituting Al by one trivalent or three monovalent basic radicles; the esecond formula is derived from the hypothetical salt Al₄(Si₈O₈), by substituting one, two, or three Al atoms by equivalent basic radicles. When F is present it is regarded as forming part of one or other of the monovalent groups Mg.F or Al:F₂. If the ratio of O to Si is greater than 40:Si(SiO₄) the excess of O is looked on as combined with metal to form a basic group, such as Al:O; if the ratio of O to Si is less than 40:Si the group Si,O, is supposed to be present. The micas are all capable of being represented as isomorphous mixtures of various constituents, the compositions of which fall within the limiting formulæ.

The chlorites are treated by Clarke (l.c.) similarly to the micas. In Am. S. [3] 43, 198 he gives the following general formulæ which summarise the composition of the chief micas

and chlorites :-

Normal orthosilicate Al (SiO,) ..

Micas. Muscovite Al₃(SiO₄)₃R₃. Normal Biolite Al₂(SiO₄)₃R₃. Normal Phlogopite Al (SiO) Rg. Clintonite RII: O.: Al(SiO.)R...

Normal orthosilicate Mg, (SiO,)20 Chlorites. Aphrosiderite Mg3(SiO4)2R2. $\begin{cases} \mathbf{Mg}_2(\mathrm{SiO}_4)_2\mathbf{R}_4, \\ \mathbf{Mg}(\mathrm{SiO}_4)_2\mathbf{R}_6. \end{cases}$ **Orthochlorites** Amesite O:Mg,(SiO,)R2.

Preparation of silicates.-Alkali silicates are formed by dissolving moist amorphous SiO, in boiling solutions of alkalis or alkali carbonates. also by fusing SiO2 with alkalis or with alkali salts of acids which volatilise by heat. Many other silicates are obtainable by double decompositions between alkali silicates (which are sol. water) and metallic salt solutions; also by heating various metallic oxides or carbonates

with SiO2.

Some naturally occurring silicates have been prepared by the following methods:-1. Emerald Be, SiO, clivine Mg, SiO, and enstatite MgSiO, by heating SiO, with BeO or MgO mixed with boric acid in a porcelain-oven, till the boric acid volatilised (Ebelmen, A. Ch. [3] 22, 211).—2. Anorthite Al₂Ca(SiO₄)₂, abradorite 3SiO_Al₂O₃,K₂O, and oligoclase 9SiO₂,2Al₂O₃,2K₀O, by strongly heating SiO₂ with K₂CO₃ in boric acid, or by adding CaO to molten boric acid and SiO, at a very high temperature (E., C. R. 32, 710; Fouquet a. Lévy, C. R. 90, 620).—3. Zirconite ZrSiO,, and kyanite (AlO), SiO3, by heating to redness ZrO2 in vapour of H₂SiF_s, or SiO₂ in vapour of AlF_s (Deville a. Caron, A. Ch. [4] 5, 113; Fremy a. Feil, C. R. 85, 1032).—4. Enstatite MgSiO_s, and leucite Al₂K₂(SiO₃)₄, by heating Mg, or Al mixed with KOH, to low redness in H and SiCl₄ vapour (St. Meunier, C. R. 90, 349, 1009).—5. Ortho-clase AlKSi₂O₈, albite AlNaSi₂O₈, petalite AlLi(Si₂O₈)₂, by fusing a mixture of Al₂O₃, SiO₂, and tungstate or vanadate of K, Na, or Li; with and tungstue of vanadate of R, Na, of Li; with excess of Al₂O₂ leucite Al₂K.(SiO₂), is obtained (Hautefeuille, C. R. 90, 378, 541).—6. Orthoclase AlKSi₂O₈, by heating Al₂O₂ and SiO₂, in the ratio Al₂O₂:6SiO₂, with KVO₂ (Hautefeuille a. Perrey, C. R. 107, 786).—7. Phenacite Be₄(SiO₄) mixed with a lithia felspar, quarts, and tridymite, was obtained by heating for fifteen days at 600°-700° a mixture of 4.8 g, 8iO., 1.5 g, BeO, 20 g, LiVO., and 1.5 g, Li₂CO., (H. a. P., C. R. 106, 1800).—8. Crystals of emerald heating a mixture of 12.506 g. SiO₂, 3.58 g. Al₂O₃, 2.64 g. BeO, 6 g. Cr₂O₃, and 92 g. acid Li molybdate (ratio = Li₂O:2½MoO₃); the mixture was placed in a Pt crucible, which was heated in a muffle to low redness for twenty-four hours, when the temperature was raised to 800° and kept thereat for fourteen days. The product was washed with water.

Properties and Reactions of Silicates.—All silicates except those of the alkalis are insol. water; most of them are also insol. dil. acids. For the action of water on certain silicates when the mixtures were rapidly rotated in cylindrical

vessels v. Daubrée (C. R. 64, 839). Many silicates are decomposed by evaporation with HClAq or HNO, Aq, with separation of SiO, xH,O, which is changed to SiO, by heating somewhat above 100°. Some of those silicates which are not thus decomposed are acted on, with separation of SiO₂.xH₂O, by evaporating with 8 parts conc. H₂SO₄ and 3 parts water. Almost all silicates are decomposed by heating with conc. HClAq or H.SO, and a little water in sealed tubes to c. 200°. Heating with conc. HFAq, or in HF gas, decomposes silicates with formation of SiF4; when a silicate is mixed with 3 parts AmF or 5 parts powdered CaF2, and the mixture well moistened with H2SO4, and heated in a Pt dish. all the Si is given off as SiF. Fusion of a finely-powdered silicate with 4-6 parts mixed K2CO, and Na2CO, gives K and Na silicate (which is sol. water), while the metal remains as oxide. Silicates which contain F generally lose HF or silicofluoride when strongly heated; any alkali or alkaline metal, or Fe or Al, which was present in the silicate in combination with F remains as oxide (Rammelsberg, W. 7, 146). Clarke a. Schneider (Am. S. [3] 40, 303, 405, 452) have studied quantitatively the interactions of various natural silicates with HCl gas and also with HClAq; their results make it probable that in the magnesian silicates gaseous HCl attacks only the Mg which is present as the basic monovalent radicle Mg.OH.

The following account of individual silicates does not refer to silicates which occur in rocks. but only to those salts which have been prepared in the laboratory; the chief naturally occurring silicates that have been prepared artificially are mentioned under the heading

artinially are mentioned under the heading Preparation of silicates (supra).

Barium silicates. The normal meta-salt BaSiO₃.xH₂O is formed by ppg. dil. Na₂SiO₃Aq (v. Sodium silicates, infra) by dil. BaCl₂Aq or Ba(NO₃)₂Aq; not quite insol. hot water, easily sol. dil. HClAq; retains water at 100° (Ammon, J. 1862. 138). Lefort (J. Ph. [3] 39, 31) says that BaO.3SiO₂. 3aq (? BaH_Si₂O₈. 2aq) is formed by ppg. a dil. Ba salt solution by a dil. solution by ppg. a dil. Ba salt solution by a dil. solution

of 9SiO,.2Na,O.

Calcium silicates. The compounds 3SiO₂.CaO, 2SiO₂.CaO, 3SiO₂.2CaO, and SiO₂.2CaO, are said to be produced by very strongly heating mixtures of quartz and marble in the proper proportions. By adding CaCl₂Aq to solution of 3SiO₂.K₂O, a gelatinous pp. is obtained which becomes crystalline after a botained which becomes crystainine after a time; dried at 100°, the solid is said to be 3SiO_x.CaO. 2aq (? CaH_xSi_xO_x.aq). The normal mcta-salt CaSiO_x is said to be formed by ppg. Na_xSiO_xAq by dil. CaCl_xAq (v. A., l.c.; L., l.c.). Calcium silicates form the bases of most hydraulic cements (v. Cements in Dictionary of APPLIED CHEMISTRY).

The normal meta-salt Cerium silicate. Ce(SiO₃)₂ is said to be formed by fusing Ce oxychloride with SiO₂ and CaCl₂ or NaCl (Didier, C. R. 101, 882).

Cobalt silicate. The normal ortho- salt Co₂SiO₄ is formed, according to Bourgeois (C. R. 108, 1177), by very strongly heating CoO with

CoCl, and a large excess of SiO₂.

Nickel silicate. Normal ortho-salt Ni₂SiO₄

formed like the Co salt (B., I.c.).

Magnesium silicate. The gelatinous pp. obtained by adding MgCl₂Aq to solution of 8SiO₂.K₂O is said to be 2SiO₂.MgO.2H₂O (? MgH₂(SiO₃)₂, aq acid meta-salt) (Heldt, J. pr. 94, 129, 157). The normal meta-salt MgSiO₂.xH₂O is obtained, according to Ammon (l.c.), by ppg. Na₂SiO₂Aq by dil. MgCl₂Aq. Potassium silicates. The normal meta-salt

K₂SiO₂ is prepared by fusing 1 part SiO₂ with 2½ parts dry K₂CO₃. If this product is dissolved in a little water, and alcohol is added, a gelatinous pp. is formed, which, if slightly washed and squeezed, is said to be 4SiO₂-K₂O; but Fremy (J. 1856. 353) gives the composition 9SiO₂-2K₂O aq to this pp., and this is confirmed

by Lefort (J. 1861. 205).

The name potash water-glass is given to the mixture of K silicates obtained by fusing together quartz and pearlash in a proportion about equal to 4SiO_xK_xO. Water-glass is a clear transparent solid, like glass; it is completely sol. hot water; a conc. solution, with c.28 p.c. silicate, is syrupy, somewhat turbid, and has S.G. 1.25. The solution is decomposed by acids, even by CO_x with separation of SiO_xxH_xO; alkaline carbonates and chlorides, especially AmCl, ppt. SiO_xxH_xO; BaO, SrO, CaO, Al.O_x, and PbO decompose the solution, forming a double silicate with the whole of the silica and a portion of the K. The solution yields pps. with solutions of most of the salts of earth metals and heavy metals. Water-glass is also formed by boiling SiO_x with KOHAq under pressure. Sodium silicates. The normal meta-salt

Na,SiO, is prepared by fusing 1 part SiO, with 13 parts dry Na₂CO₃. The salt is obtained with 8H,O, in monoclinic crystals, by dissolving SiO, in an equivalent quantity of NaOH in solution, decanting, evaporating, as much as possible out of contact with air, till Na,CO, begins to settle out, cooling to -22°, stirring till the whole solidifies, straining from motherliquor, dissolving in a little water, and allowing to stand (Ammon, J. 1862. 138; cf. Ordway, Am. S. [2] 40, 186). By adding freshly ppd. AlO₃H₄ to a boiling solution of Na₂SiO₃ and NaOII, the double salt Na₂SiO₃Al₄(SiO₄)₃ is obtained; and the salt Na, SiO, Al, (SiO,) is ppd. by adding Na, SiO, Aq to a hot solution of alum (A., l.c.). Mixtures of Na silicates are known as soda water-glass (cf. supra, Potash water-glass). For effect of time on composition of solutions of Na silicates v. Kohlrausch (Z. P. C. 12, 773).

Strontium silicate. The normal meta-salt SrSiO₂ is said to be formed by adding Na,SiO₃Aq to dil. SrCl.Aq (Ammon, l.c.).

Thorium silicates. The normal ortho-salt

Thorium silicates. The normal ortho-salt ThSiO₄ and the normal meta-salt Th(SiO₃), are formed, according to Troost a. Ouvrard (O. R. 105, 220), by fusing ThO₂ with SiO₂ and CaCl₂ and treating with dil. HClAq. ThSiO₄ is not isomorphous with ZrSiO₄ (T. a. O., l.c.).

Zine silicates. The normal meta-salt ZnSiO₈

Zinc silicates. The normal meta-salt ZnSiO₂ is obtained in rhombic crystals by ppg. ZnSO₄Aq by Na₂SiO₂Aq, and strongly heating the dried powith boric acid for several days (H. Traube, B.

26, 2735).

A systematic arrangement of the naturally occurring silicates will be found in Groth's Tabell. Uebersichte, pp. 108-151 [Brd ed.].

M. M. P. M.

SILICIC ACIDS v. SILICA, HYDRATES OF, p. 447).

BILICIDES. Binary compounds of Si with metals. These compounds are formed (1) by heating amorphous Si with metallic chlorides in presence of such a reducer as Na; (2) by heating K₂SiF₆ with metals; (3) by electrolysing a mixture of an alkali fluoride with a metallic oxide; (4) by heating metals with Si (v. Aluminum, Cerbum, Copper, Iron, Magnesium, Manganese, Nickel, Platinum, silicides of). M. M. P. M.

SILICO-BORATES. Certain minerals consist of compounds of silicates and borates; the name silico-borate is sometimes applied to such O:Si.O.

compounds. Datholite O.Si.O Ca.CaB₂O₄, aq,

and botryolite, the same formula with 2aq, are examples of borosilicates. Tourmalines Al(BO₂)(SiO₄)₂RI₅ are also silico-borates (R¹ may be replaced by its equivalent of R¹¹).

M. M. P. M. SILICO-BROMOFORM SiHBr₃. (Silicon hygen bromide. Tribromo-silico-methane.) drogen bromide. Obtained, not quite pure, by Baff and Wöhler (A. 104, 99) by leading HBr gas over heated Si, distilling the product, shaking with Hg, and distilling again. Gattermann (B. 22, 193) obtained pure SiHBr, as follows. Crude Mg silicide, prepared as described under Silicon, Preparation, No. 1 (p. 456), is freed from MgO by powdering, adding little by little to HClAq (1:2), shaking with this acid for some hours, washing till the wash-water is neutral, and drying thoroughly. The Si thus obtained is heated in a tube in a stream of HBr, the tube being connected with a well-cooled receiver; the details and precautions described under Silicon TETRICIDENTIE, Preparation, No. 2 (p. 458) must be observed. The HBr required may be made by the action of H.SO, Aq on KBr; G. used a cold mixture of 45 c.c. conc. H2SO, and 15 c.c. water, and let this drop on to 75 g. KBr; he dried the gas by H₂SO₄. The liquid is distilled, and then fractionated till a portion boils at 115°-117°; most of the remainder boils at c. 153° and is SiBr. A colourless liquid, boiling 115°-117°; S.G. 2.7 at ordinary temperature (G., l.c.). Fumes much in air, and takes fire, probably because the heat produced in the decomposition of a portion by the moisture of the air suffices to start rapid oxidation (G., l.c.). Ice-cold water forms silico-formic anhydride (4. v., p. 455). Combines with PH3, when compressed, to form a solid, unstable compound (Besson, C. R. 112, 530). M. M. P. M.

SILICO-CHLOROFORM SHCI, (Silicon hydrogen chloride, Trichloro-silico-methane.)
Mol. w. 135-41. V.D. 67.

Formation.—1. Dry HCl gas is passed over Si heated below redness; the product is condensed in a flask in a freezing mixture and fractionated (Friedel a. J. adenburg, A. 143, 118; cf. Buff a. Wöhler, A. 104, 94).—2. Dry HCl gas is passed over siliceous pig-iron containing 15 p.c. Si (Warren, C. N. 60, 158).

Preparation.—Si, prepared by reducing sand by Mg (v. Sillicon, Preparation, No. 1, p. 456) and removing MgO as described under Sillico-BROMOFORM (supra), is carefully heated in a stream of dry HCl gas in a tube connected with a receiver surrounded by a very good freezing mixture. The directions given for preparing SiCl, must be carefully followed (v. Silicon tetrachloride, Preparation, No. 2). [Gattermann recommends to make the HCl in a Kipp's generator, using conc. H₂SO₄ and fused NH₄Cl.]
The liquid in the receiver is fractionated from a flask with a side tube 75 cms. long; if this is done, no condenser is required; the flask must be warmed by water at 90°, if a naked flame is used explosions of part of the SiHCl, may result (Gattermann, B. 22, 190).

Properties and Reactions .- A colourless, mobile liquid, with a very disagreeable smell; boils at 35°-39° (F. a. L., l.c.). Non-conductor

of electricity.

The vapour takes fire very easily in air, e.g. by bringing a hot glass rod to the mouth of a vessel in which a little SiHCl, has been shaken. Mixture of the vapour with air is explosive. Decomposed to Si and HCl by passing through a narrow tube heated to redness. Water at 0° forms Si₂O₃H₂ (v. Silicoformic anhydride, p. 455) and HCr; at the ordinary temperature SiO,xH,O, HClAq, and H are produced. Chlorine reacts at ordinary temperatures, forming SiCl, and HCl; bromine reacts similarly at 100°. Alcohol produces SiH(OEt), (v. SILICON TETRA-HYDRIDE, Preparation, No. 1, p. 460). Combines with phosphorus hydride, under pressure, to form a solid unstable body (Besson, C. R. 112, 530).

M. M. P. M. 530).

SILICO-ETHANE, PENTA-BROMO- DERI-VATIVE OF, Si.HBr. (Disilicon hydrogen pentabromide. Pentabromo-silico-ethane.) In pentabromide. Pentabromo-silico-cihane.) In making SiBr, by passing SiH, into Br, Mahn (J. Z. 5, 163) obtained a solid in the form of white needles, melting at 89° and boiling (out of contact with air) at 230°, and giving numbers on analysis agreeing with the formula Si. HBr. Takes fire when heated in air. M. M. P. M.

SILICO-FLUORHYDRIC ACID H.SiF,Aq. (Hydrofluosilicic acid.) Known only in aqueous solution.

Preparation.—SiF₄, prepared by the interaction of CaF₂, SiO₂, and H₂SO₄ (v. Silicon TETRAFLUORIDE, p. 459), is passed into water, the exit tube dipping beneath a little Hg in the bottom of the vessel which contains the water; the vessel is shaken frequently to break up the gelatinous silica which forms in the water; when the liquid becomes thickish from separated silica, it is filtered through linen, the silica is pressed, and more SiF, is passed into the filtrate, as before.

(1) SiF₄ + 3H₂O + Aq = SiO_{...}H₂O + 4HFAq; (2) 4HFAq + 2SiF₄ = 2H₂SiF₆Aq. The solution of H2SiF6 may be evaporated in a Pt vessel till

it contains c. 34 p.c. of the acid.

To prepare the acid solution on a large scale, Tessié du Mothay recommends to fuse a mixture of fluorspar, silica, and charcoal in an oven, and to lead the gas that is given off through condensers containing water; c. 68 p.c. of the F in the fluorspar is thus obtained as H₂SiF_s (C. C. 1868. 432).

Properties and Reactions. - H2SiF4Aq is a strongly-acid liquid, smelling like HClAq, and burning the skin. If kept in glass vessels it gradually withdraws alkali, lime, and iron

oxide (H. Rose, P. 80, 408). Truchot (C. R. 98, 821) gives H.F. [SiF',2HFAq] = 17,000 (cf. Sabatier, A. Ch. [5] 22, 91). Thomsen gives [SiO'Aq,0HFAq] = 32,800; and the heat of neutralisation as [H2SiF6Aq,2NaOHAq] = 26,600 (Th. 1, 236). The following table is given by Stolba (J. pr. 90, 193):-

S.G. P.c. S.G. H_SiF_Aq H_SiF_ H_SiF_Aq	P.o. H.Sif.
1.0040 0.5 1.1559	18
1.0080 1 1.1653	19
1.0161 2 1.1748	20
1.0242 3 1.1844	21
1.0324 4 1.1941	22
1.0407 5 1.2038	23
1.0491 6 1.2136	24
1·0576 7 1·2235	25
1.0661 8 1.2335	26
1.0747 9 1.2436	27
1.0834 10 1.2537	28
1.0922 11 1.2639	29
1.1011 12 1.2742	30
1.1100 13 1.2846	81
1.1190 14 1.2951	32
1·1281 15 1·3056	33
1.1373 16 1.3162	84
1.1466 17	

The S.G. for any percentage of H_2SiF_6 , when n = number of half-per-cents., is given by the formula; S.G. = $1 + n \cdot 004 + \frac{n(n-3) + 2}{n(n-3) + 2}$ 100000

By passing SiF, into fairly conc. HFAq until the liquid is saturated, hard, colourless, very hygroscopic crystals of the hydrate H.SiF. 2H.O separate; the crystals melt at 19°, and decompose at a higher temperature (Kessler, C. R. 90,

H.SiF.Aq acts as a dibasic acid (the heat of neutralisation confirms this), giving salts M12SiF6 and MuSiFa; with excess of a strongly basic metallic oxide it forms metallic fluoride and $\begin{array}{l} \mathrm{SiO}_{2}\mathrm{\cdot H}_{2}\mathrm{O} - \mathrm{thus} \\ \mathrm{\cdot H}_{2}\mathrm{SiF}_{0}\mathrm{Aq} + 3\mathrm{K}_{2}\mathrm{O} - \mathrm{SiO}_{2}\mathrm{\cdot H}_{2}\mathrm{O} + 6\mathrm{KFAq}. \end{array}$

H.SiF. Aq is decomposed by conc. H.SO., also by HCl gas, with formation of SiF. and withdrawal of water. Boric acid separates SiO2.xH2O and forms fluoboric acid (q.v., vol. i. М. М. Р. М. p. 530)

Salts of H₂SiF₆ (v. preceding article). These salts are formed by dissolving various metalse.g. Fe or Zn-in H.SiF.Aq, or by neutralising the acid solution by the proper quantities of basic oxides or hydroxides; if excess of a strongly basic oxide is added to H₂SiF₆Aq, SiO₂·H₂O is separated and a fluoride is formed. Most of the silicofluorides are sol. water; the salts of Ba, K, Na, Ce, and a few elements allied thereto, are only slightly sol. water and insol. alcohol. Aqueous solutions of silicofluorides have an acid reaction to litmus. Silicofluorides are generally decomposed by heat, giving off SiF, and leaving fluorides; heated with AmCl, metallic chlorides remain (Stolba, J. pr. 101, 157). Some silicofluorides are de composed by heating strongly with Fe or K, forming fluoride and Si. Conc. H₂SO₄ evolves H₂SiF₄, when heated HF is given off; conc. HClAq and HNO₃Aq react similarly, but more slowly and less completely; but H.SiF.Aq

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partially decomposes most chlorides and nitrates in solution. Truchot (C. R. 98, 821, 1330) gives the heats of formation of alkali silicofluorides. M. M. P. M.

By the action of SILICO-FORMIC ACID. water on (?) Sil, Friedel a. Ladenburg (A. 203, 247) obtained a white solid that gave off H when treated with KOHAq; the amount of H obtained agreed fairly well with the formula SiH₂O₂. If this formula is correct, the compound is probably the Si analogue of formic M. M. P. M.

H,Si,O, SILICO-FORMIC ANHYDRIDE HŞi:O

This body represents among Si com-HŠi:O. pounds the hypothetical formic anhydride ÎIÇ:0

Prepared by slowly distilling SiHCl, HĊ:O. into water kept at 0°, filtering quickly the solid that separates, washing with ice-cold water, drying in vacuo over H.SO, and then at 150° the SiHCl, is distilled from a small flask and the distillation-tube is fused on to an inverted funnel which dips beneath the water; 2SiHCl₃+3H₂O = 6HCl+Si₂H₂O₃ (Friedel a. Ladenburg, A. 143, 118; cf. Buff a. Wöhler, A. 104, 101; also Gattermann, B. 12, 186). A white, amorphous, light powder; floats in water, sinks in ether; sl. sol. water. Does not decompose at 300°, but at higher temperatures it glows and gives off H which takes fire explosively; burns when heated in O, emitting a brilliant light; burns when heated in a covered crucible, with formation of some amorphous Si. Heated in tube, SiH, is given off and a thin layer of amorphous Si remains. Not acted on by acids, except HFAq which dissolves it with rapid evolution of H. Alkali and alkali carbonate solutions, including NH3Aq, dissolve this compound, giving off H, and forming alkali silicates. A freshly-prepared aqueous solution of H2Si2O, acts as an energetic reducer; AuClaAq is reduced to Au; Pd salts probably to Pd mixed with Pd silicate; SeO2Aq, SO2Aq, TeO2Aq, and HgCl2Aq are reduced to Se, S, Te, and HgCl. CroaAq, indigo solution, and salts of Pt and Ir are not reduced.

The substance obtained by Wöhler, by the action of light and water on the body he named silicone (v. Silicon, compounds of, with hydrogen AND OXYGEN, p. 459), and called by him leukon (A. 127, 268), and also the substance called by (A. 121, 200). The solid control of the solid contr

SILICO-IODOFORM SiHI₃. (Silicon hydrogen iodide. Tri-iodo-silico-methane.) Formula probably molecular, from analogy of SiHCl, Obtained in small quantities by the interaction of HI and crystalline Si at red heat (Buff a. Wöhler, A. 104, 99); better prepared by diluting the HI vapour with H; the product, which is a mixture of SiI, and SiHI, is repeatedly fractionated; SiI, boils at 290°, SiHI, at c. 200°. A mixture of SiI, and SiHI, is also obtained by heating SiH, with I (Mahn, J. 1869. 248). colourless, refractive liquid; S.G. 3:362 at 0°, 8:314 at 20°; boils at c. 200°. Water produces Si₂H₂O₂ (Friedel, A. 149, 96) (v. Silico-formio M. M. P. M. ANHADRIDE, supra).

SILICO-MOLYBDATES. Compounds con-

taining SiO₂, MoO₃, and basic radicles; v. Molyberts, vol. iii, p. 427.

SILICON. Si. (Silicium.) At.w. 28·3; mol.w. unknown.

H.F. [Si, O'] = 219,240 amorphous Si; 211,120 crystalline Si (Troost a. Haute-feuille, C. R. 70, 252). C.E. (linear at 40°) 00000763 (Fizeau, C. R. 68, 1125). For other properties v. Properties, p. 456.

Historical.—The existence of aspecial earth in rocks that could be melted to glass-like substances was indicated by Pott in 1746. Scheele (Opuscula, 2, 67) and Bergmann (Opuscula, 26) showed that this earth could not be changed into lime or alumina; Smithson in 1811 found that the earth acted like an acid; Berzelius, in 1823, isolated the element of this earth, and in 1854 Deville obtained the same element in crystalline form. The new element was shown to resemble carbon by the researches of Buff and Wöhler and of Friedel and Ladenburg. The name silicon was given from acidum silicum or silex.

Occurrence.—Si is not found uncombined; compounds of Si are very widely distributed in vast quantities; next to oxygen, Si (in combination) is the most widely distributed element. Silicates occur in very many rocks and soils and in plant-ashes; SiO2 is found in many mineral springs and in sea-water (Forchhammer, Pr. E. 2, 303; Bunsen, A. 62, 7, 25), and in small quantities in various animal organisms (von Gorup-Besanez, A. 61, 46; Henneberg, A. 61, 261). Si is found in pig-iron; it is generally supposed to exist therein as crystallised Si, but the experiments of Jordan a. Turner (C. J. 49, 215) make it probable that the Si is combined with Fe as a silicide.

Formation. - Amorphous silicon. - 1. By passing the vapour of SiCl, over heated K, removing excess of SiCl, by a current of dry air, and washing out KCl with water (Berzelius, Lehrb. (1st ed.) 3, 327).—2. By passing vapour of H,SiF, over heated K, washing with water, heating the residue in a covered crucible (to remove H and C), washing with HFAq (to remove SiO₂) and then with water (B., l.c.).—3. By heating a mixture of K₂SiF₄ and K, and washing with water (B., l.c.); Wöhler (A. 104, 107) heats a mixture of Na, SiF, with NaCl and Na.-4. By heating Mg in SiF, vapour (Warren, C. N. 58, 215).-5. By reducing SiO₂ by heating with Mg (v. Preparation, No. 1) .- 6. By elec trolysing a fused silicate in a carbon crucible, with Pt as the positive, and gas-carbon as the negative, electrode (Hampe, Chem. Zeitung, 12, 841). Crystalline silicon .- 7. By heating a mixture of K. SiF., Na, and Zn (v. Preparation, No. 2).—8. By reducing K₂SiF₆ or a silicate by Al (v. Preparation, No. 3).—9. By passing H and SiCl₄ vapour over Zn heated to reduces in a porcelain tube (Beketoff, Bl. 1, 22) .-- 10. By heating a mixture of SiO₂, K₂CO₃, Iceland spar, and Na (Deville, A. Ch. [3] 49, 62).—11. By passing vapour of SiF₄ or SiCl₄ over Si heated to redness (Troost a. Hautefeuille, C. R. 73, 443).-12. By passing vapour of SiCl, over heated Na, or Al, and heating the product (Si with excess of Na or Al) in a carbon crucible (Deville, A. Ch. [8] 49, 62).-13. A piece of siliceous pig-iron is con nected with the positive pole of a battery and

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immersed in dilute H2SO4Aq, in which a Pt plate connected with the negative pole of the battery is also placed; after some hours the iron has dissolved: the mixture of graphite, amorphous Si and SiO, which remains is heated to full redness for some time with Zn and the fused mass is treated with dilute HClAq (Warren, C. N. 57, 54).

Preparation. - Amorphous silicon. 1. An intimate mixture of 10 g. Mg powder and 40 g. thoroughly dry sand is placed in a testtube, of fairly thick glass, c. 2-3 cms. diameter and c. 15 cms. long; the tube is heated throughout by a large flame, and then the lower part is very strongly heated, when reduction quickly occurs. If the tube is gradually moved downwards so that one part is strongly heated after another, the whole of the SiO2 is reduced in a few minutes. The contents of the tube are shaken out, pulverised, and treated with HClAq (1:2), the solid being added to the acid in small successive quantities (to prevent explosion from evolution of SiH, (Gattermann, B. 22, 186). Crystalline silicon .- 2. A mixture of 15 parts dry K2SiF4, 20 parts dry granulated Zn, and 4 parts dry Na in small pieces is placed in a clay crucible, which is covered and heated to redness; when the reduction of the K2SiF6 is effected (there is a visible, but not violent, reaction) the temperature is raised till the mass melts, care being taken not to heat to the b.p. of zinc, else considerable loss will occur. The crucible is broken when cold, the regulus is heated to the m.p. of zinc, the molten zinc is poured off, and SiO2, Zn, &c., are removed by treatment, in succession, with conc. HClAq, conc. boiling HNO,Aq, and HFAq. The Si, mixed with a little K,SiF, thus obtained is placed in a crucible and covered with a layer of powdered glass; the grucible is set inside another, and heated to the m.p. of pig-iron (c. 1100°). When all is melted the crucible is allowed to cool to dull redness and is then plunged into water; the regulus is separated from the slag, and is treated with HFAq and then washed with water (Caron, A. Ch. [3] 63, 26; Deville a. C., A. Ch. [3] 67, 485).—3. A mixture of 1 part Al with 20-40 parts thoroughly dry K.SiF. or Na.SiF. is heated to c. 950° in a Hessian crucible, and the contents are kept molten for c. a quarter of an hour; the crucible is broken when cold, the regulus is separated, crushed, heated with conc. HClAq as long as H is given off, then with HFAq, and washed with water and dried (Wöhler, A. 97, 261). Or, a mixture of 10 parts powdered cryolite and 5 parts K2SiO3 or powdered glass is divided into two equal parts; one part is placed in a Hessian crucible, 1 part Al is added, the rest of the mixture is placed over this, and the whole is heated to redness for half an hour. The regulus is treated with conc. HClAq, HNO, Aq, &c., as directed above.

Properties. - Si exists as a brown amorphous powder, and also as greyish-black, very lustrous.

octahedral crystals.

Amorphous silicon is a lustrous, brown powder, which adheres to the fingers or to glass tenaciously. The S.G. has not been determined, but the powder is heavier than oil of vitriol; it is a non-conductor of electricity; burns when

heated in air or O, but the SiO, formed soon stops the process; dissolves in cold HFAq, forming SiF, and H; also dissolves in warm alkali solutions; is oxidised with incandescence when thrown into molten nitre; combines with S when warmed therewith. After being strongly heated in a covered Pt crucible, and the SiO2 formed has been removed by HFAq, amorphous Si is a dark chocolate-brown powder, which is not burnt by heating in air or O, is insol. HFAq and boiling alkali solutions, does not combine with S, and is not acted on by molten

KNO, or KClO,

Crystalline silicon is obtained in leaflets The leaflets are opaque, very or needles. lustrous, metal-like, greyish black, resembling graphite; they consist of regular octahedra. The needles are also octahedral. Crystalline Si has S.G. 249 at 10° (Wöhler, J. 9, 437); 2 194 to 2 197 (Winkler, J. 17, 208). Scratches glass, but not topaz. According to Deville (C. R. 39, 321) crystalline Si 'conducts electricity like graphite.' M.P. between those of pig-iron and steel, i.e. between c. 1100° and c. 1300°. Crystalline Si is not changed when heated, even to whiteness, in O; it is unacted on by HFAq; dissolves in warm alkali solutions; combines with S vapour. When heated in the electric are crystalline Si melts and then boils, and the ends of the electrodes become covered with crystals of SiC (Moissan, C. R. 117, 423).

For the lines in the emission spectrum of

Si v. B. A. 1884. 441.

Deville (A. Ch. [3] 49, 70) thought that a graphite-like form of Si existed different from the ordinary crystalline (or diamond-like) form; but Miller (P. M. [3] 31, 397) showed that both the leaflets and the needles consisted of octahedra. Kopp (A. Suppl. 5, 72) found differences between the specific heats of crystalline Si and the graphite-like form prepared by the interaction of K.SiF. and Al, and these differences were confirmed by Winkler (J. pr. 91,

Warren (C. N. 63, 46) thought he had obtained a crystalline form of Si (oblique octahedra) different from the ordinary by the action of impure Al on K,SiF, at a very high temperature; he described the crystals as very perfect, and sometimes half-an-inch across the

Specific heat of silicon. Kopp, Regnault, and others obtained values for the S.H. of Si varying from '138 to '173 at c. 30°-100°. In 1875 Weber (P. M. [4] 49, 161, 276) showed that S.H. of crystallised Si increased rapidly from -40° to c. 200°, and attained an almost constant value at the latter temperature. Weber's results gave the following values for S.H. of crystallised Si:-

3.H.
186
1833
196
2011
2029
١

The atomic weight of Si has been determined (1) by finding the ratio of Si to SiO, formed therefrom (Berzelius, P. 1, 226 [1824]); (2) by converting BaSiF, into BaSO, (B., P. 8, 20 [1828]); (8) by ppg. CI in SiCl, by Ag (Pelouze, C. K. 20, 1047 [1846]; Dumas, A. Ch. [3] 55, 183 [1859]); (4) by converting SiCl, into AgCl (Schiel, A. 120, 94 [1861]); (5) by decomposing SiBr, by water and determining SiO₂ produced (Thorpe a. Young, C. J. 51, 576 [1887]); (6) by finding V.D. of SiH, SiCl, SiBr, SiF, &c.; (7) by determining S.H. of Si. The atom of Si is tetravalent in the gaseous molecules SiH, SiCl, SiBr, SiF, SiHCl, &c. The molecular weight of Si is unknown.

Si is closely related to C, and less closely to Ti, Ge, Zr, Sn, Ce, Pb, and Th (v. Carbon Group

OF ELEMENTS, vol. i. p. 682).

Reactions and Combinations.—I. Amorphous silicon which has not been heated .- 1. Heated in air or oxygen burns to SiO2, which coats the Si, so that the process soon stops. -2. Heated with sulphur forms SiS, (Berzelius).-3. In molten nitre forms potassium silicate, with incandescence.-4. Dissolves in cold solution of fluorhydric acid to form SiF, and H.-5. Dissolves in conc. alkali solutions on warming, forming H₂SiO₃Aq (or Na₂SiO₃Aq) and H. For differences between amorphous silicon before and after heating, v. Properties of amorphous silicon, p. 456. II. Crystalline silicon.—6. Is not acted on by oxygen, nor by fluorhydric acid.—7. Heated in dry chlorine forms SiCl,; in bromine vapour forms SiBr,; in a mixture of iodine vapour and CO, forms SiI,; takes fire in fluorine, forming SiF, (Moissan, C. R. 103, 256).—8. Heated with sulphur vapour forms SiS2-9. Strongly heated in nitrogen forms Si₃N₄.—10. Heated to c. 800° in a mixture of oxygen and chlorine, Si,OCl, is formed (Troost a. Hautefeuille, Bl. [2] 35, 360). 11. Dissolves slowly in warm alkali solutions of medium concentration, giving off II.—12. Burns when heated with alkali carbonates, separating C, and giving off CO.—13. SiS₂ is produced (according to Sabatier, Bl. [2] 38, 153) by heating to bright redness in hydrogen sulphide.—
14. Schutzenberger (C. R. 114, 1089) obtained a mixture of Si₃N₄ and a carbide (to which he gives the formula SiC) by heating to bright redness, in a carbon crucible placed inside another crucible packed with lamp-black, a mixture of 1 part Si and 2 parts SiO2.—The following reactions apply generally to silicon .- 15. Heated in hydrogen chloride SiHCl3 is formed; in hydrogen iodide mixed with H, SiHI, is produced; and SiHBr, is obtained by heating in hydrogen bromide.—16. Heated with silicon tetrachloride, Si₂Ol₂ (and ?SiOl₂) is formed.—17. Oxidised by hydrogen iodide solution (o. Ditte, Bl. [2] 13, 322).—18. With molten caustic soda or potash, H is given off and a silicate formed; similar but slower reactions occur with baryta and lime (v. Berzelius, A. 49, 247) .-19. Heated with several metallic oxides, such as PbO or Ag₂O, reduction occurs, generally with formation of a silicide. If a mixture of powdered Si, Al, and PbO is heated, a violent explosion occurs.—20. According to Colson (Bl. [2] 88, 56), Si₂C₂O is formed by heating Si in carbon dioxide; SiS, SiSO, and Si,C,S are formed by heating Si to white heat in carbon disulphide SiCO, is formed by heating with bensene; and Si,C,O, is produced when Si is heated to whiteness in a carbon crucible.

Silicon, amidonitride of. By the interaction of NH₂ and SiCl, or SiF, Harris (C. C. 1889 [ii.] 283) obtained a snow-white powder, to which he gave the formula Si.NH₂.N.

Silicon, carbide of. According to Schutzen-berger (C. R. 114, 1089), a compound of Si and C, having the composition of SiC, is formed along with a little Si₂N₄, by placing a mixture of 1 part crystallised Si and 2 parts SiO₂ in a covered gas-carbon crucible, imbedding this in lamp-black in a larger crucible, and this again in more lamp-black in another larger crucible, and heating to bright redness for some hours: boiling with moderately conc. HFAq dissolves SiO, and Si, N, and leaves the SiC. Heated to low redness in chlorine, SiC is said to give SiCl. and C. Moissan (C. R. 117, 425) obtained colourless crystals of SiC by fusing C and Si in an electric furnace. The crystals are very hard, act strongly on polarised light, S.G. 3.12; they are not acted on by O or S vapour at 1000°; Cl begins to react at c. 600° and the action is complete at 1200°; the crystals are not acted on by boiling HClAq, HNO3, H2SO4, aqua regia, or a mixture of HNO, and HFAq, nor by fused KNO, or KClO,; molten KOH gradually forms K₂CO₃ and K silicate.

Silicon, bromides of. Two bromides of Si

are known, Si₂Br, and SiBr,

DISTLEON HEXABRONIDE Si₂Br_s. (Silicon tribromide SiBr_s.) Formula probably molecular from analogy of Si₂Cl_s. A colourless liquid, boiling at c. 240°. Formed by adding the proper quantity of Br to Si₂I_s in CS_s, pouring off from I, purifying by shaking with Hg, filtering in dry air, and fractionating (Friedel a. Ladenburg. 4. 203, 254).

SILICON TETRABROMIDE SiBr. Mol. w. pro-

bably 347.3.

Preparation.—Amorphous Si, prepared as described under Sillon, Preparation, No. 1 (p. 456), after being partially purified from SiO₂ by HClAq, washing, and drying, is heated in a glass tube, while Br vapour is passed over it; the tube passes into a small flask, which is surrounded by cold water. A mixture of SiBr, and Br collects in the flask; this is fractionated, and the last traces of Br are removed by shaking with Hg and distilling (Gattermann, B. 22, 186). SiBr, may also be prepared by heating a mixture of SiO₂ and C (cf. Sillon Tethachloride, p. 458) in Br, shaking with Hg, and fractionating (Serullas, P. 24, 341; modified by Reynolds, C. J. 51, 500).

Properties and Reactions.—A colourless liquid, having a disagreeable odour, and fuming much in air. S.G. 2.8128 at 0°. B.p. 153.4° at 762.5 mm. (Piorre, A. Ch. [3] 20, 26; Freyer a. Meyer, Zeit. für anorgan. Chemie, 2, 1); 148° to 150° (Sorullas, Lc.). Solidifies at c. -12°. (F. a. L., Lc.). Decomposed by water to HBrAq and SiO₂; shaken with conc. sulphuric actd, slowly changes to Br and SiO₂. Heated to 250° with lead oxide gives PbBr, and Pb silicate (Friedel a. Ladenburg, A. 147, 362). Ammonia probably forms SiBr, NH₂ (Persoz, A. Ch. [2] 44, 315). Phosphorus hydride forms a white amorphous compound, by repeated compression with SiBr, the pressure being maintained for some hours (Besson, C. R. 110, 240).

For the compounds SiBraH and SiBraH v.

SILICOBROMOFORM, and SILICO-ETHANE, PENTA-BBOMO- DERIVATIVE OF, pp. 453, 454.
Silicon, bromochlorides of. Three compounds

of Si with Br and Cl have been isolated. The V.D. of SiBr, Cl, and also that of SiBrCl, has been determined; the formulæ of all are pro-

bably molecular.

SILICON BROMO-TRICHLORIDE SiBrCl. Mol. w. 214.16. A colourless liquid, boiling at c. 80°, fuming in air, and decomposed by water. 80°, tuming in air, and decomposed by water. Prepared by heating Br and SiHCl₃ at 100°; SiHCl₃+Br₂=SiBrCl₃+HBr (Friedel a. Ladenburg, A. 145, 187). Also by the interaction of Br and SiCl₃SH (? SiCl₃SH+3Br=SiBrCl₃+SBr+HBr) (F. a. L., l.c. p. 179). V.D. 104°7 at c. 130° (F. a. L., l.c.). Reacts with NH to form an emerglous compound. with NH, to form an amorphous compound, 2SiBrCl₂.11NH₂, easily decomposed by water (Besson, C. R. 112, 788).

SILICON DIBROMO-DICHLORIDE SiBr.Cl. A colourless liquid, boiling at 103°-105°, and not solidifying at -60° . Prepared by heating SiHCl, and Br above 100° (F. a. L., Lc.). Also by passing the vapour of HBr and SiCl, through a red-hot porcelain tube (Besson, l.c.). Combines with NH₃ to form SiBr₂Cl₂.5NH₃, decom-

posed by water.

SILICON TRIBROMO-CHLORIDE SiBr.Cl. Mol. w. 302.92. A colourless liquid, fuming in air, boiling at 140° – 141° , not solidifying at -40° ; S.G. $2\cdot432$. V.D. $150\cdot5$ at c. 185° (Reynolds, C. J. 51, 590). Obtained, along with SBr., by passing Br vapour over a mixture of SiO, and C heated in a wind-furnace, passing dry H through the warm product, shaking with Hg, and fractionating (R., l.c.). Besson (C. R. 112, 788) seems to have obtained the same compound, along with SiBr,Cl, by passing the vapours of HBr and SiCl, through a redhot porcelain tube. B. gives the b.p. 126°-128°, and m.p. -39°; he says a compound SiBr.Cl.11NH, is formed by interaction with

NH...
Silicon, brome-iodides of, v. Silicon iodo-

BROMIDES, p. 461.

Silicon, chlorides of. Two chlorides of Si have been isolated with certainty, Si2Cla and SiCl.; these formulæ are molecular. There are indications of the existence of another chloride, SiCl.

SILICON HEXACHLORIDE Si2Cls. (Silicon tri-

chloride SiCl₂.) Mol. w. 268-22.

Preparation.—1. By heating HgCl₂ with Si₂I_e, fractionating, and distilling the portion boiling at 146°-148° from HgCl₂ (Friedel a. Ladenburg, A. 203, 253).-2. Vapour of SiCl, is passed over Si kept molten in a porcelain tube (3SiCl₄ + Si = 2Si₂Cl₃); the product is rapidly cooled, and fractionated from SiCl₄, Si oxychlorides (and ? SiCl2) (Troost a. Hautefeuille, A. Ch. [5] 7, 459).

Properties. — A colourless, mobile liquid, boiling at 146°-148°; S.G. 1.58 at 0°; solidifies st. 14° to large leaflets, which melt at 1° (F. a. L., l.c.). V.D. 140 at c. 240° (T. a. H., l.c.). Fumes in air, de imposed by water; vapour takes fire when Si_.Cl₄ is heated in air.

Reactions and Combinations.—1. Decomposed to SiCul and Combinations.—1.

posed to SiCl, and Si by heat in a closed tube; decomposition is extremely slow at 350°, nearly complete at 800°; heated rapidly above 1000° the dissociation-pressure falls: the compound is stable below 350° and above 1000° (T. a. H., l.c.).—2. Decomposed by water. At ordinary temperatures products remain in solution, and are ppd. by NH₃Aq; at 0° Si₂H₂O₄ is formed (v. Silico-oxalic acid, p. 463) (F. a. L., l.c.).— 3. Caustic potash forms SiO₂ and gives off H (F. a. L., A. 203, 254) .- 4. Phosphorus hydride is changed to the solid hydride at -10° (Besson, C. R. 110, 516).-5. Combines with ammonia to form Si,Cls.5NH, (B., l.c.).

SILICON TETRACHLORIDE SiCl. 169.78. Boils at 57.57° at 760 mm. pressure (Thorpe, C. J. 37, 327). S.G. 30 1.52408 (T., l.c.). V.D. 85.5 at 100° (Dumas, A. Ch. [2] 33, 368). S.H. of SiCl, vapour, at 90° to 234°, = 1322, at constant pressure, referred to equal weight of water; 12, at constant volume, referred to equal weight of water (Regnault, Acad. 26, 1). Regnault (l.c.) gives the vapour-pressures of SiCl, as follows:—

Temp.	•	Vap	our-pro	essure.
-20°.		. 26.49	mm.	mercury
-10.		. 46.46	"	,,
0.	•	. 78.02	"	,,
+10 .	•	. 12 5·90	,,	,,
20 .	•	. 195.86	"	**
30 .	•	. 294·49	,,	**
40.	•	. 429.08	"	,,
50 .	•	. 607·46	**	**
60 .		. 837.23	,,	,,

H.F. $[Si,Cl^4] = 157,640$ (Troost a. Hautefeuille, A. Ch. [5] 9, 70).

Formation.-1. By passing dry Cl, or HCl gas, over a mixture of SiO, and C at full red heat (Oerstedt, B. J. 6, 119; Deville, A. Ch. [3] 43, 23). According to Weber (P. 112, 649) C is not necessary if the temperature is high enough. 2. By heating crystalline Si, or Si containing H, in Cl (Berzelius, C. J. 4, 91).—3. Favre (C. R. 107, 339) heats impure Si, and passes HCl and vapour of naphthalene over it.—4. By heating iron containing c. 15 p.c. Si in Cl (Warren, C. N. 60, 158).—5. By passing vapour of BCl_3 over SiO_2 heated to dull redness $(4BCl_3 + 3SiO_2 = 3SiCl_4 + 2B_2O_3$; Troosta Hautefeuille, A. Ch. [5] 7, 476).

Preparation.-1. Amorphous SiO, is mixed with an equal weight of lampblack, and the mixture is made into a paste with oil. Small pellets are made of this paste; these are imbedded in charcoal powder, and strongly heated. The dry pellets are placed in a porcelain tube, which is heated to very bright redness in a furnace while a stream of Cl (dried by H₂SO₄ and then by CaCl.) is passed through. The exit end of the porcelain tube is connected with a U-tube, from the bottom of the bend of which a short tube passes down into a small flask; the U-tube and small flask are surrounded by a freezing mixture. The SiCl, which condenses in the flask is shaken in a dry flask with Hg and a few pieces of K, and then distilled with sodium.

L. Meyer (A. 270, 238) recommends the use of charcoal-powder in place of lampblack, and starch-paste rather than oil.—2. Gattermann (B. 22, 186) places impure amorphous Si (containing some Mg, &c.), prepared as described under Silicon, Preparation, No. 1, in a tube c. 2 cms. wide, leaving a space of c. 1 cm. above the Si along the tube; he bends this tube at right angles, and connects it with a U-tube placed in a freezing mixture; he then passes dry Cl through the apparatus, while he heats the tube, laid in an iron trough in a gas-furnace so that the tips of the flames just touch the iron trough. The temperature must not get too high, else the Si glows, and MgCl, and O are formed, and the O oxidises the Si to SiO.

Properties.—A colourless, very clear, and very mobile liquid, with a disagreeable odour resembling that of cyanides; reddens litinus; Does not become viscid fumes in moist air.

at -75° (Haase, B. 26, 1052).

Reactions and Combinations .- 1. Heated to redness with hydrogen a little SiHCl, is formed (Friedel a. Ladenburg, Bl. [2] 12, 92).-2. Oxychlorides are produced by the action of oxygen under the influence of induction sparks (Troost a. Hautefeuille, A. Ch. [5] 7, 465).—3. SiCl, is decomposed by passing the vapour with dry air through a white-hot tube, giving Si_2OCl_a and Cl (F. a. L., *l.c.*). Berthelot (A. Ch. [5] 15, 185) says that SiO_2 is also produced. 4. Water produces H.SiO, and HClAq .- 5. Hydrogen sulphide forms SiCl, SH, when SiCl, and H,S are passed through a red-hot tube (F. a. L., A. 145, 179; Pierre, A. Ch. [3] 24, 300). 6. Many metals-e.g. K, Na, Zn, Ag-withdraw all Cl from SiCl, when heated to redness in vapour of SiCl, (F. a. L.; cf. Rauter, A. 270, 235). 7. Most metallic oxides form SiO, and metallic chlorides when heated with SiCl, (R., l.c.); CaO, MgO, Al₂O₃, and BeO form silicates and crystalline SiO₂ (Daubrée, C. R. 39, 135); TiO₂ is not changed (T. a. H., A. Ch. [5], 7, 476).—8. Decomposed by heating with alkali carbonates, potassium chlorate or nitrate, and various oxidising salts (R., l.c.) .- 9. SiO2 and HCl are produced by reaction with sulphuric acid. -10. Ammonia forms SiCl. 6NH, (Persoz, A. Ch. [2] 44, 315); also, according to Gattermann (B. 22, 194), Si.NH, N.-11. Phosphoretted hydro. gen does not react at ordinary temperatures; but at -40° c. 40 vols. of PH, are absorbed by SiCl,, forming a solution which does not solidify at -60° (Besson, C. R. 110, 240). A colourless crystalline compound is produced by compressing PH3 and SiCl, and then decreasing pressure to 20 atmospheres at 10° (B., l.c.).—12. Heated with sodium silicate, NaCl is formed. If SiCl, vapour is passed through a tube containing fragments of felspar, at a white heat, KCl, SiO2, and Si,OCl, are formed (F. a. L., l.c.).

For the compound SiHCl, v. SILICO-CHLORO-

говм, р. 453.

? SILICON DICHLORIDE SiCl. In the preparation of Si_.Cl_s by the reaction of SiCl_s with Si, Troost a. Hautefeuille (A. Ch. [5] 7, 463) obtained a liquid which took fire when heated in air, and reacted with ice-cold water to form a hydroxide of Si having reducing properties.

Silicon, chlorobromides of, v. Silicon Bromo-

CHLORIDES, p. 458.

Silicon, chlorohydrosulphide of, SiCl, SH. (Trichloro-silico-mercaptan.) Mol. w. 167-39. This compound may be looked on as a derivative of hypothetical ortho-thio-silicic acid Si(SH),, obtained by replacing 3SH by 3Cl.

Prepared by passing dry H.S into SiCl, in a

retort, and then passing the mixed vapours of H.S and SiCl, through a red-hot porcelain tube connected with a receiver surrounded by a freezing mixture, and fractionating the liquid that condenses (Friedel a. Ladenburg, A. 145, 179). Colourless liquid, with sharp, disgusting smell; boils at 96°; S.G. 1.45. V.D. 83.5 at c. 167°. Decomposed by moist air, more rapidly by water, to H₂S, S, HClAq, and SiO₂xH₂O; bromine produces SiBrCl₃ and HBr. Alcohol in excess forms Si(OEt), H₂S, and HCl; by reacting in the ratio 3EtOH: SiCl₂SH, F. a. L. (l.c.) obtained a liquid boiling at 164°-167°, probably Si(OEt) SH; this liquid could not be obtained pure, as it changed to Si(OEt), HCl, and H.S.

Silicon, chloro-iodides of, v. Silicon iodo-

CHLORIDES, p. 461.

Silicon, compounds of, with carbon and oxygen. According to Colson (Bl. [2] 38, 56), the compound SiCO, is formed by heating Si with benzene vapour, the compound Si₂C₃O₂ by heating Si to whiteness in a carbon crucible, and

the compound Si₂C₂O by heating Si in CO₂.
Silicon, compound of, with carbon and sulphur. Colson (Bl. [2] 38, 56) says that a compound, to which he gives the formula Si,C,S, is produced by heating Si to a white heat

in CS. vapour.

Silicon, compounds of, with hydrogen and oxygen. The compounds of the form SiO, xH,O are described under SILICA, HYDRATES OF (p. 447); the compounds Si₂H₂O₃ and Si₂H₂O₄ are described as silico-formic anhydride and silicooxalic acid respectively (pp. 455, 463). Wöhler (A. 127, 257) obtained a substance, by the decomposition of impure Ca silicide by HClAq, to which he gave the name silicone, and either the composition Si₄H₄O₃ or Si₃H₃O₂. On account of the yellow colour of this body, Miller proposed to call it chryscone. Silicone is described as orange-yellow leaslets, insol. water, alcohol, CS, SiCl, or PCl; when heated below redness it takes fire, burning to SiO, and amorphous Si; heated out of air, H is given off and SiO₂ and amorphous Si remain; not acted on by Cl, fuming HNO₃, or conc. HSO₄; caustic alkali solutions, even dilute NH, Aq, produce SiO, with rapid evolution of H; acts as an energetic reducer towards solutions of many metallic salts.

Silicon, fluorides of. The existence of any compound of Si and F except SiF, is doubtful. Troost a. Hautefeuille (A. Ch. [5] 7, 464) obtained a fine dust by passing SiF, over molten Si and suddenly cooling, which was probably a lower fluoride than SiF.

SILICON TETRAFLUORIDE SiF. Mol. w. 104.3. Formation.—1. By passing BF, vapour through a red-hot porcelain tube (Troost a. Hautefeuille (A. Ch. [5] 7, 464).—2. By the interaction of HFAq and SiO2 or silicates.

Preparation. -A fair-sized flask is one-third filled with a mixture of equal parts of powdered CaF, and quartz or white sand; sufficient conc. H.SO, is added to thoroughly moisten the mixture; the flask is gently warmed, and the gas that comes off is collected over Hg

 $(2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4)$. Properties.—A colourless gas, with a dis-greeable odour and sour taste; reddens dry litmus paper; fumes strongly in air. V.D. 51-9 (Dumas, A. Ch. [2] 83, 368). Condensed to a colourless mobile liquid at -106.5° and 9 atmospressure (Faraday, T. 1845, 155). According to Olszewski (M. 5, 127) SiF₄ solidifies at -102° . Acts as a powerful poison (v. Cameron, Dublin

J. of Med. Sci. Jan. 1387).

Reactions.-1. Decomposed by electric sparks with separation of Si (T. a. H., C. R. 43, 443).-2. Potassium and iron, when hot, burn in SiF,, forming fluorides and Si.—3. Moist air forms Si,O,F.OH (Landolt, A. Suppl. 4, 27, and v. DIMETASILICIO FLUORHYDRIN, infra).—4. Water absorbs SiF., forming SiO.xH.20 and H.SiF.Aq (v. SILICOFLUORHYDRIC ACID, p. 454).-5. Ammonia forms SiF₄.2NH₃ (J. Davy, T. 1812. 352); also, according to Harris (C. C. 1889 (ii.) 283), SiNH, N (v. SILICON AMIDONITRIDE, p. 457).

Combinations. - 1. Combines with dry phosphoretted hydrogen, when the gases are strongly compressed at -22° and 50 atmospheres in the ratio 2PH₃:3SiF₄, to form lustrous crystals (Besson, C R. 110, 80).-2. Alcohol absorbs SiF₄ freely, forming an acid liquid which gives off SiF₄ in the air (Knop, J. 1858, 146).—3. SiF₄ is absorbed by many metallic oxides.

Dimetasilicic fluorhydrin Si₂O₂OH.F. Landolt (A. Suppl. 4, 27) obtained this compound as a white crystalline solid (v. also Schiff,

J. 1865. 196).

Silicon, haloid compounds of. The com-pounds of Si with halogens belong to the forms Si₂X₆ and SiX₄; the compounds SiX₄, where X is a single halogen, have been gasified, and the compound Si₂Cl₈ has also been gasified. The formulæ are probably all molecular. There are also indications of the existence of some compounds of the type SiX₂. Besides the compounds where X is a single halogen, there exist the compounds SiXX'₃, SiX₂X'₂, and SiX'X₃, where X and X' are Br and Cl, I and Cl, and I and Br respectively; the only one of these compounds that has been gasified is SiBr,Cl.

Silicon, hydrides of. The compound SiH, has been isolated and examined. The existence of another hydride, probably SigHg, is

likely.

SILICON TETRAHYDRIDE SiH. (Silicitretted hydrogen.) Mol. w. 32·3. Si and H do not combine directly, even in the electric arc (Friedel, C. R. 73, 497).

Formation.—1. Al containing Si is made the positive pole in NaClAq (Buff a. Wöhler, A. 103, 218).—2. Crude Mg silicide is decomposed by dilute HClAq (v. Preparation). These processes yield mixtures of SiH, and H.—3. By the reaction of Na with SiH(OEt), (v. Prepara-

tion).

Preparation .- 1. Small pieces of Na are dropped into SiH(OEt), (v. infra), and the liquid is gently warmed; the escaping gas is allowed to drive out the air (if the Na or SiH(OEt), was moist H comes off, and the gas takes fire), and is then collected over Hg (Friedel a. Ladenburg, 143, 123). The SiH(OLt), is prepared by adding dry absolute alcohol to pure SiHCl, in a longnecked flask, in the ratio 3EtOH : SiHCl_s, distilling after some time, and collecting the liquid that boils from 134° to 137°.-2. Impure SiH,, mixed with considerable quantities of H, is prepared by placing coarsely-pulverised crude Mg silicide (for preparation, v. infra) in a small

two-necked flask, fitted with a funnel tube and a short wide delivery tube; the flask and de-livery tube are quite filled with water from which all air has been driven out by boiling, the delivery tube is made to dip under boiled water. and the bell-jar to receive the gas is filled with boiled water; conc. HClAq is added, little by little, by the funnel tube. The gas, which comes off very rapidly, is collected in a bell-jar fitted with a stop-cock; this jar is then connected with a U-tube containing CaCl, and carrying a short, narrow piece of glass tubing, which is made to dip under a dry vessel full of Hg. By depressing the bell-jar, the gas is forced out; it burns in the tubes till the air is exhausted, when it passes into the vessel full of Hg, where it is collected.

Preparation of the crude Mg silicide. A mixture of 1 part finely-powdered, dry, white sand and $1\frac{1}{2}$ parts Mg powder is heated in a stout glass tube; reduction takes place with production of much light, and a bluegrey, semi-molten mass is obtained (Gattermann, the Mg silicide required, v. Wöhler (A. 137, 369), Warren (C. N. 58, 215), and Mermet (Bl. [2] 47, 366).

Properties .- A colourless gas; insol. water; liquefied at -11° and 50 atmos., -7 and 70 atmos., or -1° and 100 atmos. pressure (Ogier, A. Ch. [5] 20, 5). V.D. 15.9 (F. a. L., A. 143, 123). H.F. [Si,H⁴] = 32,900 (O., l.c.). Does not react with N, NO, NH₃, H₂SO₄Aq, or HClAq.

Reactions.—1. Decomposed completely to Si

and II by heating to above 400° (O., l.c.). 2. Induction sparks cause increase of volume from 100 to 121-129; H is produced, and yellow solid separates, probably Si_.H₁ (v. Disilicon tri-Hydride, infra). --3. SiH₁ takes fire in air when slightly heated, or when the pressure is decreased; if the pure gas is passed into a tube filled with Hg, the pressure is lowered to 100-150 mm., and air is admitted, the gas takes for (F. a. L., l.c.). The gas as prepared from Mg silicide is mixed with H, and takes fire in air at ordinary temperature and pressure.-4. Burns in chlorine with violent explosion .-5. Conc. potash solution forms K.Sio, and H; the volume of H is four times that of the SiH, (SiH₁ + 2KOHAq + H₂O = K₂SiO₂ + 8H) (F. a. L., l.c.).-6. Reduces solutions of many metallic salts; ppts. Ag and Si from AgNO, Aq, Pd from Pd salts, Cu silicide from CuSO, Aq, &c. Does not react with PtCl, Aq or Pb(C, H, O,), Aq.— 7. The action of electric discharges on SiH. mixed with nitrogen produces NH,, and (?) Si₂H, which combines with some of the N (Ogier, A. Ch. [5] 20, 31).

Disilicon TRIMYDRIDE Si₂H₃. This formula is given by Ogier (A. Ch. [5] 20, 31) to a yellow solid obtained by the action of induction sparks on SiH. The composition of the substance is somewhat doubtful. It takes fire when rubbed or heated in air; heated in H or N, inflammable SiH, is produced, or at higher temperatures Si

and H are formed.

Silicon hydrogen bromides v. Silico-Bromo-FORM, p. 453, and SILICO-ETHANE, PENTABROMO-DERIVATIVE OF (Si.HBr.), p. 454.
Silicon hydrogen chloride v. Silico-chloro

FORM, p. 453.

Silicon hydrogen iodide v. Silico-rodoform, b. 455.

Silicon, hydroxides of, v. Silica, hydrates of, p. 447; Silico-formic acid, p. 455; Silico-formic ametardre, p. 455; Silico-formic ametardre, p. 455; Silico-oxalic acid, p. 463; and Silicone, under Silicon, compounds of, with hydrogen and oxygen, p. 459.
Silicon, iodides of. Two compounds have

Silicon, iodides of. Two compounds have been isolated, SiI, and Si₁I₆, and a third, which is probably SiI₂, seems also to exist.

SILICON TETRA-IODIDE SII. Mol. w. 534'42. Melts at 120'5°; boils at 290°. V.D. at 360° = 268'5. H.F. [Si,F⁴] = 58,000 (Berthelot).

Preparation.—1. The crude product obtained by reducing a mixture of 4 parts fine white sand by heating with 1 part Mg powder (v. SILLCON, Preparation of, No. 1, p. 456) is strongly heated in a mixture of dry CO, and I vapour, in a tube which projects c. 20 cm. .rom the furnace; Sil, collects in the cold part of the tube, it is dissolved in CS₂ (1 part CS₂ dissolves c. 2·2 parts SiI₄), shaken with Hg till colourless, and the CS₂ is evaporated by passing dry CO₂ through it at the lowest possible temperature (Gatternann, B. 22, 190).—2. A mixture of CO₂ and I vapour is passed over Si strongly heated in a porcelain tube; the SiI₄ that collects in the cold part of the tube is purified as in 1 (Friedel, A. 149, 96).

Properties and Reactions.—Colourless, transparent, regular octahedra; isomorphous with CI₄. (For M.P., &c., v. supra.) The vapour burns when heated in air, with separation of I. Water produces SiO₂xH₂O and HIAq. Alcohol forms EtI, HI, and SiO₂. Ether, at 100°, produces Si(OEt), and EtI (F., l.c.).

SILCON HEXA-IODIDE Si.L. Formula probably molecular, from analogy of Si.Cl. Prepared by heating SiI, with finely-divided Ag (formed by reducing AgCl) to 290°–300° for some hours, removing SiI, by washing with a little dry CS₂ (1 part CS₂ dissolves c. '26 parts SiI, and c. 2'2 parts SiI,), dissolving in much hot CS₂, and crystallising (Friedel a. Ladenburg, 4. 203, 254). Colourless, six-sided, double refractive plates. Melts at 250° in vacuo, with partial decomposition. When heated, decomposes to SiI₄, and a substance that is probably SiI₄. Fumes in air; with water gives H₂Si₂O₄ and HIAG.

SILION DI-IODIDE. The yellow solid that is formed by heating SiI, is probably SiI,; it is insol. in the ordinary solvents; with water becomes grey, perhaps forming H₂SiO₂ (v. Silico-forming ACID, p. 455) (Friedel a. Ladenburg, A. 203, 247).

For the compound SiHI, v. Silico-iodoform, p. 455.

Silicon, iodobromides of. Three compounds, corresponding with the three bromochlorides and the three iodochlorides, are formed by passing IBr (alone or mixed with H) over crystalline Si heated to dull redness; also by passing the vapour of a solution of I in SiBr, over crystalline Si at a low red heat (Besson, O. R. 112, 1447). The compounds are solids which decompose in air with separation of I; they all combine with NH, to form white compounds that are decomposed by water.

SILICON IODOTRIBROMIDE SiIBr_s. Melts at 14° and boils at 192°. Prepared as described above, also (probably) by the interaction of I and

SiHBr_a at 200°-250°, also by passing HI over SiBr_a heated to low redness (B., *l.c.*).

SILICON DI-IODODIBROMIDE Sil₂Br₂. Melts at c. 88° and boils at 230°-231°. SILICON TRI-IODOBROMIDE Sil₂Br. Melts at

c. 55° and boils at c. 255°.

Silicon, iodochlorides of. Three compounds have been isolated, corresponding with the three bromochlorides, and the three iodobromides. The V.D. of none has been determined, but from the analogy with the bromochlorides the simplest formulæ are probably molecular.

SILION IDDOTRICHLORIDE SIICI₃. Obtained by passing HI mixed with SiCl₄ vapour through a red-hot tube, also by the interaction of HI and SiHCl₅ at 200°-250°, also by distilling ICl over crystallised Si heated to redness (Besson, C. R. 112, 60, 1314). A colourless liquid, boiling at 113°-114°; fumes in air; decomposed by water; I separates on standing, especially in sunlight. With NH₃ forms white amorphous 2SilCl₃.11NH₄.

SILICON DI-IODDICHLORIDE SIL, Cl., Formed from HI and SiCl., also from ICl and Si; also by heating HI with Sil, Cl at 2502. Colourless liquid, boiling at 172°. With NH4 forms amorphous SiL, Cl., 5NH4 (B., Lc.).

SILICON TRI-IODOCHLORIDE SII,Cl. A solid obtained in preparation of the two former compounds; melts at 2°. Fumes in air, with separation of I.

Silicon, nitrides of. Schutzenberger (C. R. 114, 1089) obtained small quantities of a compound to which he gave the formula Si,N., along with a carbide of Si, by heating 1 part Si and 2 parts SiO, in a covered carbon crucible, imbedded in lampblack in an outer crucible, imbedded in lampblack in an outer crucible, imbedded in Porcelain tube kept at a white heat, Colson (C. R. 94, 1710) found a black layer in the hottest part of the tube, which was probably a mixture of Si and nitride of Si. A compound of Si, N, and H, probably Si.NH₂,N, was obtained by Harris (C. C. 1889 (ii.) 283) by the reaction of NH₂, with SiCl, or SiF₄. Silicon, oxide of, SiO₂; v. Shlea, p. 446.

Silicon, oxide of, SiO₂; v. Silico, p. 446.
Silicon, oxychlorides of. The compound
Si₂OCl₆ is formed by heating SiCl₄ vapour in air
or O. According to Troost a. Hautefeuille
(Bl. [2] 35, 360) several oxychlorides are formed
by passing a mixture of SiCl₄ vapour and O
through a red-hot tube, or, better, by passing a
mixture of 1 vol. Cl and ½ to ½ vol. O over crystalline Si heated to not above 800°. T. a. H.
isolated the following oxychlorides:—

Si,O,Cl₁₀; liquid, b.p. 1522–154°, Si,O,Cl₁₀; liquid, b.p. 198°–202°. Si,O,Cl₂; cily liquid, b.p. above 400°. Si,O,Cl₂; solid, m.p. above 400°.

SILICON OXYCHLORIDE SLOCI. (Perchlorosilico-methyl ether (SiCl₃).O.) Mol. w. 28478. Prepared by passing vapour of SiCl₄ through a porcelain tube heated in a wind furnace burning coke, condensing the product, repeating the operation with the portion which boils above 70°, fractionating, and separating the liquid boiling at 187°-178° (Friedel a. Ladenburg, 4. 147, 365). A colourless liquid, boiling at 137°-138°. V.D. 144 at c. 200°. Furnes in air, decomposed by water to HClAq and SiO₁₀-HO. Miscible in all proportions with OHCl₂, CCl₄, OS₂₀ SiCl, and Et.O. Alcohol produces Si₂O₇(Et),; zinc ethide at 180° forms SiEt, and Si OEt, (F. a. L., l.c.)

The compound SiP,O,Cl, is described as SILICOPHOSPHORIC OXYCHLORIDE (p. 461).

Silicon, oxysulphide of. According to Colson (Bl. [2] 38, 56), a compound SiOS is formed, along with SiS and Si₄SC₄, by heating Si to white

heat in CS₂.
Silicon, sulphides of. The only compound of Si and S certainly isolated is SiS2. Colson (Bl. [2] 88, 56) says that silicon monosulphide, SiS, is produced, along with SiOS and Si, SC., by heating Si to white heat in CS₂; he describes SiS as a yellow solid, decomposed by water giving off H₂S, sol. in very dilute KOHAq with evolution of H. SiS is also said to be formed, along with SiS, by heating Si to redness in H_2S (Sabatier, Bl. [2] 38, 153).

SILICON DISULPHIDE SiS2. Mol. w. not determined. Sabatier (Bl. [2] 38, 153) gives H.F. [Si,S²] = 19,900. Amorphous Si and S combine when strongly heated (Berzelius). Prepared by heating Si to redness in a stream of dry H2S; the other products are a yellow solid, probably SiS, and a brown substance that is likely a mixture of SiS, and SiS, or of SiS, and Si (S., l.c.; v. also Fremy, A. Ch. [3] 38, 324). Also prepared by strongly heating dried pellets of oil and SiO2 (separated from SiF4) in a slow stream of dry CS₂, quickly separating the white needles that form on the cooler part of the tube, and keeping in a closed tube (Fremy, *l.c.*). The residue that remains on distilling the products of the interaction of SiCl, and H₂S (v. Silicon Chlorohydrosoulphide, p. 459) contains SiS, and S; S may be removed by carefully heating in a stream of N (Gay-Lussac a. Thénard, A. Ch. [2] 69, 204). Long, lustrous, white needles; volatilised at very high temperatures (Fremy, l.c.). Unchanged in dry air at ordinary temperatures; decomposed by moist air to H₂S, and crystalline SiO₂ pseudomorphous with SiS2; burns to SO2 and SiO2 when heated in air. Decomposed rapidly by water to SiO₂xH₂O and H₂S; also decomposed by alcohol and ether (Fremy, l.c.). HNO, oxidises rapidly, producing H.SO. M. M. P. M.

Silicon, sulphocyanide of; v. p. 463. SILICON, ORGANIC COMPOUNDS OF.

Silicic ethers are described elsewhere -v. AMYL, AMYLPHENYL, ETHYL, METHYL, PHENYL, THYMYL, TOLYL, and XYLYL SILICATES.
Tetra-methyl-silicane SiMe. • Mol. w. 88.

(31°). V.D. 3·08 (calc. 3·04). Formed by heating SiCl, with ZnMe, at 120° (Friedel a Crafts, A. 136, 203). Light oil, burning with bright flame emitting SiO2. Not attacked by potash or HNO, (S.G. 1.4).

Mol. w. 144. Tetra-ethyl-silicane SiEt,. (153°). V.D. 5·13 (calc. 4·99). S.G. 2·834. Prepared by heating SiCl, with ZnEt, at 160°. Formed also by the action of ZnEt, and Na on ethyl silicate (Friedel a. Crafts, Bl. 1863, 468; 1865, 358; A. 127, 31; 138, 19). Oil, insol. H.SO. Chlorine forms liquid Et.SiC.H.Cl (185°), converted by alcoholic KOAc at 180° into Et,SiC,H,OAc (2080-2140), whence alcoholic

Formed by distilling Si, I, with ZnEt, (Friedel a. Ladenburg, A. 203, 251). Oil, burning with bright flame.

'Silicopropionic acid' EtSiO.OH. Got by heating its ortho- ether with HIAq (Ladenburg, A. 159, 271; 164, 305). Amorphous powder, insol. water and Na CO Aq, sol. conc. KOHAq.

Methyl ortho- ether EtSi(OMe),. (126°). S.G. 2 9747. Formed from Si(OMe), sodium, and ZnEt, (Ladenburg, B. 5, 1081). Oil.

Ethyl ortho-ether EtSi(OEt), (159°).
S.G. 2 927. Formed by the action of Na and

ZnEt, on ClSi(OEt), or Si(OEt), Oil. Converted by BzCl into EtOBz and EtSiCl, (100°), which fumes in the air and is converted by water into silicopropionic ether.

'Silicodiethyl ether' Et2Si(OEt)2. (156°). V.D. (H=1) 87 (calc. 88). S.G. 9 ·875. Formed from Na, ZnEt₂, and silicic ether. Oil, sol. alcohol and ether. AcCl (1 mol.) at 200° forms EtOAc and Et₂SiCl(OEt) (147°). A larger quantity (2 mols.) of AcCl at 250° forms Et.SiCl₂ (129°), which is decomposed by water, forming syrupy SiEt₂O (above 360°), which may also be got by boiling SiEt, (OEt), with HIAq.

'Silicoheptyl ether' SiEt. OEt. Mol. w. 160. (153°). S.G. $\stackrel{4}{\sim}$ *840. V.D. (H = 1) 80°8 (calc. 80). Formed from SiEt. (OEt)₂. Na, and ZnEt₂. Oil, sol. alcohol and ether. Sol. conc. H₂SO₄. AcCl at 180° forms SiEt₃Cl (144°), S.G. SiEt,OH.

Tri-ethyl-silicol SiEt,OH. Mol. w. 132. (154°). S.G. 2 871. Formed by dropping SiEt, OEt into NH, Aq, or by heating it with Ac, O at 250° and decomposing the resulting SiEt₃.OAc with Na₂CO₃Aq. Thick liquid, smelling like camphor. Insol. water, miscible with alcohol and ether. Burns with bright flame. Sodium forms SiEt, ONa, which, in ethereal solution, combines with CO2, forming SiEt3, CO2Na, an amorphous deliquescent solid, decomposed at a red heat into Si₂Et_aO and Na₂CO₃. AcCl forms HOAc and SiEt₃Cl. HIAq at 200° forms ethane and SiEt₂O. Oxidising agents have no action. Fuming H2SO4 forms EtSiO2H, ethane, H, and SO4

Acetyl derivative SiEt₃OAc. (168°). S.G. ²·903. Formed by heating SiEt₃.OEt with Ac₂O at 250°. Liquid with ethereal odour.

'Silicoheptyl oxide' (SiEt₃)₂O. Mol. w.246.

(231°). S.G. 2 859. Formed as above, and also by the action of P2O, on tri-ethyl-silicol. Got also from SiEt, Cl and KOHAq. Colourless syrup, sol. H.SO, and separated unchanged on dilution, if heating be avoided.

(107°). S.G. (8). Formed, Tri-ethyl-silicane SiEt.H. ² ·751. V.D. (H = 1) 59 (calc. 58). together with SiEt,, by the action of excess of ZnEt, and Na on Et,SiO,. Liquid, insol. water and H.SO,, sol. alcohol and other. Fuming H₂SO, converts it into (SiEt₃)₂O. HNO₃ attacks it vigorously. Bromine added slowly to the cooled liquid forms SiEt₃Br (161°), which is converted by NaOHAq into (SiEt,),O, and by NH3Aq into SiEts.OH.

Bilicoformic acid. Ethyl ortho- ether SiH(OEt)3. (134°). Formed from SiHCl2 and Dotash at 120° forms oily Et. SiC.H.OH (190°).

Hexa-ethyl di-silicane Si.Et. (252°).

S.G. § 851; 38 840. V.D. 8.6 (calc. 7.96). Hygroscopic liquid, decomposed by alkalis with absolute alcohol (Friedel a. Ladenburg, A. 143, 123; Bl. [2] 7, 322; Gattermann, B. 22, 190). svolution of H. Sodium decomposes it into

SiH, and Et,SiO,.

Chloro-silicoformic ether v. ETHYL SILICATE. 'Silicoacetic acid.' Ethyl ortho- ether CH₃.Si(OEt)₃. (145°-151°). S.G. 2 .928. Formed by heating silicic ether with ZnMe. Oil, sol. alcohol. Converted by HIAq into amorphous silico-acetic acid CH., SiO., H., which is insol. water and ether (Ladenburg, B. 6, 1029).

The term silicoacetic acid is also sometimes used to denote $H_2\mathrm{Si}_2\mathrm{O}_3$, which is got by decomposing $\mathrm{Si}_4\mathrm{I}_5$ by water at 0° (Friedel a. Ladenburg, $A.\ 203,\ 249$; $v.\ \mathrm{Silico-oxalic acid,}\ infra). A compound <math>\mathrm{Si}_2\mathrm{O}_3\mathrm{O}_2$ is formed, as a bottle-green powder, by heating silicon to whiteness in a

crucible lined with lampblack. It is insol.

KOHAq and HFAq (Colson, C. R. 94, 1316).

Tetra-propyl-siticane Si(C₂H₁), (213°).

S.G. ² 7979; ¹⁵ 7883. V.D. 99.7 (obs.).

Formed, together with SiHPr₃, by heating ZnPr₂. (2 pts.) with SiHCl, (1 pt.) at 150° (Pape, B. 14, 1872; A. 222, 370). Colourless oil, sol. alcohol, and ether, insol. H₂SO₄. Br has no action in Colourless oil, sol. alcohol. the cold, but on warming it forms oily SiC₁₂H₂,Br, converted by alcoholic potash into oily SiC₁₂H₂₆ (206°-210°).

Tri.propyl-silicane SiHPr_s. (170°). S.G. 7723; ¹⁵ 7621. V.D. 82 (obs.). Formed as above. Oil, v. sol. alcohol and ether, insol. Formed conc. H2SO4. Burns with bright flame, forming SiO₂. Br acts violently, forming SiPr₃Br (213°), a fuming liquid, which is slowly converted by

water into SiPr. OH.

Tri-propyl-silicol SiPr₃.OH. (205°-208°). Formed by the action of NH3Aq on SiPr3Br, or of Na₂CO₃Aq on SiPr₃.OAc (Pape). Oil.

Acetyl derivative SiPr. OAc. 216°). Formed from SiPr, Br and AgOAc. Oil.

Hexa-propyl-di-silicyl oxide (SiPr₃)20. (280°-290°). Formed by warming SiHPr, with H₂SO₄ and, together with SiPr₈.OH, by boiling SiHPr, with Na₂CO₃Aq (Pape, A. 222, 369). Liquid, sol. alcohol, ether, and H₂SO₄.

Silicon sulphocyanide Si(CNS). (c. 300°). Formed by distilling lead sulphocyanide with SiCl, (Miguel, A. Ch. [5] 11, 343). Colourless prisms, insol. ether and CS₂, soluble in a solution of HCNS in benzene. Burns with violet flame. Dyes the skin red. Decomposed

by water into HCNS and SiO...

Tetra-phenyl-silicane SiPh.. [233°]. (above 860°). S.G. 20 1.0780. Formed from chlorobenzene, SiOl., and Na in presence of a little EtOAc (Polis, B. 18, 1540; 19, 1012; 20, 3331). Dimetric crystals; a:o=1:440, sol. hot benzene, sl. sol. alcohol and ether. May be sublimed. Sulphonated by fuming H2SO4. HNO8 forms Si(C₄H₄,NO₂), [105°], a yellow powder, v. sol. benzene. Converted by PCl₃ into liquid SiPh₂Cl₂ (234° at 90 mm.) and SiPh,Cl [89°], from which water produces tri-phenyl-silicol SiPh, OH [141], which separates from ether in colourless crystals.

Phenyl-tri-chloro-silicane SiPhCls. (197°). Formed by heating SiCl₄ with HgPh₂ at 300° (Ladenburg, B. 6, 379). Oil. Decomposed by hot water, or by NH₂Aq, yielding 'silicobenzoic acid' SiPh(OH)₂ [92°]. Absolute alcohol forms 'silicobenzoic' ethyl ortho- ether SiPh(OEt)₂ (237°). S.G. 2 1.018; ¹² 1.006. Silicobenzoic acid is converted at 100° into amorphous 'ailicobenzoic anhydride' (SiPhO),O.

Phenyltriethyl-silicane SiPhEt. S.G. 2 904. Formed, together with SiEt, and SiPh₂Et₂ (c. 810°), by heating SiPhCl₃ with ZnEt₄ at 150°. Oil, smelling like cloves. Yields a bromo-derivative (270°-280°). Ol forms SiC₁₂H₁₃Ol (260°-265°), S.G. 2 1 0185.

Tetra-m-tolyl-silicar : Si(C.F) (above 550°). S.G. 20 1.119. .med from m-bromo-toluene, SiCl,, and Na (Polis, B. 19, 1021). Pale-yellow needles (from ether), v. sol. benzene and chloroform, insol. alcohol.

Tetra-p-tolyl-silicane Si(C,H_r)₄. [228°]. (above 360°). S.G. ²² 1-079. Formed from p-bromo-toluene, SiCl₄, and Na (Polis, B. 18, 1542). Colourless crystals, sol. benzene.

p-Tolyl-tri-chloro-silicane C,H,SiCl₂. (219°).
Formed from Hg(C,H₂), and SiCl₄ at 310° (Ladenburg, A. 173, 165). Fuming liquid, decomposed by water. Converted by NH₃Aq into viscid C,H,SiC₂H, which is converted at 200° into the solid anhydride (C,H,SiO),O, which is not melted at 200°.

Tetra-benzyl-silicane v. vol. i. p. 502.

Silicon tetra-phenyl-tetra-amide Si(NHPh)4. [138°]. Formed from SiBr, and excess of aniline diluted with benzene, the product being distilled in a current of H at 105° (Reynolds, C. J. 55, 477). Colourless monoclinic crystals; $a:b:o = 985:1:1\cdot043$; $\beta = 110^{\circ}20'$. V. sol. benzene, sol. CS., insol. ligroin. Decomposed by water and alcohol. Not decomposed by heating at 210°. HCl forms SiCl, and aniline.

Silicon di-chloro-di-phenyl-di-amide SiCl₂(NHPh)₂. Formed from SiCl, and aniline (Harden, C. J. 51, 40). Amorphous solid. Decomposed by water into aniline hydrochloride and silica.

Silicon tetra-o-tolyl-tetra-amide

Si(NHC,H,)₄. Formed from SiCl₄, o-toluidine, and benzene (Reynolds). Prisms, v. sol. benzene and CS₂. The compound SiCl₂(NHC,H,)₂, which is also formed from SiCl, and o-toluid-ine, is a white granular powder (Harden).

Silicon tetra-p-tolyl-tetra amide

Si(NHC,H₁), [132°]. Formed from SiCl, and p-toluidine in benzene (Reynolds). Botryoidal aggregate of needles, v. sol. benzene and ether, decomposed by water and alcohol.

Silicon tetra-naphthyl-tetra-amide Si(NHC₁₀H₁). Formed from (\$\beta\$)-naphthylamine and SiCl₄ (R.). Nodules, decomposed by water. Sl. sol. ligroin, sol. benzene.

SILICO-NITRATES. SiO₂ seems to form some compounds with N₂O₃ and basic oxides the salt 3SiO₂N₂O₃.7Ag₂O (=3Ag₄SiO₄.2AgNO₄) was obtained, in ruby-coloured prisms, by Rousseau a. Tite (C. R. 114, 294), by heating AgNO, with a little water and fragments of marble in a sealed tube at 180°-300° for several hours; heated to dull redness, it gave off N oxides, and Ag and Ag₂SiO₃ remained.

M. M. P. M.

SILICO-OXALIC ACID $H_2Si_2O_4 = {\begin{array}{c} O:Si.OH \\ O:Si.OH \\ \end{array}}$

This compound is obtained, as a white amorphous powder, by the interaction of water and Si₂Cl₆ or Si₂I₆ at 0°; the gelatinous pp. is washed with ice-cold water, dried in vacuo and then at 100° (Friedel a. Ladenburg, A. 203, 118). It is also produced by the interaction of Si.I. with

absolute alcohol. The compound is decomposed even by weak bases, with evolution of H. M. M. P. M.

SILICO PHOSPHORIC OXIDES. (Silicophosphoric acids.) SiO₂.P₂O₃ and SiO₂.P₂O₃.4H₂O. The compound SiO₂.P₂O₃.

= SiP₂O₃ is formed by dropping SiO₂, prepared by decomposing SiF, by water and drying the pp., into molten HPO, and washing with water (Hautefeuille a. Margottet, C. R. 96, 1052; v. also Skey, C. N. 16, 187). Large, hard, transparent crystals; S.G. 3·1 at 14°; melts when strongly heated to a glass-like mass. The crystals are polymorphous; they are hexagonal under 300°; at c. 300° they form leaflets resembling tridymite, between 700° and 800° they are regular octahedra, and between 800° and 1000° they assume the form of clinorhombic prisms. Water attacks the hexagonal, but not the octahedral or prismatic, crystals. Molten AgNO₂ forms Ag₂PO₄ and SiO₂ with all the forms (H. a. M., C. R. 99, 789).

The compound SiO₂.2P₂O₅.4H₂O was obtained (H. a. M., C. R. 104, 56) by one-fourth saturating H,PO,Aq with SiO,xH,O, heating the solution in a Pt dish to 125° for 7-8 hours, and drying the solid which separated. The compound is a crystalline powder; decomposed by moist air: sol. water at 0°, but decomposed by water at the ordinary temperature to H,PO Aq and gelatinous SiO, xH,O. M. M. P. SILICOPHOSPHORIC OXYCHLORIDE M. M. P. M.

SiP₂O₄Cl₄. (Silicopyrophosphorylchloride.) Prepared by heating SiCl₃.OEt, or Si(OEt), with excess of POCl₄ to 180° for 2 hours, distilling off EtCl, and SiCl, if prepared from SiCl, OEt, and heating the solid that remains to 150°-200° in a stream of dry air to remove adhering POCl₃. A white, loose, very hygroscopic, amorphous powder. Very sol. water, but with separation of SiO₂xH₂O; easily sol. alcohol, insol. ether. Decomposed very slowly below 200°, more rapidly above 200°, giving off POCl₂; at a red heat P₂O₃ comes off, and a glassy mass remains, probably consisting of SiO₂ and SiO₂·P₂O₃. Addition of excess AgNO₃Aq to solution in water (with a little alcohol to prevent separation of silical, followed by HNO.Aq note Accil tion of silica), followed by HNO, Aq, ppts. AgCl, and on filtering this off and adding NH, Aq drop by drop Ag,P₂O, is ppd. mixed with some Ag,PO, Heated to 100° with PCl, the equation SiP₂O₃Cl₂+4PCl₅ = SiCl₄+6POCl₃ is realised. The constitution of the compound is probably O.PO.CI

either
$$Si \leqslant_{O_2:PO.Cl}^{O_2:PO.Cl}$$
 or $O:Si \xrightarrow{O}$ (Stokes,

Bulletin U.S. Geolog. Survey, No. 90 [1892] 47; M. M. P. M. also in B. 24, 933).

SILICOTITANATES. Compounds of silicates and titanates are found in certain minerals; sphene, for instance (CaO.3SiO.2CaTiO.), may be called a silicotitanate. M. M. P. M.

SILICOTUNGSTATES. Compounds containing SiO₂, WO₃, and basic radicles; v. Tungsto-silicates.

SILICOVANADATES v. VANADO-SILICATES.

SILK v. Proteïds.

SILVER. Ag. At. w. 107.66. Mol. w. not known (v. infra, Properties). Melts at c. 950°;

Person (A. Ch. [8] 27, 250) gave 1000°, Daniell (T. 1830. 237) 1024°, Violle (C. R. 85, 543) 954°, Becquerel (J. 1863.) 916°, Deville (B. 12, 791) 916°. B.p. not known; Meyer (B. 12, 1428) says that Åg does not appreciably evaporate at c. 1570°. S.G. c. 10.5; Playfair a. Joule (C. S. Mem. 3, 66) gave 10.53, and 9.13 to 9.28 for molten Ag, Dumas (C. N. 37, 82) gave 10.512 for Ag heated in vacuo, Roberts-Austen gave 10.57, and 9.46 to 9.5 for liquid Ag (Pr. 23, 495); for further data v. Clarke's Table of Specific Gravities [new ed.] 14. S.H. 0°-100° = '0557 (Dulong a. Petit, A. Ch. [2] 7, 113); '0559 (Bunsen, P. 141, 1); '05722 (Louguinine, A. Ch. [5] 27, 398). C.E. '00002 between 0° and 1002 (n. Methicaen, P. 120, 50. 12. 3. 3. 100° (v. Matthiessen, P. 130, 50; Fizeau, C. R. 68, 1125); 00003721 from 0° to the m.p. (Roberts-Austen, Pr. 23, 495). T.O. 100 (that of copper = 73°6, and of Au = 53°2, Wiedermann a. Franz, A. 88, 191); heat sufficient to raise 109.6 mgm. water from 0° to 1° passes in i second through each sq. mm. of a plate of Ag 1 mm. thick, the two sides of which differ in temperature by 1° (Weber, B. B. 1880. 467). E.C. (Hg at 0°=1) 57-226 for soft Ag, 63-845 for hard Ag (Siemens, P. 110, 1); 62·12 (Benoit, C. R. 76, 382). H.C. [Ag²,O] = 5.900 (Th. 3, 381). Heat of fusion (for 108 g.) 2.275 (Person, A. Ch. [3] 24, 275); 2.67 (Pionehon, A. Ch. [6] 11, 100). S.V.S. c. 10.3. Emission spectrum gives a line 5464 in the yellow, 5200.9 in the green, and many lines in the orange, green, blue and violet (v. B. A. 1884. 442); for absorptionspectrum of Ag vapour v. Lockyer a. Roberts-Austen (Pr. 23, 344). Refraction equiv.

 $=\frac{\mu-1}{d}$. At. w. = 12.62 (Kanonnikoff, J. R. 1884.

[1] 119); 13·2 (Gladstone, Pr. 18, 49)

Occurrence.-Found native, generally alloyed with Au, Cu, &c. The chief compounds found in ores are Ag.S (frequently in combination with Cu.S, Fe,S., Sb,S., As,S., Bi,S., PbS, &c.), AgCl, AgBr, AgI, compounds of Ag with Sc, Te, As, Sb, Bi, &c. Ag is also found in small quantities in most lead ores. According to Malaguti (J. pr. 42, 422; cf. Field, D. P. J. 143, 397), traces of salts of Ag (c. 1 mgm. Ag in 100 litres) are found in sea-water. Small quantities of Ag, probably as AgCl, have been found in volcanio dust (Mallet, Pr. 47, 277). Silver has been known and used from the earliest times (for a full historical account of silver, including the derivation of the name, v. Silber in Ladenburg's Handwörterbuch der Chemie, 10, 635).

Formation.-1. By heating Ag₂S with PbO or PbSO,, SO, and a compound or alloy of Ag and Pb are formed; the Pb may be separated from this alloy by cupellation.—2. By shaking AgCl with Hg and water, HgCl and an amalgam of Ag and Hg are formed; Ag remains when the Hg is removed from this amalgam by heating.— 3. Ag is ppd. from solutions of its salts by Zn, Cu, Fe, &c.-4. AgCl is reduced to Ag by treatment with many reducing agents, such as Zn and H₂SO₄Aq, also by fusion with Na₂CO₄ and C .- 5. Most easily-oxidised metals ppt. Ag from solutions of its salts. For an account of the extraction of Ag from its ores v. Dictionary or APPLIED CHEMISTRY, vol. iii. p. 886.

Preparation.—Silver coins are dissolved in

pure dilute boiling HNO,Aq, the solution is evaporated to dryness, the residue is heated till it melts, after cooling it is dissolved in NH, Aq, after standing forty-eight hours the liquid is passed through a filter made of specially good paper, and the filtrate is diluted till it contains not more than 2 p.c. of Ag. This ammoniacal solution contains AgNO, and Cu(NO,)2; the whole of the Ag is ppd. by ammoniacal solution of (NH₁)₂SO₃ at 60°. A solution of (NII₁)₂SO₃ is prepared by saturating pure NH₃Aq with SO₄ (made by heating pure Cu with pure H.SO. diluted with $\frac{1}{2}$ to $\frac{2}{3}$ its volume of water); a measured quantity of this solution is mixed with excess of pure NH, Aq, heated to boiling, and the ammoniacal solution containing AgNO. and Cu(NO₃)₂ is run from a burette into the boiling liquid until there is the faintest trace of blue colour in the liquid above the ppd. Ag. Cuprous sulphite is formed, and this reduces the AgNO, in the ammoniacal liquid; when all the AgNOs is reduced, the blue colour of the ammoniacal copper nitrate appears. The whole of the ammoniacal solution of AgNO, and Cu(NO₂), is now mixed with the proper quantity of ammoniacal (NH₄) SO₃Aq required for complete reduction of the AgNO₃, the mixed liquids are set aside in a closed vessel for fortyeight hours, when c. 1/3 of the Ag is ppd.; the blue liquid is decanted off and heated on a water-bath to 60°-70°, whereby the whole of the Ag in solution is ppd. The two quantities of ppd. Ag are washed with ammoniacal water, by decantation, until the washings show no trace of blue colour on standing (or until BaCl₂Aq gives no trace of pp.), the Ag is kept in contact with conc. NH₃Aq for some days, and is then washed with water until every trace of NH, is removed. If it is desired to have the Ag in bars, the finely-divided metal obtained by ppn. is mixed with 5 p.c. of its weight of pure borax which has been strongly heated, and 5 p.c. pure NaNO, fused in a porcelain crucible and poured into kaolin moulds lined with a paste made of a mixture of kaolin that has been strongly heated and unignited kaolin; when cold the bars are cleaned with fine sand, then strongly heated with pure KOHAq (to remove traces of kaolin) and washed with water. The bars may be cut with a chisel of very hard steel; if this is done the pieces must be warmed for some time with pure conc. HClAq, washed with NH₃Aq, and then with water (Stas. Rech. 88 et seq.). The Ag may be freed from traces of absorbed gases by distilling it; this is done by placing the Ag in a hole in a block of strongly-heated marble; this hole communicates, by a slit in the marble, with another hole from which an opening passes upwards to the surface of the marble; another opening admits the nozzle of an O-H blowpipe, so that the flame plays on the surface of the Ag. (For flame plays on the surface of the Ag. (For details v. Stas, l.c.) Dumas (A. Ch. [5] 15, 289) found that 1 kilo. of Ag considered pure gave from 59 to 174 c.c. O when heated in a Sprengel vacuum; it was supposed by some chemists (v. Mallet, T. 1880. 1003; Clarke, Recalculations of the Atomic Weights, 262) that this result proved that Ag made by Stas' process was not quite pure; but Brauner has proved experimentally (C. J. 55, 899) that Ag prepared YOL IV,

by Stas's method described above, and distilled by the O-H flame in a block of burnt marble, gives off no O when heated in vacuo (v. also Stas, Bull. Acad. roy. Belg. [8] 18, 23; abstract in C. J. 58, 561).

Properties.—A white, very lustrous metal. Crystallises in forms in the regular system, chielly cubes, octahedra, and rhombododecahedra; these crystals are obtained by slowly cooling molten Ag, or by the electrolytic deposition of the metal; they are also sometimes found native. Finely divided Ag—as obtained, for instance, by reduction of AgCl—is a grey powder, which becomes white and lustrous when compressed with a flat iron. A thin deposit of

Ag on glass transmits bluish light.

Ag is harder than Au and softer than Cu. Ag reflects light and heat strongly; its absorptive power is very small. It is very mallcable; Ag foil has been obtained 003 mm thick. Ag is very ductile; '06 gram may be drawn to a wire 130 metres long; it is so tenacious that a cold-drawn wire of 2 mm. diameter does not break till it is loaded with 80-85 kilos (Baudrimont, A. Ch. [3] 30, 304). Ag is slightly volatile at a low-red heat in vacuo, but not at the ordinary pressure at this temperature, nor in vacuo at 410°-450° (Stas, Bull. Acad. rov. Belg. [3] 18, 23). It may be distilled, by heating, by the O-H flame, Ag placed in a block of burnt marble. Stas distilled 50 g. Ag in c. 15 mins.; part of the Ag appeared as a blue vapour during the distillation. When an alloy of Ag with a more volatile metal, such as Hg, Pb, or Sn, is heated, part of the Ag volatilises with the other metal. Molten pure Ag absorbs c. 20 times its volume of O from the air (v. Lucas, A. Ch. [2] 12, 402; Gay-Lussac, A. Ch. [2] 45, 221; Graham, P. M. [4] 32, 503; Neumann, M. 13, 40; Levol, J. pr. 57, 192); as the Ag cools it 'spits' and gives off the O it has absorbed; Dumas' experiments (A. Ch. [5] 15, 289) show that a little O is retained, but Brauner (C. J. 55, 399) has proved that no O remains if the Ag is distilled in a block of burnt marble. (For the chemical action of O on Ag v. Reactions, No. 1.) Pure Ag suffers no change when heated in air, H, or CO (van der Plaats, Mandblad voor Natuur-wetenschappen, 1886. No. 2). Molten Ag ab-sorbs P, but the whole of the P, except c. :002 p.c., separates on cooling (Warren, C. N. 56,

The at. wt. of Ag has been determined (1) by finding the ratio of Ag to Cl in AgCl (Berzelius, P. 8, 17 [1826]; Turner, T. 1829. 297 [1829]; Marignac, A. 44, 23 [1842]; ibid. Bibl. univ. Genève, 46, 354 [1843]; Maumené, A. Ch. [3] 55, 134 [1859]; Stas, Stas. Rech. 38 et seg. [1860]); (2) by finding the ratio of Ag to Br in AgBr, and of Ag to I in AgI (Marignac, l.c. 46, 360 [1843]; Stas, Stas. Nouv. R. 158 et seg. [1865]); (3) by determining the ratio of Ag to Ag.8 formed therefrom (Dumas, A. Ch. [3] 55, 147 [1859], Stas, Stas. Rech. 53 [1860]); (4) by reducing Ag.SO., to Ag (Struve, A. 80, 203 [1851]; Stas, Stas. Rech. 125 [1860]); (5) by converting Ag.SeO., into Ag (Pettersson a. Ekman, Bl. [2] 27, 205 [1876]); (6) by converting Ag.NO. (Marignac, A. 59, 289 [1843]; Stas, Stas. Rech. 50 et seg. [1860]); (7) by determining

S.H. of Ag; (6) by finding V.D. of AgCl at white heat (Biltz a. Meyer, B. 22, 725). The classical work of Stas has placed the value for the at. wt. on a very sure foundation.

Ramsay (C. J. 55, 521) measured the depression of the vapour-pressure of Hg by dissolving Ag therein; assuming that the mol. w. of liquid Hg is 200, and that equal volumes of dilute solutions of metals in Hg contain equal numbers of molecules, the results led to the conclusion that the mol. w. of Ag is the same as the at. wt.

AgCl is the only compound of Ag the vapourdensity of which has been determined; the value found shows that the atom of Ag is monovalent in the gaseous molecule AgCl.

Ag is fairly closely related chemically to Cu and Au (v. Copper group of Elements, vol. ii.

p. 250).

Allotropic forms of silver. According to Schneider (B. 25, 1281, 1440), an aqueous solution of Ag, containing c. 20 g. Ag per litre, is obtained by mixing 150 g. FeSO, 7aq in 500 c.c. water and 280 g. Na citrate in 700 c.c. water, pouring the mixture into 500 c.c. of 10 p.c. AgNO, Aq (it is best to divide the mixture into five parts, as small quantities are more easily dealt with), removing liquid from ppd. Ag after half an hour (by a pipette), filtering through a good filter under decreased pressure, and dissolving the ppd. Ag in as little water as possible; by adding absolute alcohol, and filtering, after some days, with help of a good waterpump, colloidal Ag containing from '3 to '5 p.c. of Fe salts is obtained. A very little HClAq ppts. Ag with a little AgCl and Ag.Cl (?) from solution of colloidal Ag. Carey Lea has carried out a series of researches on the properties of Ag ppd. from solutions of its salts by ferrous citrate, ferrous tartrate, and dextrin in presence of alkali (Am. S. [3] 37, 476; 38, 47, 129, 237; 41, 179, 259; P. M. [5] 31, 238, 320, 497; 32, 937). The pps. of Ag show almost every shade of colour, such as blue, red, green, purple, golden; some of the pps. are soluble in water, and some are not; most of the pps. are very sensitive to light, but they vary much in this respect; some of the pps. yield ordinary Ag when heated; ordinary Ag is also ppd. from solutions of soluble colloidal Ag by a little very dilute HClAq. In no case does any so called allotropic Ag seem to have been obtained quite free from organic compounds; the percentage of Ag in the pps. varied from c. 90 to c. 98. For accounts of the properties of the various coloured pps. the memoirs of Carey Lea must be consulted; v. also Schneider, B. 24, 3370; Barus a. Schneider, Z. P. C. 8, 278; Prange, R. T. C. 9, 121; Muthmann, P. 20, 983. B. a. S. determined many of the physical properties of a solution of colloidal Ag, and concluded that the colloidal variety consists of extremely minute particles of ordinary Ag that remain suspended in the liquid for a considerable time.

Reactions and Combinations.—1. According to Debray (C. R. 66, 735), Ag is partially oxidised by very strongly heating in the O-H flame, using excess of oxygen. According to Le Chatelier (Bl. [2] 48, 342) pure ppd. Ag is oxidised by heating in oxygen at 300° under 15 atmos. pressure; after 50 p.c. of the Ag was

oxidised the change stopped .- 2. Ozonised oxygen acts on moist, finely-divided Ag at the ordinary temperature, forming a peroxide (v. Silver Peroxide, p. 471).—3. Ag combines easily with chlorine, bromine, iodine, and sulphur (v. SILVER CHLORIDE &c.); also, by heating, with selenion, arsenic, and phosphorus (v. SILVER SELENIDE &c.).-4. Finely-divided Ag'is said to dissolve, with oxidation, in ammonia solution in presence of air (Carey Lea, Zcit. filr anorg. Chem. 3, 180).—5. Ag reacts with steam at a white heat, absorbing O while H is given off.— 6. Finely-divided Ag is oxidised by hydrogen peroxide (Berthelot, A. Ch. [5] 21, 164).—
7. Finely-divided Ag is said to be oxidised by heating with oxides and salts that readily give up oxygen-e.g. MnO₂, Pb₃O₄, Pb(NO₃)₂, &c.-8. Hydrogen sulphide forms Ag.S. Alkali sulphides also produce Ag2S .- 9. Molten sodium chloride forms AgCl, some Na vapour being given off; solution of sodium chloride, as also of potassium or ammonium chloride, dissolves some Ag as AgCl.-10. Potassium iodide solution, in air, forms soluble AgI.KI.-11. Hot solution of potassium cyanide dissolves Ag, forming AgK(GN)₂ (v. Christomanos, Fr. 7, 301).—12. Fusion with silicates, such as glass, forms Ag₂O, which dissolves in the molten silicate .- 13. Ag dissolves in solution of ferric sulphate on warming; as the solution cools the Ag, SO, is again decomposed, with formation of Fe₂(SO₄)₃ and ppn. of finely-divided Ag.—14. A compound of Ag and Si is said to be formed by strongly heating Ag with potassium silico-fluoride and potassium (Warren, C. N. 60, 5).— 15. Ag dissolves in moderately dilute nitric acid, forming AgNO₃, and giving off N oxides; the gaseous products are N₂O and NO, according to Montemartini (G. 22, 384, 397, 426).—16. Conc. hydrobromic and hydriodic acids dissolve Ag on warming, with evolution of H; the dissolved AgBr or AgI is ppd. on dilution.—17. Hot conc. sulphuric acid dissolves Ag, giving off SO₂; if a little Fe2(SO4)3 solution is added the Ag goes into solution without heating. Very finelydivided Ag, obtained by reduction of Ag saits by milk-sugar and alkali, is dissolved by very dilute H₂SO,Aq (Carcy Lea, Zeit. für anorg. Chem. 3, 180). Friedheim (B. 19, 2554; 20, 307) says that Ag dissolves in dilute H2SO, Aq containing KMnO₄Aq.—18. Chromic acid (i.e. solution of CrO₃ in water) produces red Ag₂CrO₄; HNO₃Aq, S.G. 1·2, in which K₂CrO₄ is dissolved, gives a red deposit on the surface of Ag; this test is used to distinguish Ag from other white metals, such as Sn.-19. Ag in pieces is scarcely acted on by hydrochloric acid, even when hot and conc.; very finelydivided Ag is said to form a little AgCl, with evolution of H. Hydrofluoric acid is without reaction. - 20. Ag is not acted on by molten alkalis or alkaline carbonates; hence KOH, &c., may be fused in dishes of Ag.-21. Ag alloys with many metals (v. Silver, alloys or).

Silver, alloys of. Ag forms alloys with many metals. They are generally formed by heating the metals together; in a few cases—e.g. alloy with Ba or Mn—they are formed by heating Ag with metallic cyides and C.

heating Ag with metallic oxides and C.

With aluminium. An alloy of 100 parts
Al with 5 parts Ag is harder and more easily

4.4

the properties of Al: it is used for making the pans, &c., of balances. Hirzel (J. 1858. 137) obtained alloys corresponding in composition with the formulæ Ag,Al, Ag,Al, and AgAl (v. also Tissier, C. R. 43, 885; 52, 931; Debray, C. R. 43, 925).

With antimony, and with arsenic; v. SILVER

ANTIMONIDE and ARSENIDE, infra.

With copper. Ag becomes harder, more elastic, more capable of being polished, and more slowly worn away when alloyed with Cu without losing much in malleability and ductility. Alloys with less than 50 p.c. Cu are white, with more than 50 p.c. Cu the colour becomes reddish. The S.G. of a Ag-Cu alloy is rather smaller than the mean of those of the constituent elements (v. Karmarsch, D. P. J. 108, 278). The composition of these alloys is rarely identical throughout a mass (v. Levol, A. Ch. [3] 36, 193). Alloys of Ag and Cu are used for making silver vessels and ornaments, and for coinage; the standard silver coinage alloy of the United Kingdom contains 925 parts Ag and 75 parts Cu per 1,000.

With mercury. The amalgams of Ag are formed (1) by the action of Hg on AgNO₃Aq, (2) by the action of finely-divided Ag on HgCl, Aq, (3) by dissolving Ag in Hg. The compositions of many of these amalgams can be represented by formulæ, but it is very doubtful whether any of them are definite compounds. For accounts of these amalgams v. Campani, J. 1870. 373; Joule, C. J. [2] 1, 378; Crookewitt, J. 1847-48. 393; Malaguti a. Durocher, Ann. M. 17, 336;

Gay-Lussac, A. Ch. 58, 218.

Alloys of Ag with the following metals have been described :- Ba (Clarke, G. A. 62, 373; Lampadius, S. 15, 146); Cd (Wood, C. N. 6, 135); Au (G. Rose, P. 23, 181; Levol, A. Ch. [3] 15, 55; 27, 310); Ir; Fe; Pb (Levol, A. Ch. [3] 39, 173); Mg; Mo; Ni; Pd (Graham, J. 1868. 144); Pt; K; Rh; Na; Sn; Zn (v. Wright a. Thompson, Pr. 48, 25).

Silver, antimonide of. The mineral dyskrasite has approximately the composition Ag, Sb; when heated to dull redness in H, the compound Ag, Sb is said to remain (von Bonsdorff, S. 34, 225). The compound Ag, Sb is also obtained by ppg. AgNO, Aq by Sb hydride; using conc. AgNO, Aq the compound Ag, Sb.3AgNO, was formed (Poleck a. Thümmel, B. 16, 2435)

Silver, arsenide of. No definite compound of Ag and As has been obtained. By heating Ag powder with As about 16 p.c. of As is absorbed by the Ag to form a grey, brittle solid By passing As hydride into conc. (Gehlen). AgNO, Aq the compound Ag, As. 3 AgNO, was obtained (P. a. T., l.c.).

Silver, bromide of, AgBr. (Argentic bromide.) Formula probably molecular, from analogy of AgCl. Occurs native in Chili and Mexico.

Preparation. - HBrAq or alkali bromide solution is added to AgNO, Aq till ppn. is complete; the pp. is washed with water in the dark and dried.

Properties.-A pale-yellow solid; melts at c. 434° (Carnelley, C. J. 29, 489). S.G. 6.245 at

polished than Al, but otherwise has most of For effects of heat on AgBr v. Rodwell (Pr. 25. 280). Obtained in octahedra by crystallising from HBrAq. Solubility of AgBr dried at 100° in NH Aq S.G. 986, = 051 (Pohl, J. pr. 82, 52). Granular AgBr is slightly sol. water above 50° flocculent AgBr is slightly sol. water above 33° (Stas, A. Ch. [5] 3, 289). Sol. hot Hg(NO₂), Aq; AgBr crystallises out on cooling (Debray, C. R. 70, 995). Sol. solutions of alkali bromides. H.F. [Ag,Br] = 22,700 (Th. 3, 381). According to Berthelot (Bl. [2] 39, 19), the reaction [Ag,Br] has the value 23,700 when crystalline AgBr is formed, and the value 20,000 when the AgBr is amorphous (in both cases using liquid Br). B. also says that in the formation of AuBr by add. ing KBrAq to AgNO3Aq 20,700 cals. are produced, and that when AgNO, Aq is added to KBrAq only 17,600 cals. are produced at first, but that temperature then rises until 20,600 cals, are evolved; B. thinks that two forms of AgBr are formed, one more stable than the other. Vogel (B. 16, 1160) distinguishes two modifications of AgBr, one ppd. from aqueous solutions and very sensitive to blue rays, the other ppd. from solutions in absolute alcohol and sensitive to the violet rays. Stas (A. Ch. [5] 3, 289) distinguishes six forms of AgBr:—(1) flocculent, white, by adding dilute alkali bromide solution to excess of cold AgNO₃Aq; (2) flocculent, yellow, by using excess of bromide as pptant.; (3) powdery, white, by shaking (1) or (2) with water; (4) intense yellow, by heating (4); (5) granular, white-yellow, by pouring the flocculent or powdery variety, shaken with water, into boiling water, also by adding very dilute NH BrAq to boiling AgNO₃Aq (1:1000); (6) pure yellow, crystalline variety.

Reactions and Combinations. — 1. AgBr darkens rapidly when exposed to sunlight. Carey Lea says that the dark product of the action of light on AgBr reacts with HNO,Aq to re-form AgBr, and Ag which dissolves in the acid (Am. S. [3] 15, 189). The action of light on the Ag haloids is treated more fully under Silver chloride (q. v.).-2. Heated in chlorine, AgCl and Br are produced. - 3. Dissolves slowly in hot silver nitrate solution; the salt AgBr.AgNO, separates on cooling (Risse, A. 111, 43; Riche, A. 111, 39).-4. Combines with silver chloride and iodide to form compounds AgaBrbIcCld (v. SILVER IODOBROMOCHLORIDES, p. 470).

AgBr resembles AgCl in most of its reactions; NH, is not absorbed by dry AgBr (Rammelsberg, P. 55, 248).

Silver, bromo-iodochlorides of, v. Silver IODOBROMOCHLORIDES (p. 470).

Silver, carbides of. Gay-Lussac noticed that Ag absorbed c. 3 p.c. C when heated with lampblack (A. Ch. [2] 58, 222); Ag,C requires 2.7 p.c. C. A yellow powder, approximately agreeing with the composition Ag.C. was obtained by Gerhardt and Cahours (A. Ch. [3] 1, 76) by heating Ag cuminate; the same compound was probably produced by Liebig by heating AgCN (A. 38, 21). By heating an aqueous solution of Ag pyrotartrate, filtering from the brown pp. produced, and boiling the pp., Berzelius obtained 0°, 5·595 at m.p. (Rodwell, Pr. 31, 291). S.H. a dark-brown, metal-like pp., probably AgC (P. (15° to 98°) ·07891 (Regnault, A. Ch. [3] 1, 129). 36, 28; of. Regnault, A. 19, 153).

Silver, chlorides of. The isolation of a chloride | 1 of Ag containing less Cl than AgCl is not yet certain. Cl is given off when AgCl darkens in sunlight, but whether the darkened product is a chloride or an oxychloride is not finally determined (v. Action of light on silver chloride,

SILVER SUBCHLORIDE ? Ag2Cl. chloride.) According to Güntz (C. R. 112, 861), Ag₂Cl is formed by passing dry HCl over Ag₂F (v. Silver subfluoride, p. 469) as long as darkening occurs and the solid continues to gain in weight. The compound is also said to be formed by passing vapour of CCl, SiCl, or PCl, over dry Ag.F. A subchloride is formed, according to von Bibra (J. pr. [2] 12, 55), by digesting with conc. HClAq the product of the reduction of Ag citrate by H at 100°; after drying, the black solid is said to have the composition Ag, Cl3, and with NH_3 Aq to give Ag and $AgCl.3NH_3$. bury (Am. 8, 196) failed to obtain any subchloride by this method; he also found that the reduction of Ag citrate by H at 100° does not yield any definite compound, but probably a mixture of unchanged citrate and Ag.

SILVER CHLORIDE AgCl. (Argentic chloride.) Mol. w. 143.03. V.D. 80 at c. 1700° (Biltz a. Meyer, B. 22, 725). Melts at c. 457° (Carnelley, C. J. 29, 489). S.G. at 0°=5505; at m.p. = 4*919 (Rodwell, Pr. 31, 291). S.H. (13° to 98°) .09109 (Regnault, A. Ch. [3] 1, 129). For expansion of AgCl by heat v. Rodwell (Pr. 25, 280). H.F. [Ag,Cl] = 22,700 (Th. 3, 381); 29,200 (Berthelot, Bl. [2] 39, 19). For solubilities in various liquids v. Properties.

Occurrence. - Native, as hornsilver, Siberia, Mexico, Peru, the Harz, Alsace, &c.

Preparation .- 1. By adding dilute HClAq, or solution of a chloride, to solution of any salt of Ag except Ag2S,O3, washing the white curdy pp., drying, and heating to incipient fusion. Obtained in octahedral crystals by dissolving in large quantity of conc. HClAq and evaporating.— 2. By heating Ag to redness in a stream of Cl or HCl gas.-3. By fusing NaCl with finely divided Ag, washing, and drying.-4. Very slowly by the action of HClAq on Ag in the presence of air.

Properties .- A white solid. According to Cooke (Am. S. [3] 21, 220) AgCl is very slightly sol. cold water, and very distinctly sol. boiling water; he found that 1.4561 g. AgCl washed with 66 litres boiling water lost 2241 g. = 15.39 p.c.; the solvent action was entirely prevented by the addition of 05 g. AgNO, per litre of water. Stas (C. R. 73, 998) distinguished four forms of AgCl: (1) gelatinous; (2) curdy, flocculent; (3) powdery; (4) granular, crystalline, or fused. The curdy, flocculent form is the most sol. in water; it is formed by ppg. cold dilute AgNO Aq by a chloride solution; on shaking it changes to the less sol. powdery variety. The granular, crystalline, or fused form is insol. cold water (10 million parts cold water dissolve 1 part) but it begins to dissolve at 30° (cf. Berthelot, A. Ch. [5] 29, 241, for the heats of solution in KCNAq of different preparations of AgCl). AgCl is sol. conc. HClAq and in saturated solutions of various metallic chlorides; Vogel (C. C. 5, 578) gives the following table :-

100 a	e. cold HClAq S.G. 1.165	dissolve	-298	6	78QI
	boiling ,, cone, HClAq diluted with	90	•560		*
	1 nt. H.O	,	-056	*	0.
99	conc. HClAq diluted with 2 pts. H.O		-018		,
-	conc. HClAq diluted with 8 pts. H ₂ O	99	-0089	"	*
**	conc. HOlAq diluted with 5 pts. H.O	, ,,,	-0085	11	gi
"	saturated BaCl.Aq	39	*0143	"	97
99	" SrCl ₂ Aq	**	*0884	17	4
,,	, OaOl, Aq	29	-0930	"	n
,,	MgCl ₂ Aq	99	•171	19	**
	NaClAq		•095	**	10
"	KClAq	"	·0472	17	**
"	NH.OlAq		·1575	**	99

One part AgCl dissolves in 50,000 parts boiling conc. HNO, Aq (Thorpe, C. N. 25, 198). NH, Aq dissolves AgCl; 1 litre NH, Aq S.G. 924 dissolves 69.5 g. freshly ppd. AgCl, according to Millon and Comaille (C. R. 56, 309). AgCl crystallises from solutions in NH3Aq, on evaporation; explosive silver is obtained from boiling solutions (v. SILVER NITRIDES, p. 470). According to Terreil (Bl. [2] 51, 598), crystals of AgCl.2NH, separate from a hot solution of AgCl in NH,Aq; these crystals lose NH, in the air. AgCl dissolves easily in Na,S2O3Aq, forming Ag2Na,(S2O3)3Aq; AgCl also dissolves readily in KCNAq forming AgK(CN), and in NH, HSO, Aq forming double Ag-NH, sulphites (v. Svensson, B. 4, 714). A hot solution of AgNO, Aq dissolves AgCl; Risse says that a double compound of AgNO, and AgCl separates on cooling (A. 111, 39), but Debray asserts that simple solution occurs (C. R. 70, 995). Hg(NO₃), Aq also dissolves AgCl; Wackenroder (A. 91, 317) and Field $(\tilde{J}.~1857.~255)$ say that AgCl separates on cooling a hot saturated solution; Stas (A. Ch. [5] 3, 180) found that a little AgNO, is formed.

Reactions.—1. AgCl is reduced to Ag by many metals, e.g. Zn or Fe, in presence of dilute acid; Cu reduces AgCl in presence of NH₂Aq, with formation of Ag and CuO.H₂O.— 2. Heated in hydrogen, or with carbon, or with several organic compounds, AgCl is reduced to Ag.—3. Solution of hydriodic acid forms AgI and HClAq.—4. Caustic alkali solutions pro-

duce Ag₂O.

Action of light on silver chloride. AgCl darkens when exposed to sunlight in ordinary air. During the darkening Cl is given off (Scheele; von Bibra, J. pr. 122, 39; Hitchcock, Am. 11, 474; Béchamp, Bl. [3] 6, 836; Richardson, C. J. 59, 536; Baker, C. J. 61, 728). Only a small portion of the AgCl is changed to the dark compound (v. R., l.c.; B., l.c., got 09 g. of the dark body from 51 g. AgCl). AgCl does not darken in thoroughly dried oxygen (B., l.c.; nor in dried air according to Carey Lea, Zeit. fur anorg. Chem. 3, 184). AgCl does not darken in vacuo, when thoroughly dry (Abney; B., l.c.). Carey Lea (l.c.) found that AgCl darkened under dry petroleum; Baker noticed darkening under benzene in absence of air, and he showed that the dark substance was Ag. B. (l.c.) noticed darkening, with formation of Ag, under CCl,, but he proved that if the CCl, contained no trace of free Cl darkening did not occur. For the influence of HCl and chlorides in water upon the rate of darkening of AgCl in the water v. Richardson (l.c.). The dark substance was supposed by some to be a subchloride, but Baker

has shown that it contains O (Hodgkinson had formerly arrived at this conclusion; v. Meldola's Chemistry of Photography [1889], p. 856). B. kept pure AgCl, dried at 150°, in sunshine, in a current of air freed from CO. and dried by H2SO4, until it darkened; he measured the O obtained from the darkened product, by decomposing by Cl, and also determined the Ag and Cl; the results agreed approximately with the formula Ag, OCl; the atomic ratio of Ag to Cl found in various experiments was almost exactly 2:1, and of Ag to O was nearly 5:2; the darkened product dissolved in conc. KClAq, on dilution AgCl was ppd. and the solution had a slightly alkaline reaction, as would be expected if an oxychloride were present in the dark-coloured substance. B. also found that a little H2O was obtained by heating the dark substance in dry H; Richardson (C. J. 59, 536) failed to obtain any water by treating darkened AgCl in this way; R. also failed to get O from the darkened AgCl by heating it to the m.p. in connection with a Sprengel pump. B. (l.c.) found that the darkcoloured product became white when left in the dark for some days, and that a small quantity of O was absorbed during this change; he, therefore, concludes that two oxychlorides of Ag are formed, one of which is dark-coloured and absorbs a little O to form another, white, oxychloride. Carey Lea (Am. S. [3] 38, 356) thinks that the darkening action of light on AgCl is preceded by the formation of what he calls a photochloride. The photochloride is supposed to contain less Cl than the normal chloride; and probably to be a compound of AgCl with a subchloride or oxychloride; it is extremely sensitive to the action of light, and undergoes many changes of colour when exposed to light (Am. S. [3] 33, 349, 480, 489; 34, 33; and full abstract in C. J. 54, 1). For the application of the effects of light on AgCl to photography v. Photography CHEMISTRY, this vol. p. 154; and Photography, in Dictionary of Applied Chemistry, vol. iii.

Combinations .- 1. With several metallic chlorides, especially the alkaline chlorides; generally forming compounds of the type AgCl.MCl. Wells and Wheeler (Am. S. [3] 44, 155) obtained the compound AgCl.2CsCl.— 2. With ammonia gas. According to H. Rose (P. 20, 157), 2AgCl.3NH, is formed. Isambert (C. R. 64, 1259; v. also Horstmann, B. 9, 749) studied the vapour-pressures of the NH, given off, and concluded that two compounds are formed when NH, is absorbed by AgCl-viz. 2AgCl.3NH, and AgCl.3NH, (v. curves given in Drssocarron, vol. ii. p. 397). Bodländer (Z. P.C. 9, 730) measured the reduction of the freezingpoint of water produced by the compound 2AgCl.3NH₂; as this reduction was much larger than the normal, he concluded that the compound is dissociated in aqueous solution; a similar conclusion was come to by measuring the electrical conductivities of aqueous solutions. The dissociation cannot have been into NH, and AgCl, says B., else AgCl would have separated out; hence the dissociation must be electrolytic, and the solution must contain Ag and Ol as free ions. This conclusion was confirmed by finding that PbAc,Aq ppd. PbCl, from 2AgCl.3NH, in NH,Aq, KIAq ppd. AgI, and (NH,),SAq ppd. Ag₂S; confirmatory evidence

was also found in the fact that addition of NH₄Cl or AgNO₃ reduced the solubility in water of 2AgCl.3NH₃, in keeping with the law regarding the effect on the solubility of an electrolyte of the presence of one of its ions. B. concludes that 2AgCl.3NH₃ is a definite compound, which is electrolytically dissociated in aqueous solution.—3. With silver iodide and bromide; v. SILVER IODORROMOCHLORIDES, p. 470.

Silver, chloro-iodobromides of; v. Silver iodobromochlorides, p. 470.

Silver, cyanide of; v. vol. ii. p. 346.

Silver, ferricyanide of; v. vol. ii. p. 340.

Silver, ferrocyanide of; v. vol. ii. p. 837.

Silver, fluorides of. Two fluorides of Ag

Silver, fluorides of. Two fluorides of Ag probably exist, Ag_2F and AgF, although there is still some doubt as to the isolation of the first of these.

SILVER SUBFLUGRIDE (? Ag.F). (Argentous fluoride.) By electrolysing saturated AgFAq, using Ag electrodes, and a current so strong that the liquid became hot, Güntz (C. R. 110, 1337) noticed the separation of brass-coloured crystalline plates at the negative pole (if a weaker current was used, Ag was deposited). Treatment of these crystals with water gave AgFAq and Ag, the ratio of Ag separating to Ag going into solution being practically unity; hence G. gives the formula Ag.F to the yellow crystals. G. says that the same compound is obtained by heating finely-divided Ag with AgFAq in a sealed tube to nearly 90°. Ag.F does not change in dry air; it decomposes slowly in moist air, and rapidly in water. Heated in dry HCl, CCl., PCl., &c., Ag.Cl is said to be formed (G., C. R. 112, 861).

SILVER FLUORIDE AgF. (Argentic fluoride.) Formula probably molecular, from analogy of AgCl. Prepared by dissolving Ag.CO, that has been freshly ppd. and well washed, in HFAq, evaporating to dryness in a Pt dish, with constant stirring, dissolving the black residue in water, filtering, and evaporating in vacuo over H2SO,, in the dark (Moissan, Bl. [3] 5, 456; cf. Güntz, A. Ch. [6] 3, 42). A yellow, transparent, elastic solid; sol. water; melts at c. 435° (M., l.c.). S.G. 5.852 at 15.5° (Gore, Pr. 18, 157). Fremy (A. Ch. [3] 47, 39) obtained large colourless prisms, to which he gave the formula AgF. 2aq, by evaporating a solution of Ag₂CO₂ or Ag,O in HFAq; these crystals lost 2aq in vacuo, but some oxyfluoride was always formed (cf. Marignac, Ann. M. [5] 15, 270). Heated in air, AgF is decomposed, by the moisture present, to Ag, O, and HF, according to Gore (i.c.). AgF interacts violently with POCl₃, PCl₃, SiCl₄, and BCl₃, giving AgCl and fluoride of P, Si, or B (Moissan, *l.c.*). Molten AgF attacks vessels of Ag or Pt. The dry salt is said to absorb c. 800 times its volume of NH, (Gore, l.c.). Heating with I produces AgI and IF, (Gore, Pr. 30, 70; where a few other reactions of compounds with AgF are given).

Silver, fulminating; v. Silver nitrides, p. 470; Silver fulminate (q. v., vol. il. p. 317) is sometimes called fulminating silver.

Silver, hydroxides of; v. Silver oxides and hydrated oxides, p. 470.

Silver, iodides of. The isolation of an iodide other than AgI is very doubtful.

SILVER SUBIODIDE (? Ag.I). Güntz (C. R. 112, 861) states that this compound is formed by the interaction of HI and Ag.F; but no

analyses are given.
Silven lodide Agl. (Argentic iodide.) Formula probably molecular, from analogy of AgCl. Melts at c. 530° (Carnelley, C. J. 29, 489); at 527° (Rodwell, Pr. 25, 280). S.G. at 489); at 527° = 5·522; maximum density at 142° (R., l.c.). V.D. said to be 214 (Dewar a. Scott, B. A. 1881. 597). S.H. (15° to 98°) ·06159 (Regnault, A. Ch. [3] 1, 129; v. also Bellati a. Romanese, Pr. 34, 104). H.F. [Ag,I] = 13,800 (Th. 3, 381); 14,300 for crystalline AgI (Berthelot, Bl. [2] 39, 18).

Occurrence .- As iodite in Peru, Mexico, the Harz, Spain, &c.; forms hexagonal tablets; also in combination with AgBr as iodobromite

in small quantities in Nassau.

Preparation .- 1. By adding HIAq, or solution of an iodide, to AgNO₃Aq, washing, and drying.—2. By the interaction of finely-divided Ag with HIAg, H is evolved at ordinary temperatures and AgI formed; a solution saturated by heating HMq with Ag deposits crystals of AgI.xHI on cooling (v. infra, Combinations, No. 2), and the liquid decanted from these deposits hexagonal crystals of AgI on standing in air .-8. Crystals of AgI are also obtained by boiling saturated AgNO₃Aq with HgL, and allowing to cool (Field, J. 1857, 255).—4. The interaction of a mixture of HClAq and HIAq with Ag produces only AgI, according to Deville (A. 101,

Properties.—As obtained by adding alkali lodide to excess of AgNO3Aq, AgI is a curdy pp., yellow, with a slight orange tint; by adding AgNO.Aq to excess of alkali iodide, a pure yellow, powdery pp. of AgI is formed; the former pp. is sensitive to light, the latter, after washing in the dark, is not discoloured by light. AgI melts to a yellow liquid, which becomes red and then dark-red as temperature rises; the liquid solidifies to a yellow, horny, crystalline mass.. Rodwell (Pr. 25, 280) found that AgI contracted considerably at the moment of solidification; regular contraction then took place to 142° whereat there was sudden and considerable expansion accompanied by change from the amorphous to the crystalline form; this was followed, as temperature fell, by slight expansion (for measurements v. R., l.c.). AgI exists in two forms: above 142° up to the m.p. it is yellow, transparent, and flexible; below 142° it is pale green, crystalline, opaque, and brittle (R., I.c.). AgI is nearly insol. NH3Aq; according to Martini (S. 56, 153) 1 part AgI requires 2560 parts NH, Aq, S.G. 96, for solution. AgI dissolves in Na,S₂O,Aq, in KCNAq, and in NaClAq; it dissolves readily in hot Hg(NO₄),Aq, and crystallises therefrom on cooling (v. also Combinations).

Reactions .- 1. Heated in chlorine, AgCl is formed .- 2. Reduced by contact with metals, such as Zn or Fe, in presence of acids. Most of the reactions of AgI closely resemble those of AgCl.

Combinations .- 1. Dry AgI absorbs ammonia; Rammelsberg (P. 48, 170) says that 2AgI.NH, is formed (for dissociation-pressures of this compound v. Isambert, C. R. 64, 1259). By heating

AgI with excess of NH, Aq in a sealed tube at 100°, Terreil obtained crystals of AgI.2NH, (Bl. [2] 41, 598).—2. AgI dissolves in hot conq. hydriodic acid solution; the liquid deposits large, colourless, unstable crystals of AgI.HI (?) (Deville, C. R. 42, 895); Berthelot obtained transparent crystals of 3AgI.HI.7H₂O (A. Ch. [5] 23, 89).—3. According to Preuss (A. 29, 328) a solution of AgI in a hot solution of mercuric nitrate deposits crystals of 4AgI.2Hg(NO2) aq on cooling.-4. AgI dissolves in silver nitrate solution containing more than 3 p.c. AgNO. (Vogel); water re-ppts. AgI. For accounts of different compounds obtained v. Kremers (J. pr. 71, 54), Stürenberg (Ar. Ph. [2] 143, 112), Weltzien (A. 95, 127), Riche (A. 111, 39), Risse (A. 111, 43). AgI also combines with silver nitrate and lead nitrate, and with antimonide, arsenide, phosphide, and sulphide of silver (v. Poleck a. Thümmel, Ar. Ph. [3] 22, 1).—5. With alkali iodides and alkaline earth iodides (v. Boullay, A. Ch. [2] 34, 377; Berthelot, Bl. [2] 39, 24; Johnson, C. N. 37, 110; Maxwell Simpson, Pr. 27, 120).

Silver, iodobromochlorides of. Rodwell (Pr 25, 292) prepared various compounds of AgI AgBr, and AgCl by melting the constituents together. R. studied especially the effects of heat on the S.G., change of volume, and m.p. of these bodies. The formula xAgI.yAgBr.zAgCl expresses the composition of the compounds examined; x varied from 1 to 4, y was always 1,

and z varied from 1 to 2.

Silver, nitrides of. Raschig (A. 233, 93) has shown that the explosive substance first prepared by Borthollet, by the action of conc. cold NH₃Aq on Ag₂O, and supposed by B. to be a compound of Ag₂O and NH₃, is a nitride of Ag, Ag, N, mixed with finely-divided Ag. Ag, N is best prepared by allowing a conc. solution of Ag₂O in NH₃Aq to stand in air, or by adding alcohol. Ag₃N dissolves in KCNAq,

forming AgCN, KHOAq, and NH₃.

The Ag salt of HN₃ may be called silver nitride; v. Hydrazoro Acid, vol. iii. p. 559. Silver, nitroprusside of, v. vol. ii. p. 341.

Silver, oxides and hydrated oxides of. Only one oxide of Ag has been certainly isolated; the existence of any hydrated oxide is doubtful.

SILVER OXIDE Ag,O. (Argentic oxide.) Mol. w. not known.

Formation.-1. By heating Ag much above the temperature of volatilisation in the O-H flame, using excess of O (Debray, C. R. 66, 735).-2. By passing an electric current through KNO₃Aq, using a plate of Ag as positive electrode (Wöhler, A. 146, 264).—3. By boiling freshlyppd. AgCl with KOHAq, S.G. 1·25 to 1·3 (Mohr, A. 66, 65).

Preparation .- KOHAq is added in slight excess to AgNO₃Aq, the pp. is thoroughly washed with hot water, best in air freed from CO₂, and

dried at c. 80°.

Properties.-A black powder (brownish when ppd.), with an unpleasant, metallic taste. S.G. 7.52 (Schröder, B. 9, 1888); 7.15 (Playfair a. Joule, C. S. Mem. 3, 84): 7.25 (Boullay, A. Ch. [2] 43, 266). H.F. [Ag²,O] = 5,900 (Th. 3, 381). Slightly sol. water; 1 part dissolves in 3,000 parts water according to Bineau (C. R. 41, 509). but according to Abl in 96 parts water at 18.50

(Oester. Zett. f. Pharm. 8, 201 [1884]). Sol. NH.Aq (for so-called explosive silver, formed by dissolving in conc. NH, Aq, v. SILVER NITRIDES. p. 470). Also sol. aqueous solutions of alkali thiosulphates, chlorides, and cyanides. Sol. aqueous MeNH₂ and EtNH₂ (Wurtz, A. Ch. [3] 80, 453). Moist Ag₂O absorbs CO₂ from the air, forming Ag₂CO₃, and reacts with many salts like the alkalis (v. Reactions). Ag₂O is decomposed to Ag and O by heat (v. Reactions).

Reactions and Combinations. - 1. Decomposed to Ag and O by heat; Carnelley and Walker (C. J. 53, 79) say that O begins to come off at c. 100°, rapid decomposition occurs at c. 270°, and reduction is complete at 300'-340° (v. also H. Rose, P. 85, 317; Joulin, Bl. [2] 19, 349; cf. Hydrated Silver oxide, infra).— 2. Antimony sulphide, arsenic sulphide, finely-powdered sulphur and selenion, amorphous phosphorus, and some organic compounds, are ignited by rubbing with Ag₂O (Böttger, J. 1863. 284).— 3. Reduced to Ag by heating to 100° in hydrogen (Wöhler, A. 30, 4).-4. Finely-divided Ag₂O under water is reduced to Ag by cadmium, copper, tin, and zinc (not reduced by Fe or Hg) (Fischer, P. 10, 605).-5. AgI and HIO, are formed by the reaction of iodine with Ag2O suspended in water (Naquet, Bl. 1860, 123); with chlorine the products are AgCl, HClOAq, AgClO, and AgClO, (Stas). - 6. Moist Ag2O decomposes many metallic salts in solution, ppg. metallic hydroxides, e.g. salts of Bi, Cr, Co, Cu, Fe, Hg (v. H. Rose, B. 1857. 245).—7. The moist oxide removes halogens from many halogencontaining organic compounds, replacing the halogen by OH (e.g. 2NMe,I+Ag,O.H,O halogen by OH (e.g. $2NMe_1I + Ag_2O.H_2O$ = $2NMe_4OH + 2AgI).$ —8. Ag_2O reacts with acids as a decidedly basic oxide, forming salts Ag2X, where $X = SO_4$, $2NO_{31}$ &c. -9. A little $AgNO_2$ is said to be formed when nitric oxide is passed into water with Ag.O suspended therein (Sabatier a. Senderens, C. R. 114, 1476).—10. Ag.O combines with lead monoxide; by allowing a mixture of PbO.xH2O and freshly ppd. Ag2O to stand in contact with NaOHAq, a compound was obtained, probably 2Ag₂O.PbO (E. Aston, C. J. 59, 1093).

HYDRATED SHIVER OXIDE (? AgOH). According to H. Rose (P. 85, 904), no compound of Ag₂O and H₂O exists. By ppg. an alcoholic solution of AgNO₃ by KOHAq at -40°, Bruce obtained a white flocculent pp. which he supposed to be a hydroxide of Ag (no analyses are given); the pp. darkened on heating, forming Ag₂O and H₂O according to B. (C. N. 50, 208). Carey Lea (Am. S. 1892, 249) found that ppd. Ag₂O retained some water after drying at 100° for 40 hours, and that all water was removed at 160°-165° but some O went off also. Carnelley and Walker (C. J. 53, 79) say that the product of drying ppd. silver oxide in air for 6 months had the composition AgOH, and that this was scarcely decomposed at 100°, but that above this temperature it gave off water and a little O, and was gradually changed to Ag.O mixed with a little Ag. Some reactions of moist Ag2O point to the existence of such a compound as AgOH (v. SILVER OXIDE, Reactions, Nos. 6 and 7).

OXIDE OF SILVER WITH LESS OXYGEN THAN Ag.O. (Silver suboxide.) Many experiments are recorded on the interactions of reducing

agents and Ag salts whereby salts of a lower oxide than Ag₂O were supposed to be formed, and the corresponding oxide was supposed to be ppd. from these salts by alkali. Wohler (4.30, 1) reduced Ag citrate by heating in H; W. a. Rautenberg reduced ammoniacal solutions of chromate, molybdate, and tungstate of Ag (A. 114, 119); W. reduced arsenate and phosphate of Ag by FeSO, (A. 146, 263); H. Rose reduced AgNO₃ in NH₃Aq by ferrous and manganous salts (P. 101, 264, 321, 497; v. also Weltzien, A. 142, 105). More recent experiments have shown that the products of such reductions in presence of alkali are mixtures containing Ag (v. Pillitz, Fr. 27, 496; Newbury, Am. 8, 196; Muthmann, B. 20, 983; Bailey a. Fowler, C. J. 51, 416).

Faraday (Q. J. S. 4, 268) supposed that a suboxide of Ag was formed by the action of air on an ammoniacal solution of Ag2O; but Bailey and Fowler (l.c.) have shown that the substance is a mixture of Ag₂O with a little explosive

silver.

The result of a long series of experiments by O. v. d. Pfordten (B. 18, 1407; 20, 1458; 21 2288, 3375) on reducing AgNO, Aq by H, PO, Aq, alkali bisulphites, and tartaric acid, is that the black pp. thus obtained is not a suboxide of Ag (for some time it was asserted to be AgiO); the accuracy of this result has been strengthened by the critical experimental work of Bailey (C. N. 55, 263; C. J. 51, 466), and especially of Friedheim (B. 20, 2554; 21, 307). F. regards the supposed Ag₄O as a mixture of finely-divided Ag with more or less Ag,O, or with some organic compounds. V. d. P. (B. 21, 2288, 3375) thinks his latest work points to the black substance being a compound of Ag, H, and O in the ratio 4Ag:2H:O; he gives it the formula Ag. H2O, or Ag. OH.H, and calls it silver hydrate. According to Güntz (C. R. 112, 861) Ag,O is produced by the action of steam on Ag₂F at 160

The question of the existence and isolation of a compound with less O than Ag.O cannot be

regarded as settled.

OXIDES OF SILVER WITH MORE OXYGEN THAN Ag₂O. By electrolysing conc. AgNO₂Δq, using Pt as positive and Ag as negative electrode, Ritter obtained a black deposit on the Pt; to this black substance R. gave the formula Ag.O. and described it as crystallising in octahedra, S.G. 5.474, giving up half its O when carefully heated, with NH3Aq evolving N, and with H2O2Aq production Ag, H.O, and O. A similar production of what seemed to be a peroxide of Ag was noticed by Fischer (J. pr. 33, 237) and by Wöhler (A. 146, 264). Böttger (B. 6, 1398) noticed that the peroxide produced by electrolysis formed explosive Ag and rapidly evolved N, with NH,Aq. Ag peroxide is formed by the action of ozone on Ag, according to Schönbein (J. pr. 41, 821); and of ozone on Ag2O according to Schiel (J. 1864. 118). Ag peroxide is an energetic oxidiser; it sets fire to H2S, and Au suiphide when rubbed therewith (v. Böttger, l.c.).

The analyses made by Fischer (J. pr. 33, 237), Mahla (A. 82, 289), and Gmelin (J. 6, 105) of the peroxide showed the presence of H₂O and AgNO₃; their preparations were probably impure. The analyses of Wallquist (J. pr. 31, 179) agreed well

with the formula AgO (or Ag.O.).

The supposed peroxide of Ag, prepared by secrelysing AgNO.Aq, is regarded by Berthelot (Bl. [2] 34, 138) as a compound of AgNO, with an oxide to which he gives the formula Ag.O.. By the interaction of H₂O₂Aq with Ag₂O, Berthelot (l.c.) obtained black flocks, which were separated from Ag by washing; to this substance B. gives the formula Ag,O, as the result of a not very complete analysis; he looks on it as probably identical with the product of the interaction of moist ozone and Ag or Ag₂O. This substance loses O when dried over H,SO,; with acids it gives salts of Ag₂O and evolves O.

Silver, oxychlorides of. The action of light on AgCl probably produces two oxychlorides of Ag; v. SILVER CHLORIDE, Action of light on,

p. 468.

Silver, oxyfluoride of. To the yellow crystals obtained by evaporating an aqueous solution of AgF, Pfaundler gives the composition AgF.AgOH

(W. A. B. 46 [2] 259).

Silver, phosphides of. Molten Ag absorbs P: according to Pelletier (A. Ch. 13, 101), some of the P remains in combination on cooling, but Warren (C. N. 56, 113) says that all except c. .002 p.c. separates as the Ag cools. According to Emmerling (B. 12, 152), a compound AgP is formed by heating Ag and P in a sealed tube to a dark-red heat; on heating the compound P is given off and Ag remains (v. also Landgrebe, S. 60, 128). By heating powdered Ag in vapour of P, Schrötter obtained a grey solid, S.G. 4-63, to which he gave the composition Ag₂P₃ (J. 1869.

Fresenius and Neubauer (Fr. 1, 340) obtained a pp. said to contain Ag phosphide and Ag, by leading PH₃, or CO₂ laden with vapour of P₃, into AgNO₃Aq; using PH₂ diluted with CO₂. Poleck and Thümmel (B. 16, 2435) obtained a

compound, probably Ag₃P.3AgNO₃.
Silver, photosalts of. Carey Lea (Am. S. [8] 33, 349, 480, 489; 34, 33; abstract in C. J. 54, 1) gives the name of photosalts to variouslycoloured compounds of Ag with the halogens which are very sensitive to light. These bodies are regarded by C. L. as identical with the substances that form the latent images on exposed photographic plates. The photosalts are obtained by the action of reducers, such as FeSO Aq or FeCl Aq, on the normal Ag haloids, by reducing Ag salts by such bodies as dextrose or tannin in presence of alkali and treating the products with HClAq, or by treating finely-divided Ag with the haloid salts of Cu or Fe and certain other halogenating reagents. The photosalts are regarded by C. L. as compounds of the normal haloids with sub-haloids; from the methods of preparation it seems fairly certain that the coloured bodies called photosalts contained various substances besides Ag and halogen.

Silver, platinocyanide of, v. vol. ii. p. 344. Silver, platinosulphocyanide of, v. vol. ii.

Silver, salts of. Compounds derived from acids by replacing II by Ag. These salts belong to the type AgX, where $X = NO_3$, $\frac{1}{2}SO_1$, $\frac{1}{2}CO_4$, $\frac{1}{3}PO_4$, &c. Subsalts of the type Ag_2X possibly exist, where X is a halogen. The principal silver salts of oxyacids are: arsenate and arscnite, borate, bromate, carbonates, chlorate,

chlorite, perchlorate and hypochlorite, caromass and dichromate, jodate and periodates, molubdates. nitrate, nitrite and hyponitrite, phosphates, selenate and selenite, sulphates, sulphite and thionates, tellurates and tellurite. Several salts derived from sulphur-containing acids also exist, the chief of which are: thio-antimonates and antimonites, thio-arsenates and arsenites, thio-carbonate, thio-molybdates, thio-phosphates

and phosphites, and thio-tellurite.

Silver, selenide of, Ag2Se. Occurs native, also in combination with selenides of Cu and Pb. Obtained by heating Ag with Se, SeO₂, or H₂Se; also by passing H₂Se into solution of a Ag salt; and by heating AgNO, Aq with Se (Senderens, C. R. 104, 175). A grey solid, melting at red heat to silver-white regulus. A little Se is lost by roasting in air; sol. conc. hot HNO, Aq, crystals of Ag, SeO, separating as liquid

Silver, selenocyanide of, v. vol. ii. p. 348. Silver, silicides of. Berzelius found that Ag after fusion with SiO, and C gave a residue of SiO, when dissolved in HNO₃Aq. Percy (Silver and Gold, 1, 131) failed to obtain any compound of Ag and Si. Warren (C. N. 60, 5) obtained compounds or alloys of Ag and Si by heating Ag with K.SiF, and Na.

Silver, silico-fluoride of, Ag.SiF. 2H.O. White, deliquescent crystals, melting below Ag with some SiO₂. Obtained by evaporating a solution of Ag₂O in H.SiF₄Aq (Marignac, Ann. M. [5] 15, 270).

Silver, sulphides of. The isolation of any sulphide other than AgaS is very doubtful.

SILVER SULPHIDE Ag.S. (Argentic sulphide.)
Mol. w. not known. Occurs native as argentits on red-hot AgCl (Durocher, C. R. 32, 823). H2S quite free from admixed O is said not to react with Ag. Also prepared by passing H2S into a solution of a salt of Ag; by boiling Ag, SO, Aq or AgNO, Aq with S (Filhol a. Senderens, C. R. 104, 175); and by the contact of H2SAq with moist Ag.O. Spring formed Ag.S by subjecting a mixture of Ag powder and amorphous S to a pressure of several thousand atmospheres, powdering, and compressing again, and repeating this treatment seven or eight times (Bl. [2] 39, this treatment seven of sight times $[Bt. [2] \ 30, 526]$, [641; 41, 488, 492; cf. Friedel, $Bt. [2] \ 40, 526]$. Thomsen (Th. 3, 381) gives [Ag; 8] = 5,340. Winssinger $(Bt. [2] \ 49, 452)$ obtained a dilute aqueous solution of colloidal Ag_2S by ppg. from a very dilute solution of a Ag salt, by H.S, and dialysing; the solution was reddish brown, and did not change after keeping for more than two months.

Ag2S obtained by ppn. is a black solid; when melted, out of air, it solidifies to a greyblack, lustrous, malleable mass, that can be cut with a knife; S.G. 685 (Karsten, S. 66, 394). S.G. of argentite 7.27 to 7.82 (Dauber, J. 13, 748). Heated in air slowly goes to Ag, giving off SO₂. With conc. boiling HClAq gives AgCl and H₂S; hot HNO₂Aq forms AgNO₂Aq and H.S; cone. H.SO, produces Ag.SO, and SO. Heated in Cl. AgCl and S.Cl. are formed. Reduced to Ag by action of metals and dilute acid; also reduced by heating with PbO, CuO,

16 3 3 3 4 4 4 4 4

Fe powder, or Hg (cf. Rammelsberg, C. J. 39.

Many compounds of Ag.S with metallic sulphides occur in minerals, e.g. with Cu,S, Sb₂S₂, As₂S₃, Bi₂S₃, &c. Schneider (J. pr. 41, 414) obtained a compound of Ag.S and Bi.S. by fusing the two sulphides together in a covered crucible. Poleck and Thümmel (Ar. Ph. [3] 22, 1) obtained Ag. S. Ag. NO. by passing H. S. into conc. AgNO3Aq so long as it was completely absorbed, washing the greenish pp. with HNO₃Aq, and drying; a black amorphous powdecomposed by water to Ag.S and AgNO,Aq.

SILVER SUBSULPHIDE. According to Güntz (C. R. 112, 861), Ag,S is obtained by the action of H.S on Ag.Cl.

Silver, sulphocyanide.of, v. vol. ii. p. 352.

Silver, telluride of, Ag.Te. Occurs native as hessite. Prepared by melting together Ag and Te, by passing vapour of Te diluted with much N over red-hot Ag (Margottet, C. R. 85, 1142), and by heating AgNO3Aq with Te in a sealed tube (Senderens, C. R. 104, 175). Grey, lustrous solid; obtained in needles (octahedral) by the second method given above. M. M. P. M.

SINALBIN C30H41N2S2O16. A glucoside occurring in the seed of white mustard (Will, Z. [2] 7, 89; A. 199, 150). Prepared by washing the seeds with CS, and extracting the residue with alcohol. Concentric groups of pale-yellow needles (from alcohol), v. sol. water, insol. CS2 and ether. Reduces Fehling's solution, with formation of Cu.S. Split up by the ferment myrosin into glucose, sinapine sulphate C₁₀H₂₂NO₃H₂SO₄, and C₂H₂OCNS, a pungent oil. Aqueous AgNO₄ produces a similar decomposition, forming a pp. whence H.S removes Ag, leaving in solution sulphate of sinapine and C₈II,NO [69°]. Coloured yellow by alkalis, and yields Na₂SO₄ and sodium sulphocyanide on boiling with NaOHAq. HgCl₂ gives a white pp.

SINAMINE v. ALLYL CYANAMIDE.

SINAPIC ACID C11H12O3. [192° cor.]. Formed, together with neurine, by boiling sinapine sulphocyanide with alkalis (Von Babo a. Hirschbrünn, A. 84, 19; Remsen a. Coale, Am. 6, 50). Small yellow prisms (from alcohol), sl. sol. cold water, insol. ether. The ammoniacal solution turns brown in air. Salt .- BaA" (dried at 110°). Pp.

Acetyl derivative C11H11AcO5. [281°]. Got by boiling the acid with Ac.O. White

crystals, sol. hot water.

SINAPINE C18H23NO3. Occurs as sulphocyanide in seeds of white mustard (O. Henry a. cyanide in seeds of white mustard (U. Henry a. Garot, J. Ph. 17, 1; 20, 63; Pelouze, A. Ch. [2] 44, 214; J. Ph. 17, 271; Boutron a. Robiquet, J. Ph. 17, 279; O. Henry a. Plisson, A. Ch. [2] 46, 198; Winckler, Rep. Pharm. 41, 169; 67, 257; Simon, P. 43, 651; 44, 593; Boutron a. Fremy, J. Ph. 26, 50; Von Babo a. Tringht in A 24, 10. Ramsen a Coale Am. Hirschbrünn, A. 84, 10; Remsen a. Coale, Am. 6, 50). Formed also by the action of myrosin on sinalbine (Will a. Laubenheimer, A. 199, 162). The free base is known only in solution, and is decomposed on evaporation, leaving a resin. Boiling baryta-water splits it up into neurine C₂H₁₈NO₂ and sinapic soid.

Salts.—B'H₂SO₄2aq: rectangular plates, v. sol, water and hot alcohol, nearly insol, ether .--B'HHgCl₃: thin prisms.—B'HCNS. [176°].

SINAPOLINE v. DI-ALLYL URBA.

SINCALINE v. NEURINE.

SINISTRIN v. Inulin. SIPERINE. An amorphous, resinous, alkaloid occurring, together with bebirine, in the greenheart tree (Nectandra Rodiai or Bebeeru Sipceri). It is v. sl. sol. water, m. sol. alcohol, insol. ether (Maclagan, A. 48, 106).

SKATOLE v. METHYL-INDOLE.

SKELETINS v. Proteins, Appendix C.

SKIMMIN C₁₃H₁₀O₂. [210°]. A glucoside extracted by alcohol from Skimmia japonica (Eijkman, R. T. C. 3, 204). White needles, sl. sol. cold water. Its alkaline solutions show blue fluorescence. It is not poisonous, and does not reduce Fehling's solution.

Skimmetin C,H,O,. [223°]. Formed, to-gether with glucose, by boiling skimmin with dilute mineral acids. Colourless crystals, sol. alcohol and ether. Its solutions exhibit blue fluorescence. Does not reduce Fehling's solution. FeCl, gives a blue colour. Gold chloride gives a rose colour, turning blue and violet.

SMILACIN C₁₈H₃₀O₆(?). Occurs in sarsa-parilla root (Smilax Sarsaparilla) (Reinsch, Rep. Pharm. 82, 145; Thubeuf, A. 5, 204; 14, 76; Batka, A. 11, 305; Poggiale, A. 13, 34; Henry, A. 14, 77; Petersen, A. 15, 74; 17, 166; Wright a. Rennie, C. J. 39, 237). Nodular groups of leaflets, m. sol. hot water and alcohol, sol. alkalis.

Reference.-Parillin.

SNAKE POISON v. PROTEÏDS.

SOAP v. DICTIONARY OF APPLIED CHEMISTRY. **SOBREROL** $C_{10}H_{18}O_2$. [150°]. [a]₀ = ± 150°. A product of atmospheric oxidation of turpentime in sunlight (Armstrong a. Pope, C. J. 59, 316). Long tables (from alcohol) or monoclinic prisms (from water); a:b:c = 2.411:1: 853; $\beta = 83^{\circ}38'$. Tastes bitter. Converted by boiling dilute H.SO, into an oily isomeride of cam-phor. By crystallising a solution of equal quantities of dextro- and lævorotatory sobrerol there is obtained an inactive sobrerol [131°] crystallising from alcohol in trimetric tables; a:b:c = 2.424:1; .827.

SOCALOÏN v. ALOÏN.

SODA; v. Sodium hydroxide, p. 479. SODIUM Na. At. w. 22 995. Mol. w. very probably same as at. w. (v. infra). Melts at 95.6° (Bunsen, A. 125, 367), 97.6° (Hagen, W. 19, 436); solidifies at 97.6° (Regnault, J. 1856. 43). Boils between 860° and 950°, according to Carnelley and Williams (C. J. 35, 565); at 742° (Perman, C. J. 55, 326). S.G. 985 40 (Schröder, P. 106, 226); 9743 at 10° (Baumhauer, B. 6, 655); c. 74 at b.p. (Ramsay, C. J. 39, 49). V.D. 12.7 at 1200°-1500° (Scott, Pr. E. 14, 410; v. infra). S.H. 2734 from -28° to 6° (Regnault, A. Ch. [6] 146, 257); '21 when liquid (Joannis, A. Ch. [6] 12, 358). C.E. (0° to 50°) '00007105 (Hagen, W. 19, 436). E.C. (Hg at 0° = 1) 18·3 solid at 0°, 8·3 liquid at 120° (Matthiessen, P. M. [4] 12, 199; 13, 81). T.C. (Ag=100)=36.5 (Calvert a. Johnson, P. M. [4] 16, 881). H.C. [Na2,O] = 99,760 (Th. [8] 282). Refraction-equivalent $\frac{\mu - 1}{d}$ × at. w. = 4.4 (Gladstone, Pr. 18, 49);

4.03 (Kanonnikoff, J. R. 1884 [i.] 119). Emission spectrum characterised by a double line D, the components of which have the wave-lengths 5895 and 5889 (for detailed measurements of lines v. B., A. 1884. 443). For absorption spectrum v. Roscoe a. Schuster (Pr. 22, 362). S.V.S. solid 23.3; at b.p. 31 (Ramsay, C. J. 39, 49).

Occurrence. - Compounds of Na occur widely distributed in large quantities. NaCl is found abundantly as rock-salt, also in sea-water and many mineral springs. Large quantities of NaNO, or Chili saltpetre occur in S. America. Carbonate, sulphate, and borate of Na are found, in comparatively small quantities, in rocks, and in lake and spring waters. Cryolite is a double fluoride of Na and Al. Many silicates contain Na silicate-e.g. natrolite, albite, labradorite, &c. The ashes of many plants contain Na salts, especially NaCl, NaI, and Na,SO,; some plant ashes are free from Na salts, even when the plants grow near the sea; the ashes of algor and some other sea plants are richer in salts of K than in those of Na. NaCl, Na₂CO₃, Na₂HPO₄, and some other compounds of Na, are found in animal organishs.

Historical. - Caustic soda was decomposed by Davy in 1807 (T. 1808. 1) by electrolysis; Gay-Lussac a. Thénard heated NaOH with Fe filings and obtained Na (A. Ch. 65, 325 [1808]). Brunner (S. 71, 201) reduced Na₂CO₃ by heating with charcoal; this process was made applicable on the large scale by Deville (A. Ch. 3)

43, 5 [1855]).

The word neter is used by the older Hebrew writers to denote a substance employed for washing clothes; the same, or a similar, substance seems to have been known as vitpov or nitrum, and by the fifteenth century this name was given to saltpetre; when the existence of two similar but distinct substances having detergent properties was recognised, the name nitrum was given to one, and the other was called natrum or natron. The metal obtained from natron was called natrium; this name is retained in German, but in English and French the metal is named from soda, a word applied in the Middle Ages to designate alkaline substances, and used as synonymous with nitrum and natron. The symbol Na is universally employed for the metal.

Formation .- 1. By electrolysing NaOH (cf. Potassium, Formation, No. 1, p. 298).—2. By reducing Na₂CO₃ by heating it with charcoal, or with charcoal and very finely-divided iron (Castner, C. N. 54, 218).—3. By electrolysing fused NaCl, or conc. NaClAq, using Hg as the

negative electrode.

Preparation .- 1. An intimate mixture of 80 parts calcined Na CO3, 13 parts coal, and 5 parts chalk is heated in an iron bottle with a short exit tube, in a furnace, until vapours of Na appear at the mouth of the tube, when a small flat receiver, made of sheet iron, is adapted to the tube; when the receiver is full of Na it is removed, and the metal is taken out under mineral oil (cf. Potassium, Preparation, p. 298). As Na does not combine with CO, the difficulty which attends the preparation of K because of the formation of KCO, does not occur with Na.-2. A mixture of NaOH, C, and Fe is heated in egg-shaped iron retorts, connected with cast-iron condensers about 3 ft. long and 5 in. diameter, and having small openings near the nozzles through which the molten Na runs into pots placed beneath. The mixture of C and Fe is made by heating a mixture of very finely divided iron and pitch; this is heated with NaOH in approximately the proportion 6NaOH:2C:4Fe. (For details v. DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 422.)

The metal is purified by pressing through linen under rock oil kept at c. 100°; it must be kept under oil free from O. Rosenfeld (B. 24, 1658) recommends to soak the metal in a mixture of 1 part amyl alcohol and 3 parts petroleum, and to rub it with a rag soaked in the same mixture, till the surface is bright; then to let it remain under petroleum with 5 p.c. amyl alcohol; to wash it with pure petroleum, and to keep it under petroleum containing from 1 to 1 p.c. amyl alcohol. The film of sodium-amyl oxide which forms is easily rubbed off with filter

Properties. - A silver-white, lustrous metal: usually described as whiter than K, but according to Long (C. J. 13, 122) a clean surface has a pale rose colour. By melting Na in a glass tube, narrowed at one place, and filled with coal-gas or H, and allowing the semi-solidified metal to flow slowly through the narrowed part of the tube, Na is obtained in lustrous, white, quadratic octahedra, with a rosy sheen (Long, l.c.; cf. Böttger, B. 7, 1536). According to Linnemann (J. pr. 75, 128), the surface of a freshly-cut piece of Na shows green phosphorescence that soon disappears, but returns again at 60°-70° (cf. Baumhauer, J. pr. 102, 123, 361). A sublimate, in a very thin film on glass, shows a greenish blue colour in transmitted light (Dudley, C. N. 66, 163; Newth, N. 47, 55). The vapour obtained by boiling Na in an atmosphere of H is colourless in thin layers, and violet to purple when seen in thick layers (Roscoe a. Schuster, Pr. 22, 362; Carnelley a. Williams, C. J. 35, 565). At the ordinary temperature Na is as soft as wax; it is ductile at 0°, and fairly hard at -20° ; at c. 50° it is pasty; it melts at c. 96° , and boils at c. 750° (v. beginning of this article). Na dissolves in liquid NH3, forming a blue liquid (v. Sodium-ammonium, p. 475). A freshly-cut surface of Na exposed to air becomes rapidly covered with a film of oxide; Na is said to be unchanged at the ordinary temperature in perfectly dry air. It decomposes cold water rapidly, but the H evolved does not generally take fire. Na must be kept under a liquid free from O, such as mineral oil or naphtha (v. Preparation, supra).

The atomic weight of Na has been determined (1) by converting NaCl into AgCl (Berzelius, P. 8, 189 [1826]; Pelouze, C. R. 20, 1047 [1845]; Dumas, A. Ch. [3] 55, 182 [1859]; Stas, Stas, Rech. 78); (2) by reducing NaClO, to NaCl (Penny, T. 129 [1] 25 [1839]); (3) by converting NaCl into NaNO₃ (Stas, Nouv. R. 248 [1865]);
(4) by determining S.H. of Na.

The molecular weight of Na is not known with

certainty. Dewar a. Dittmar (C. N. 27, 121) and D. a. Scott (Pr. 29, 206 [1879]) obtained numbers that indicated a mol. w. of 23; but the values varied considerably. D. a. S. used a vessel of wrought iron. Scott (Pr. E. 14, 410 [1888]) ob-

tained fairly concordant results, giving values for V.D. varying from 11.8 to 15, using a Pt vessel heated above the m.p. of cast iron; but V. Meyer's experiments (B. 13, 391 [1880]) seemed to indicate that Na vapour attacks vessels of Ag or Pt. Mitscherlich (A. 12, 173 [1834]) found that vessels of hard glass were also attacked; and Rieth (B. 4, 807 [1871]) got no constant results by using a vessel of Cu. The values obtained by Scott were so constant that there is a large probability in favour of the monatomicity of the molecule of gaseous Na. Ramsay (C. J. 55, 521) dissolved Na in Hg and measured the decrease of vapour-pressure of the Hg thereby produced; assuming the mol. w. of liquid Hg to be 200, and assuming that equal vols, of dilute solutions in Hg contain equal numbers of molecules, the results gave values for mol. w. of Na varying from 15 to 21.5.

The V.D. of no compound of Na has been determined; from the analogy of K, Rb, Cs, and Ag, the atom of Na is probably monovalent in

gaseous molecules.

Sodium is a strongly positive element; it comes after Rb. Cs. and K in order of decreasing electropositiveness (Bunsen). In all its compounds Na reacts as a metal; it does not enter into the composition of any negative radicles. Na forms few basic salts and no oxyhaloid compounds; its haloid compounds are very stable towards heat. Na is closely related to Li, K, Cs, and Rb (v. Alkalis, METALS OF THE, vol. i. p. 114), and less closely to Cu, Ag, and Au (v. Copper group of elements, vol. ii. p. 250).

Reactions and Combinations .- 1. Heated in air or oxygen, Na₂O and Na₂O₂ are formed (v. Oxides, p. 482). According to von Bonsdorff (P. 41, 296), Na is unchanged in quite dry air at the ordinary temperature.—2. Na absorbs hydrogen at c. 300°, probably forming a compound (v. Hydride, p. 479). -3. Combines with chlorine, bromine, and iodine when heated with these elements (v. Chloride, bromide, and iodide). -4. Forms sulphides, by reacting with sulphur at the ordinary temperature; combines, when heated, with selenion and tellurium, also with arsenic and phosphorus (v. Sulphide, p. 483, Selenide, p. 482, Telluride, p. 483, Arsenide, p. 476, and l'hosphide, p. 482).—5. Alloys with several metals (v. Alloys, infra).—6. Na decomposes water at the ordinary temperature, forming NaOHAq and H; much heat is produced, but the H does not generally take fire unless the reaction is slackened, and friction is increased, by thickening the water by gum &c., or placing the Na on moist filter paper (v. Ducatel, Am. S. 25, 90; Serullas, A. Ch. [3] 40, 329). If Na is allowed to react with water in a cylinder standing over water, the H collecting in the cylinder, a violent explosion sometimes occurs, probably due to formation of a peroxide that is then decomposed with evolution of O, which mixes with the H (Böttger, J. pr. 85, 397; Griffin, J. 1856. 320) .- 7. Na reduces many oxides at high temperatures, e.g. CO, N₂O, B₂O₃, P₂O₅, As₂O₅, HgO, CuO, Ag₂O, PbO, ZnO, Fe₂O₅, &c.—8. Many carbonates, sulphates, nitrates, phosphates, and silicates are reduced when strongly heated with Na .- 9. Many metallic chlorides are reduced by heating with Na, s.g. MgCl, AlCl, &c .- 10. By heating with solid caustic potash to c. 170°, an

alloy of Na and K is formed (v. Williams, C. N. 3, 21; Wanklyn, C. N. 3, 66).-11. Heated in anmonia gas, NaNH, is formed (v. Amide, infra), and when this is more strongly heated Na₃N is formed (v. Nitride, p. 482).—12. Na reacts with aqueous solutions of acids to form salts NaX, where X is a monovalent acidic radicle.

Sodium, alloys of. Na forms alloys with many metals; these alloys are generally formed by directly melting the metals together, or by reducing the chlorides by Na. By the action of sodammonium (v. infra) on Sb. Bi. Pb. Joannis (C. R. 114, 585) says that alloys of Na with these metals are obtained agreeing in composition with the formulæ Na, Sb, Na, Bi, and NaPb. Schumann (W. 43, 101) obtained a definite alloy of Na and Hg corresponding with the formula NaHg, (v. also Sodammonium, infra).

Sodium, aluminates of, v. vol. i. p. 141.
Sodium, amide of, NaNH... (Sodamide.)
Mol. w. not determined. First prepared by Gay-Lussac and Thénard (Recherches physico-chimique, 1, 354) by heating Na in NH₃; the Na absorbed 142 to 163 vols. NH3 and 100 vols. H were produced. Prepared by Beilstein and Geuther (A. 108, 88) by driving out the air from several flasks, connected by tubes, by a stream of dry H, then placing a few grams Na in each thask, replacing the H by dry NH₃, free from CO₂ (Drechsel, J. pr. [2] 16, 203), and heating the flasks on sand-trays; the Na melts and swims on the blue-green liquid that forms. When the Na has all disappeared the liquid is allowed to cool; the solid that forms is at first brown, but when quite cold it forms a crystalline, olive-green mass. Also obtained by the gradual decomposition at the ordinary temperature (hastened by light) of sodammonium; as the liquid decomposes, crystals of NaNII₂, 1 mm., long, are formed; these crystals are said to be white (Joannis, C. R. 112, 392).

Heating in CO produces NaCN and H.O. along with NaOII and NH3. When heated in CO2 much NH3 is given off, and the final pro-[2] 21, 91). When strongly heated NaNH, given off NH, and leaves NaN, (v. Sodium nitrade, p. 482).

Sodium-ammonium or Sodammonium. Weyl (P. 121, 611; 123, 350) obtained a blue liquid, by the action of liquid NH, on Na, which he regarded as a compound or alloy of Na and NH. As Na remained when the NH, was allowed to evaporate, Seeley (C. N. 23, 169) looked on the blue liquid as a solution of Na in liquid NH.
Joannis (C. R. 109, 900, 965; 110, 238) found that the vapour-pressure of a solution of Na in liquid NH, decreased to a limit whereat it became constant if temperature remained unchanged; that on then removing more NH, a copper-red solid separated, and that NH, was then given off at constant pressure till only Na remained. When the last part of the change commenced, the copper-red substance contained

Na and NH, in the ratio Na:NH,; the evolution of NH, at constant pressure was regarded by J. due to the dissociation of a compound NaNH. The heat of formation of NH, Na from gaseous NH, and solid Na was determined by J. to be 5,200, and from liquid NH, and solid Na to be 800, cals. J. determined the lowering in the freezing-point of liquid NH, by solution in it of NaNHa, and so calculated the mol. formula of this body to be Na, N₂H₆ (C. R. 115, 820). The solution of Na₂N₂H₆ in liquid NH₅ is decomposed by Sb, Pb, and Hg, but not by Al, Cu, Ag, or Zn; the final product of the action of Pb is Pb,Na.2NH,; by dropping the liquid on to Hg, and washing the product with liquid NH, the crystalline amalgam NaHg, was obtained (J., C. R. 113, 795). According to J. (C. R. 112, 392), Na₂N₂H₆ decomposes slowly at the ordinary temperature to NaNH, and H. With excess of NaCl the blue liquid becomes colourless and NaNH, separates; the compound NH2NaCl is first formed, and is then decomposed by the liquid NH, to NaNH, and NaCl. By passing dry O into Na, N, H, in liquid NH, at -50°, J. (C. R. 116, 1370) obtained NH, Na, OH; by the prolonged action of O he obtained Na₂O₂.
Sodium, arsenates of, v. vol. i. p. 309.

Sodium, arsenide of. Gay-Lussac and Thenard found that Na combined directly with As. According to Landolt (A. 89, 210) Na, As is formed, as a silver-white solid, by heating the elements in the ratio 3Na:As. A compound of Na and As is also formed when Na is heated in AsH₃. Decomposed by water, giving off AsH₃. Sodium, arsenites of, v. vol. i. p. 307.

Sodium, aurobromate of, NaAuBr. Orangered prisms, by dissolving NaBr in AuBr, Aq (cf. vol. ii. p. 649).

Sodium, aurochlorate of, NaAuCl. By dissolving NaCl in AuCl. Aq (cf. vol. ii. p. 650).

Sodium, borates of, v. vol. i. p. 529. Sodium, boride of. The product of the reduction of B2O3 by Na may contain a compound of B and Na.

Sodium borofluoride v. vol. i. p. 526.

Sodium, bromide of, NaBr. Mol. w. not certainly known, but probably 102 745 (= NaBr). Welts at 708° (Carnelley, C. J. 33, 279); at 727° (c. Meyer a. Riddle, B. 26, 2443). S.G. 3079 at 17.5° (Kremers, P. 99, 443); 3.198 at 17.3° (Favre a. Valson, C. R. 77, 579); 2.448 when molten (Quincke, P. 138, 141). Krervers (P. 99,

40) gives	BOIDDIIITIES	88	IOHOWS:—	
Temp.	s.	- 1	Temp.	8.
0°	77.5	- 1	60°	111-1
20	88.4	- 1	80	112.5
40	104.2	- 1	100	114.9

Coppet (A. Ch. [4] 25, 506; [5] 30, 411) gives the following:-

Temp.	· 8.	Temp.	8.
44·1°	115-6	86°	118.8
51.5	116-2	90.5	119.7
55·1	116.8	100.3	120.6
60.8	117	110-6	122.7
64.5	117.8	114-8	124
74.5	118-4		

C. represents S. of NaBr as 110.84 + 1075t when twaries from 44° to 114°. S. in alcohol 90 p.c. = 6. B.P. of saturated NaBrAq = 121°. S.G.

of NaBraq given by Kremers a. Gerlach (Br. 6, 279) at 15° as follows:—

3.G. NaBrAq	P.O. NaBr	S.G. NaBrAq	P.C. NaBr
1.04	5	1.281	80
1.08	10	1.344	- 35
1.125	15	1.410	40
1.174	20	1.483	45
1.226	25	1.565	50

H.F. [Na,Br] = 85,770; [Na,Br,Ad] = 85,580 (Th. 3, 232).

Formation.-1. By passing Br vapour over Na. According to Merz and Weith (B. 6, 1518), Na remains unchanged for months in liquid Br at the ordinary temperature, and even at 100° or 200° the formation of NaBr proceeds very slowly.—2. By treating BrAq with iron filings, boiling the solution of FeBr₂Aq with NaOHAq, filtering, and evaporating (Henry, J. Ph. 15, 54).—3. By neutralising HBrAq by NaOHAq or Na CO Aq, and evaporating. -4. By decomposing CaBr.Aq by Na.SO, filtering after some time, adding Na CO, as long as turbidity is produced, filtering, and evaporating (Klein, A. 128, 237).— 5. By decomposing pure NH₄Br by NaOHAq or Na, CO, Aq, and evaporating (Castelhaz, C. R. 70, 1050).

Preparation.—Br is added, little by little, to moderately conc. pure NaOHAq (v. Sodium hydroxide, p. 479) till the liquid is slightly yellow; the liquid is evaporated to dryness; the residue of NaBrO, and NaBr is strongly heated, in a porcelain dish, till traces of Br are given off, the residue is dissolved in water, evaporated, and allowed to crystallise at a temperature not under 30° (NaBr. 2aq separates below 30°).

Properties.—Lustrous, white cubes; strong alkaline taste; reaction in water is neutral. Dissolves easily in water, with slight fall of temperature [NaBr,Aq] = -190 (Th. 3, 232); NaBr separates from this solution at c. 30° but at the ordinary temperature crystals of NaBr. 2ag are formed.

Reactions.-1. Chlorine reacts with NaBrAq to give NaClAq and Br.-2. Heated with potassium chromate and sulphuric acid, Br is given off: NaCl under similar conditions gives CrO2Cl2.-3. Conc. sulphuric acid forms HBr, Br, and SO₂; by using dilute H₂SO₄Aq (c. 30 p.c.) a mere trace of Br is obtained (v. Addyman, C. J. 61, 94).-4. Potassium permanganate does not react with NaBrAq even when boiled, but addition of a little H₂SO₄Aq causes evolution of Br (Hempel, A. 107, 160).

With water to form

NaBr.2H2O. This hydrate separates from solutions of NaBr saturated when hot and cooled to under 30°; it crystallises in monoclinic prisms, which melt at 50°, leaving NaBr.-2. With many bromides of less positive metals, e.g. with PbBr, to form PbBr, 2NaBr, and CdBr, to form CdBr, 5NaBr. 5aq (v. the various metallic bromides).—3. With arsenious oxide to form

NaBr.As,O. (Rüdorff, B. 21, 3051).
Sodium, chloride of, NaCl. (Common salt.) Mol. weight not known with certainty, but pro-bably 58-365 (= NaCl). Melts at 772° (Carnelley, C. J. 33, 280); at 851° (Meyer a. Riddle, B. 26, 2443). S.G. 2-16 at 0° (Quincke, P. 138, 141); 2-157 at 4° (Schröder, P. 106, 226); (7) 1-612 at m.p. (Braun, B. 7, 958); 2-04 after fusion (Quinoke, P. 185, 642); for other values v. Clarke's Table of Specific Gravities [2nd ed.] 20. S.H. 15° to 98° 21401 (Regnault, A. Ch. [3] 1, 129; v. also Kopp, T. 155 [i.] 71. Vol. at 40° = vol. at 0° (1 + 00012117 × 40) (Fizeau, C. R. 64, 314). H.F. [Na, Cl] = 97,690 (Th. 3, 232). Poggiale (A. Ch. [3] 8, 469) gives following data for solubility in water:—

Temp.	- 8.	Temp.	8.
-15°	32.73	40°	36.64
-10	33.49	50	86.98
- 5	84.22	60	37.25
0	35.52	70	37.88
+ 5	85.63	80	38.22
9	35.74	90	38.87
14	35.87	100	39.61
25	36.13	109.7	40.35

Coppet (A. Ch. [5] 30, 411) gives S. above 20° to $109^{\circ} = 34 \cdot 359 + 0527t$. Gerlach (Fr. 8, 281) gives the following data:—

	S.G. NaC	IAq at 15°	
1 p.c.	1.00725	10 p.c.	1.14315
2 ,,	1.01450	11 ,	1.15107
3 ,,	1.02174	12 ,	1.15931
4 ,,	1.02899	13 ,,	1.16755
5 ,,	1.03624	14 ,,	1.17580
6 ,,	1.04366	15 "	1.18404
7 ,,	1.05108	16 ,,	1.19228
8 ,,	1.05851	17 ,,	1.20098
9 ,,	1.06593	18 ,,	1.20433

1000 c.c. of NaClAq saturated at 15° contain 318479 g. NaCl and 888°669 g. water (Michel a. Kraft, J. 1854. 29°). NaClAq containing 29°4 to 29°5 p.c. NaCl boils at 109°25° (at 760 mm. pressure) and freezes at -21°3° (Karsten, Salimenkunde [Berlin, 1847] 2,38). The following freezing-points are given by Karsten (l.c.) for NaClAq (cf. Rüdorff, P. 114, 63°; and de Coppet, A. Ch. [4] 25,509):—

P.C. NaCl	F.P.	P.O. NaCl	F.P.
2	-1·32°	16	-11.69
4	-3.024	20	-14.44
6	-4.52	22	-15.78
8	 5 ·99	24	-17:11
10	-7·44	26	-18.42
12	- 8.88	1	

For freezing-points of dilute NaClAq, containing from c. 006 to c. 2.6 p.c. NaCl, v. Jones (Z. P. C. 11, 210).

Solution of NaCl in water is accompanied by lowering of temperature and contraction; 36 parts NaCl in dissolving in 100 parts water at 12:6° lower the temperature to 10:1° (Rüdorff, B. 2, 68); Thomsen gives [NaCl,Aq] = -1180 (Th. 3, 252). By mixing 36 parts NaCl with 100 parts snow, temperature falls to -21:3° (Rüdorff, P. 114, 79; 122, 337).

NaCl is insol. absolute alcohol; Girardin A. Ch. [4] 5, 146) gives the following data for S. in aqueous alcohol S.G. 9282; 10-9 at 49, 11-1 at 10°, 11-43 at 13°, 11-9 at 23°, 12-3 at 32°, 13-1 at 44°, 13-8 at 51°, 14-1 at 40°. Schiff (A. 118, 365) gives S. in alcohol at 15° as follows; 28-33 in 10 p.c. alcohol, 13-25 in 40 p.c., 5-93 in 60 p.c., 1-22 in 80 p.c. NaCl crystallises in the regular system, generally in cubes, sometimes in ootahedra.

Occurrence.—As rock salt, or halite, in very

large quantities very widely distributed; in seawater, many salt lakes, brine springs, and most mineral springs.

Fornation.—1. By burning Na in moist Cl. According to Wanklyn (C. N. 20, 271), dry Cl does not combine with Na even at the M.P. of the metal; Donny a. Marceka (C. R. 20, 817) state that Na is unacted on by liquid Cl at —80°.—2. By neutralising NaOHAq or Na₂CO₃Aq by HClAq, and evaporating.—8. By the reaction of excess of cone. HClAq with several salts of Na, e.g. Na₂SO₄.—4. By strongly heating Na₂SO₄ with excess of NH₁Cl; also by decomposing Na₂SO₄Aq by several chlorides, e.g. MgCl₂ or CaCl₂.—5. As a by-product in making KNO₃ by the reaction of KCl with NaNO₅. By the reduction of many chlorides by Na.

Preparation. - Pure NaHCO, is prepared by washing a large quantity of the ordinary ' pure salt, in fine powder, with cold water till the washings cease to be clouded on addition of a salt of Ag or Ba; after boiling with slight excess of HNO Ag, the residue is dried and heated to dull redness in a Pt dish; a boiling saturated solution of the Na₂CO₃ thus obtained is prepared, filtered, and shaken while crystallising to insure the formation of small crystals; the crystals are dried by suction by a water-pump, they are then twice moistened with cold water to remove all mother-liquor, and crystallised three times from water. The pure Na,CO, is dissolved, and NaCl is formed by passing in a stream of pure HCl gas (obtained by heating pure conc. HClAq); a little pure NH₄Cl is added to the solution (for preparation of pure NH,Cl v. vol. i. p. 197, under Ammonia, Preparation, No. 3), which is then evaporated to dryness in a Pt retort; the residue is very strongly heated, and then dissolved in water; after standing for 24 hours the solution is poured off (from any Al2O3.xH2O and SiO₂ that settle), a little pure NH₄Cl is added, the solution is evaporated to dryness in a Pt retort, the residue is strongly heated for some time, and after partial cooling the still liquid NaCl is poured off (from Pt, SiO2, and Al₂O₃) into a Pt dish; when cold, the NaCl is dissolved in water, the solution is poured off after 2 days and evaporated to dryness in a Pt retort, and the residue is fused in a Pt vessel (Stas, Chem. Proport. 275).

For preparation of Nacl from rock salt, brine, and sea-water, v. Distributor of Applied Chemistry, vol. iii. p. 429.

Properties.—A pure, white, lustrous solid; crystallises in the regular system, generally in cubes. Decrepitates when heated. NaCl is diathermanous. Solution in water is neutral to indicators, and has a bitter taste. Pure NaCl is very slightly hygroscopic, taking up c. ‡ p.e. water from moist air (Stas, Karsten). Melts at c. 772°; vapourises markedly at white heat in a stream of N (v. Stas, l.c.). NaCl is almost wholly ppd. from an aqueous solution by leading in HCl (Margueritte, C. R. 4°, 50); also ppd. from a conc. solution by cold conc. NaOHAq (Berthelot C. R. 76, 111); also by warming a conc. solution with excess of NaBr or NaI and cooling (von Hauer, J. pr. 98, 187). Saturated NaClAq deposits the hydrate NaCl. 2aq at — 7° to o. — 22°, and at c. — 23° NaCl. 10aq separates (v. Hydrates under Combinations, p. 478).

Reactions .- - 1. According to de Sanderval (C. R. 116, 641), when NaCl is vapourised around a porous tube Cl collects in the inside of the tube.—2. Electrolysis of NaClAq produces Cl and NaOHAq, but NaClOAq and NaClO, are soon formed by secondary reactions; if a diameter of the control of the collect of the tube. phragm of asbestos is used, the cathode being on one side and the anode on the other, and CO₂ is passed into the NaClAq, Cl is given off and Na₂CO₃ is formed (v. Hempel, B. 22, 2475).— 8. Fusion with potassium produces KCl and Na. 4. Fusion with sulphur is said to form Na₂S and S₂Cl₂, but this is denied by Karsten; NaCl is not decomposed by hydrogen, or oxygen, at a red heat.—5. Superheated steam has no reaction, according to Kunheim (J. 1861. 149); there is a slight reaction, according to Lunge (Soda-indusslight reaction, according to Lunge (Soda-industrie, 2, 288).—6. Sulphuric anhydride vapour is absorbed, without heating, giving S₂O₂NaCl (Na salt of SO₂(Cl).O.SO₂.OH); according to Schultz-Sellack (B. 4, 112) more SO₂ is then absorbed, and a compound approximately NaCl.4SO₂ is formed; on heating Na₂SO₃ SO₂ and Cl are produced. By heating with liquid sulphuric anhydride S₂O₃Cl₂ is formed (Rosenstiah), C. R. 53, 658).—7. Decomposed by heating the composed by heating the composed of stiehl, C. R. 53, 658).—7. Decomposed by heating to c. 500° in a mixture of air, sulphur dioxide, and water vapour, giving Na₂SO₄ and HCl (Hargreaves and Robinson's process for making Na₂SO₄; v. Dictionary of Applied Chemistry, vol. iii. p. 444). - 8. NaCl is decomposed, with formation of oxychlorides or chlorides, by heating with phosphoric, chromic, or molybdic anhydride, or with antimonic oxide; decomposition occurs with silica, boric oxide, alumina, and tungstic oxide only in presence of air or water vapour, forming silicate, borate, aluminate, or tungstate of Na, and HCl; in presence of water vapour Cl is evolved in some of these reactions (v. Schulze, J. pr. [2] 21, 407; Delalande a. Prudhomme, Bl. 20, 74; Gorgeu, A. Ch. [5] 10, 145). Lead oxide decomposes NaClAq, forming PbCl, and NaOHAq (Scheele); but molten NaCl is said not to interact with PbO. Moist NaCl mixed with caustic lime and exposed to air becomes covered with an efflorescence of Na CO, crystals. Magnesia interacts with NaclAq, in presence of CO₂, to form NaHCO₃ and MgCl₂ (Weldon; Wagner, J. 1873, 256).—9. Sulphuretted hydrogen partially decomposes hot NaCl to Na,S, more completely in presence of steam (Kingzett, C. J. [2] 11, 456).—10. Many metallic sulphides, e.g. Cu.S, produce Na.SO, and metallic chlorides (someproduce Na, 50, and metalite emotides going times Cl is set free) when roasted in air with NaCl,—11. Several metallic sulphates when fused with NaCl produce Na, 50, and metallic chlorides—c.g. PbSO, ZnSO, CuSO,; some of these sulphates react also with NaClAq. Some sulphates form Na, SO, and give off Cl when the contraction of the NaclAq. sulphates form Na, SO, and give off Ci when heated with NaCl, e.g. FeSO, (v. Barreswil, J. Ph. [8] 12, 456),—12. Fusion with potassium chlorate only decomposes a trace of NaCl (Schulze, J. pr. [2] 21, 407).—13. Ammonium oxalate heated with NaCl forms Na, CO, and disozalate heated with NaCi forms Na,CO, and distinct quantities of NaCi (Fresenius); addition of (NH₁)₂C₂O, to hot saturated NaClAq ppts. Na,CO,-—14. Potassium carbonate reacts with NaClAq to form Na,CO₂Aq and KClAq; if CO₂ is passed in NaHCO₂ ppts.—15. Ammonium bicarbonate and NaClAq produce NaHCO₂ and

NH.ClAq. Passage of CO, into NaClAq saturated with NH, ppts. NaHCO, (v. Ammonia-soda process, in Diotionary of Applied Chemistry, vol. iii. p. 494).—16. Sulphuric acid decomposes NaCl, forming HCl, and NaHSO, or Na,SO, according to the temperature. The Lebland process for making sodium carbonate takes advantage of this reaction (v. Dotionary of Applied Chemistry, vol. iii. p. 459).—17. Evaporation with excess of nitric acid produces NaNO₃ and HCl.—18. NaCl is readily decomposed by hydrofluoric acid, also by hydrofluoristicic acid.—19. Carbonic acid is said to set free some HCl from NaClAq (v. H. Müller, B. 3, 40; Funk, Chem. Zeitung, 1879. 660).—20. Repeated evaporation with excess of cashic acid completely decomposes NaCl to Na,ClQ.

Combinations.—1. With water to form hydrates. The dihydrate NaCl. 2aq separates from saturated NaClAq cooled to —7° to —22°, in large clear monoclinic crystals (v. Hankel, P. 53, 623; Mitscherlich, J. pr. 83, 485). The crystals cfiloresce at —10°, and deliquesce at 0°. Ehrenberg (P. 36, 210) and Frankenheim (P. 37, 638) obtained this hydrate by evaporating dilute NaClAq at a moderate temperature. The crystals that separate from hot NaClAq containing HCl are hydrated, according to Bevan (C. N. 35, 17), and contain 5·48 p.c. water, but after a time they change to the ordinary crystals of NaCl. According to Naumann (Thermochemie, 106), crystals of the decahydrate, NaCl. 10aq, separate from NaClAq at —23°.—2. NaCl absorbs considerable quantities of anmonia, under pressure. Joannis dissolved NaCl in liquid NH₃ at —10°; on cooling to —30° and letting NH₃ cscape at the ordinary pressure, he obtained slender white needles, probably NaCl.5NH₄ (C. R. 112, 337).—3. Sulphuric anhydride is absorbed by NaCl, forming NaCl.2SO₄, and then perhaps NaCl.4SO₄ (v. Reactions, No. 6).—4. Compounds with sodium iodate are formed, by adding excess of NaCl to NaIO₄Aq, and by boiling NaIO₄ aq was obtained by Ditte, and 3NaCl.2NaIO₄, 18aq by Rammelsberg (P. 44, 548; 115, 584).—5. With many chlorides of less positive metals, e.g. AlCl., CdCl., CfCl., PbCl., MgCl.2 (v. Chlorides of various metals).

Sodium subchloride. H. Rose (P. 120, 15) noticed that a grey-blue solid was produced by fusing NaCl with Na in H; he thought this might be a subchloride of Na. Bunsen and Kirchhoff (P. 113, 339) noticed the formation of a deep-blue substance during the electrolysis of molten RbCl; this substance dissolved in water, giving off H and producing a colourless, strongly alkaline solution; a similar reaction was obtained on electrolysing KCl; these blue substances were regarded by B. a. K. as probably subchlorides, but no analyses or proofs of composition were given.

Bodium, chromisulphocyanide of, v. vol. ii, p. 349.

Sodium, cyanide of, v. vol. ii. p. 347.
Sodium, ferrate of, v. vol. ii. p. 547.
Sodium, ferricyanide of, v. vol. ii. p. 340.
Sodium, ferrite of, v. vol. ii. p. 547.
Sodium, ferrovyanide of, v. vol. ii. p. 337.
Sodium, fluoboride of, v. vol. i. p. 526,

known with certainty, but the formula NaF is

probably molecular.

Formation .- 1. By neutralising HFAq by NaOHAg and evaporating .- 2. Formed along NaOHAq and evaporating.—2. Formed along with NaHSO, by the reaction of HFAq with Na₂SO₄ (Weldon, D. P. J. 182, 228).—3. By fusing together CaF₂, Na₂SO₄, and charcoal, and extracting with water (Jean, C. R. 66, 801, 918).—4. By boiling powdered cryolite with NaOHAq of at least 1.35 S.G. till a little taken out is entirely sol. boiling water, decanting the alkaline liquid from NaF, pressing the NaF. dissolving in boiling water, separating any Al₂O₃ in solution by Na₂SiO₃Aq, removing silica by CO₂, filtering, evaporating, and recrystallising the NaF that separates (Schuch, A. 126, 108) .-5. Berzelius (Lehrbuch [5th ed.] 3, 216) prepared NaF by adding to 100 parts Na2SiF, and 112 parts Na₃CO₃ water enough to make the whole pasty, boiling as long as CO, was given off, extracting the solid thus formed with boiling water, evaporating the solution to dryness, heating the residue gently, again extracting with hot water, filtering from SiO,, and crystal-

Preparation.—Pure Na₂CO₃ (for preparation v. Sobum chlorum, Preparation, p. 477) is dissolved in pure HFAq, till the acid is just saturated, in a Pt dish, the solution is evaporated to dryness, the residue is heated strongly for some time,

and allowed to cool.

Properties.—Clear, lustrous cubes; in presence of Na,CO₃ crystallises in octahedra. Sl. sol. water; S. at 16° = 4.78 (Berzelius), at 15° = 4 (Fremy, A. Ch. [3] 47, 32). Scarcely more sol. hot than cold water. Insol. alcohol. Güntz (A. Ch. [6] 3, 5) gives [NaF,Aq] = -600. Decrepitates on heating, and melts at a high temperature without decomposition (Berzeline)

Reactions.—1. Partially decomposed by heating to redness in water vapour, with formation of NaOH and HF (Weldon).—2. Excess of caustic potash forms NaOHAq.—3. Boiling with magnesia partially decomposes NaF to NaOHAq and forms a double Na-Nig fluoride (MgF2,2NaF) (Tissier, C. R. 56, 848).—4. Completely decomposed to NaCl by heating strongly in hydrochloric acid gas (Deville, C. R. 43, 970).—5. Partially decomposed to NaCl by heating with animonium chloride (Rose, P. 74, 579). Fusion with magnesium chloride produces NaCl and MgF2 (Geuther, J. Z. 2, 208).

Combinations.—1. With several fluorides of less positive metals; 3NaFAIF, occurs native as cryolite (v. Aluminum fluoride, vol. i. p. 145).—2. With silicon fluoride to form Na,SiF, (v. Sodium borate to form 6NaF.Na,B,O, (v. Fluoborates, vol. i. p. 530).—4. With sodium phosphate to form NaF.2Na,PO,. 19aq and 22aq, and NaF.Na,PO,. 24aq (v. Baumgarten, J. 1865. 219; Brieglieb, A. 117, 95).—5. With sodium sulphate to form NaF.Na,SO, (v. Marignac, Ann. M. [5] 12, 18).

SODIUM-HYDDOGEN FLUORIDE NaHF₂ or NaF.HF. This compound is formed, according to Berzelius (*Lehrbuch* [5th ed.] 3, 217), by the spontaneous evaporation of a solution of NaF in HFAq. Forms small rhombohedral crystals,

with a sharp, acid taste. Sl. sol. cold water, more sol. hot water. Decomposed by heat to NaF and HF (Marignac, J. 1857. 128). Güntz (A. Ch. [6] 3, 5) gives [NaF,HF] = 17,100 (to form NaF,HF).

Sodium, hydride of, Na,H. Gay-Lussac and Thénard (A. Ch. 74, 203) observed that Na absorbed H when heated therein. The process was more accurately studied by Troost and Hautefeuille (A. Ch. [5] 2, 273). They found that absorption of H by Na began at c. 300° and ceased at c. 421°, when the gas was at the atmospheric pressure. The product gave, in a Sprengel pump, 237 vols. H. for 1 vol. Na; the formula Na,H requires 238 vols. H. Na,H is a soft, silver-white solid; it can be melted without decomposition in H; S.G. 959. Traces of H are given off at 760 mm. pressure; heated in vucuto a regular dissociation takes place from 330° to 430° (for vapour-pressures of H given off v. Dissociation, vol. ii. p. 398). Moutier (C. R. 79, 1242) gives the thermal value [Na²,H] = 13,000 at c. 330°.

Sodium, hydrosulphide of, NaSH. (Sodium sulphydrate.) Sabatier (A. Ch. 46) 22, 5) obtained this compound by treating Na₂S.9aq with H₂S in absence of air, and then evaporating the liquid so formed in an atmosphere of H₂S. A white, very hygroscopic solid. Passage of CO into NaSHAq drives out H₂S and converts all the Na into Na₂CO₃. NaSHAq contains H₂S and NaOH, according to Gernez (C. R. 64, 86). NaSHAq dissolves S with evolution of H₂S; it ppts. PbS, or MnS, from a neutral solution of a Pb or Mn salt, giving off H₂S; Na₂SAq does not give off H₂S while dissolving S or ppg. PbS or MnS.

Sabatier (l.c.) obtained the hydrate

NaSH.2H.O by passing H.S over Na.S. 9aq, and then evaporating in H.S till half the water was removed; very hygroscopic needles, becoming yellow in air.

Sodium, hydroxide of, NaOH. (Caustic soda Sodium, or sodic, hydrate.) Mol. w. not determined. Melts at 1098° (v. Meyer a. Riddle, B 26, 2443). S.G. 2·13 (Filhol, A. Ch. [3] 21, 415) 1·723 (Smith, Am. J. Pharm. 53, 145). S. (colc water) c. 212 (Bineau, C. R. 41, 509). H.F. [Na,O,H] = 101.870; [Na,O,H,Aq] = 111.810 [Na*O,H*O] = 35,620 (Th. 3, 232).

Formation.—1. By the interaction of Na, of Na, of Na, of Na, of Wa, of with Ha.O.—2. By decomposing Na, CO, Ac with CaO, H2 (v. Preparation, No. 1).—3. By the action of CaO, H2 with NaFAq (Tissier J. pr. 90, 50).—4. By decomposing Na, SO, Ac by BaO or CaO ander pressure.—5. From NaClAq by interaction with PbO (Knab, B 11, 1458).—6. By heating NaNO, with char coal, or with Cu (Wohler, A. 87, 373), or Fe (Polacci, C. N. 26, 288).—7. By decomposing Na, SAq by CuO, Fe,O,, PbO, ZnO, &c. (Kopp D. P. J. 142, 341; Stromeyer, A. 107, 333).—8. By the interaction of NaF and stean (Weldon).—9. By heating soda felspar with lime

Preparation.—1. By causticising soda crystals by lime. A solution of pure Na CO₂ crystal in 4-5 parts water is boiled, in a dish of silve or polished iron, with milk of lime till a littl of the filtered liquid gives off no CO₂ whe acidified; the weight of CaO required is c. the wt. of soda crystals used, it should b

suspended in about as much water as the wt. of soda crystals used; as the boiling proceeds a little water should be added from time to time. otherwise the NaOHAq will decompose some of the CaCO, formed to CaO and Na, CO, Aq. The CaCO, formed is allowed to settle, the vessel being closed, the NaOHAq is drawn off by a siphon and evaporated to dryness in a silver dish, and the residue is heated till volatilisation begins, and allowed to cool in an exsiccator. By dissolving in absolute alcohol, allowing to settle, drawing off the liquid, evaporating it to dryness on a water-bath in a silver dish, removing resinous matter from the warm semisolid mass by a silver spatula, heating to bright redness, and pouring the molten mass on to a plate of polished iron-or, better, of silver-NaOH containing only traces of impurities, chiefly NaCl and Na_xCO₃, is obtained.—2. A large silver dish is surrounded by cold water; 2 or 3 drops of water are placed in the dish, and then a small piece of clean Na, 1 or 2 cms. long; the dish is constantly shaken, so that the Na flows over a large cold surface (explosions are thus avoided); when the reaction is finished 2 or 3 more drops of water are added, and then another piece of Na, while the dish is shaken, and so on. The semi-solid mass is heated till the water is all driven off and the NaOH melts, and the molten substance is poured on to a plate of polished iron or silver.

To obtain NaOH free from nitrites and nitrates Ilosva (Bl. [3] 2, 357) recommends to place Na in water with a layer of petroleum on the surface, the petroleum having been washed with water till free from nitrites and nitrates. He also says that if 2-4 p.o. ordinary NaOHAq is kept for some weeks in contact with granulated Zn all nitrites and nitrates are destroyed.

For preparation of ordinary caustic soda v. Dictionary of Applied Chemistry, vol. iii. p. 480.

Properties.—NaOH is a white, hard, brittle solid. Melts below red heat; volatilises at very bright red heat, higher than temperature of volatilisation of KOH. Very deliquescent; dissolves in c. 47 parts water. During solution in water much heat is produced, [NaOH,Aq] = 9,940 (Th. 3, 232); the maximum amount of heat is produced when H₂O is added to NaOH in the ratio NaOH: 20H₂O, addition of water to this solution is attended with a slight disappearance of heat (Th. 3, 84). (For hydrates v. p. 480, Combinations.) Easily sol. alcohol. NaOHAq with 36:86 p.c. NaOH boils at 130°, with 70 p.c. boils 180°, with 77:5 p.c. boils 238°, with 78:7 p.c. boils 243°, and with 82:6 p.c. boils 260° (Lunge, Soda-industrie, 2, 543).

NaOHAq acts as a strong alkali; its affinity is c. equal to that of KOHAq and LiOHAq and c. 50 times greater than NH, Aq (Ostwald). The properties of NaOHAq closely resemble those of potassium hydroxide solution (q. v. p. 302).

The table in the next column, given by Lunge, shows the composition of NaOHAq of different S.G. at 15°.

Regarding the freezing points of NaOHAq of different concentrations v. Rüdorff (P. 116, 55); de Coppet (A. Ch. [4] 24, 551); and Pickering (who gives very complete data) C. J. 63, 890).

S.G. NaOHAq	Barmé	Twaddell	100 pts. by wt.		cont	metre
Масили	B	Ę	Na _s O	NaOH	Na,O	NaOH
1.007	1	1.4	0.47	0.61	4	6
1.014	2	2.8	0.93	1.20	9	12
1.022	3	4.4	1.55	2.00	16	21
1.029	4	5.8	2.10	2.71	22	28
1.036	5	7.2	2.60	3.35	27	35
1.045	6	9.0	3.10	4.00	82	42
1.052	7	10.4	8.60	4.64	- 38	49
1.060	8	12.0	4.10	5.29	43	56
1.067	9	13.4	4.55	5.87	49	63
1.075	10	15 0	5.08	6.55	55	70
1.083	11	16.6	5.67	7.31	61	79
1.091	12	18.2	6.20	8.00	68	87
1.100	13	20.0	6.73	8.68	74	95
1.108	14	21.6	7.30	9.42	81	104
1.116	15	23.2	7.80	10.06	87	112
1.125	16	25.0	8.50	10.97	96	123
1.134	17	26.8	9.18	11.84	104	184
1.142	18	28.4	9.80	12.64	112	144
1.152	19	30.4	10.50	13.55	121	156
1.162	20	32.4	11.14	14.37	129	167
1.171	21	34.5	11.73	15.13	137	177
1.180	22	36.0	12.33	15.91	146	188 200
1.190	23	38.0	13.00	16.77	155	212
1.200	24	40.0	13.70	17.67	164	225
1.210	25	42.0	14.40	18.58	174	239
1.220	26	44.0	15.18	19.58	185	253
1.231	27 28	46·2 48·2	15.96	20.59	196	266
1.241	29	50.4	16.76	21.42	208	283
1·252 1·263	30	52.6	17.55	22·64 23·67	220 232	299
	31	54.8	18·35 19·23	24.81		316
$1.274 \\ 1.285$	32	57.0	20.00	25.80	245 257	332
1.297	33	59.4	20.80	26.83	270	348
1.308	34	61.6	21.55	27.80	282	864
1.320	35	64.0	22.35	28.83	295	381
1.332	36	66.4	23.20	29.93	309	899
1.345	.37	69.0	24.20	31.22	326	420
1.357	38	71.4	25.17	32.47	342	441
1.370	39	74.0	26.12	33.69	359	462
1.383	40	76.6	27.10	34.96	875	488
1.397	41	79.4	28.10	36.25	892	506
1.410	42	82.0	29.05	37.47	410	528
1.424	43	84.8	30.08	38.80	428	558
1.438	44	87.6	31.00	39.99	446	575
1.453	45	90.6	32.10	41.41	466	602
1.468	46	93.6	33.20	42.83	487	629
1.483	47	96.6	34.40	44.38	510	658
1.498	48	99.6	35.79	46.15	535	691
1.514	49	102.8	86.90	47.60	559	721
1.530	50	106.0	38.00	49.02	581	750

Reactions.—1. According to Deville (C. R. 45, 857), NaOH is decomposed to Na, O, and H by heating to white heat in an iron bottle.—2. Strongly heated with non-volatile acidio anhydrides, water and salts of Na are formed.—3. When molten NaOH is exposed for a considerable time to air or oxygen, some Na,O, is formed (Gay-Lussac; Thénard).—4. Moist or molten NaOH is decomposed by electrolysis, with production of Na (Davy, T. 1802. 1).—5. Heating with sulphur produces polysulphides, sulphite, and sulphate; S heated with NaOHAq forms polysulphides and sulphite. Similar reactions occur by heating with selection or tellurium.—6. Chlorine interacts with NaOHAq is

NaCIO₂Aq is formed. Bromine reacts similarly. If Cl is led into NaOHAq containing iodine in suspension, NaIO₂ is produced.—7. When NaOHAq is warmed with phosphorus, H and inflammable P hydride are given off.—8. Heated with sodium, Na₂O and H are formed.—9. Moist NaOH withdraws carbon dioxide from the air, forming NaHCO₂.—10. Reacts with acids to form Nasalts.—11. NaOHAq ppts metallic hydroxides, or oxides, from solutions of many metallic salts; in some cases the hydroxide dissolves in excess of NaOHAq—e.g. AlO₃H₃, ZnO₂H₂.—12. Molten NaOH acts generally as an oxidiser; e.g. As, Sb, Fe, Pt, &c. form arsenate, antimonate, ferrate, and platinate of Na. Salts are generally decomposed by molten NaOH, giving Na salts, and setting free the bases.—13. According to Schöne (A. 193, 241), addition of hydrogen peroxide to NaOHAq produces Na₂O₂.8H₂O (v. Sodium documpostore, p. 482).

Pickering (priv. comm.) gives the following

P.c. NaOH	S.G. NaClAq at 15° (water at 4° =1)	P.c. NaOH	S.G. NaClAq at 15° (water at 4° =1)	P.c. NaOH	S.G. Na(JAq at 15° (water at 4° =1)
0	0.999180	17	1.88707	34	1.373453
1	1.010611	18	1.199783	35	1.383815
2	1.021920	19	1.210861	36	1.394092
3	1.033109	20	1.221933	37	1.404279
4	1.044317	21	1.233062	38	1.414363
5	1.055463	22	1.244119	39	1.424353
6	1.066602	23	1.255134	40	1.434299
7	1.077733	24	1.266092	41	1.444161
8	1.088856	25	1.277063	42	1.453929
9	1.099969	26	1.287990	43	1.463623
10	1.111069	27	1.298877	44	1.473249
11	1.122165	28	1.309708	45	1.482850
12	1.133250	29	1.320496	46	1.492406
13	1.144353	30	1.331213	47	1.561927
14	1.155450	81	1.341879	48	1.511412
15	1.666538	32	1.352472	49	1.520868
16	1.177619	33	1.362991	50	1.530282

Combinations.—1. With water to form hydrates. The hydrate 2NaOH.7H,O was obtained by Hermes (B. 3, 122) by exposing NaOHAq 8.G. 1365 to the cold of a severe winter; monoclinic crystals, S.G. 1.405, melting it 6°; in vacuo gave off 3H,O. Göttig (B. 20, 543) obtained a dihydrate, NaOH.2H,O, by heating NaOH in 96.8 p.c. alcohol very gradually to 100°. By cooling NaOHAq, Pickering (C. J. 63, 890) obtained the following hydrates, with the freezing-points noted:—

Hydrate	Freezing-poin
NaOH.H.O	- 64·3°
NaOH.2H,O	12.5
NaOH.3-11H,O (sic	c) 2·73
NaOH.3·5H ₂ O	15.55
aNaOH.4H ₂ O	7.57
8NaOH.4H,O	- 1·7
NaOH.5H.O	-12·22
NaOH.7H.O	-23.51

With carbon dioxide to form NaHCO₂.
 Sodium, iodide of, NaI. Mol. w. not known with certainty, but formula NaI is probably Vol. IV.

molecular. Melts at 628° (Carnelley, C. J. 33, 278); at 650° (V. Møyer a. Riddle, B. 26, 2443). S.G. 3.45 (Filhol, A. Ch. [3] 21, 415); 3.654 at 18.2 (Favre a. Valson, C. R. 77, 579). S.H. (26° to 50°) 0881 (Schuler, P. 136, 70); (16° to 99°) 08684 (Regnault, A. Ch. [3] 1, 129). Kremers (P. 108, 120) gives the following data for solubility in water;—

Temp.	s.	Temp.	8.
0°	158.7	- 80°	303
20	178.6	100	312.5
40	208.4	120	322.5
60	$256 \cdot 4$	140	333.3

S. = $264 \cdot 19 + \cdot 3978t$, when t varies from $64 \cdot 7^{\circ}$ to $138 \cdot 7^{\circ}$ (de Coppet, A. Cl_{l} . [5] 30, 411). Gerlach (Fr. 8, 285) gives following:—

S.G. NaIAq	P.C. NaI	S.G. NaIAq	P.C. Nal
1.04	5	1.36	35
1.082	10	1.432	40
1.128	12	1.51	45
1.179	20	1.6	50
1.234	25	1.7	55
1.294	80	1.81	60

Easily sol. alcohol. Saturated NaIAq boils at 1411°. H.F. [Na,I] = 69,080; [Na,I,Aq] = 70,800 (Th. 3, 232).

Formation.—1. When Na and I are fused together only very small quantities combine (Merz a. Weith, B. 6, 1518).—2. By decomposing BaI.Aq, or Cal.Aq, by Na.CO₃ or Na.SO₄, filtering, and evaporating.—3. By neutralising HIAq by Na.CO₃, and evaporating.—4. I is added to water and iron filings till the iron is almost all dissolved, the solution is filtered, and Na.CO₃ is added so long as FeCO₂ ppts.; the liquid is filtered (if alkaline it is neutralised by HIAq) and evaporated, any Fe.O₃ which separates being filtered off (Baup, J. Ph. 9, 37, 122).

Preparation .- 1. Iodine is added to moderately conc. NaOHAq till a yellow colour is produced; finely-powdered charcoal, equal to c. 100 of the weight of I used, is added; the liquid is evaporated to dryness and the residue is heated in a covered crucible to dull redness for some time; when cold, the residue is dissolved in water, the liquid is filtered (neutralised by HIAq if alkaline) and crystallised at 40°-50°. (For more details v. Potassium iodide, Preparation, p. 304.)-2. A quantity of NaOHAq is divided into two equal portions; I is added to one part till a yellow colour remains, an equal quantity of I is then added, and then the other portion of NaOHAq is saturated with SO₂ and added, and the whole is evaporated till NaI crystallises out; the salt is purified by recrystallisation from water at 40°-50° (Stephani, J. Ph. [3] 26, 450).

Properties.—Crystallises from aqueous solutions at 40° to 50° in cubes (Mitscherlich, P. 17, 385); the hydrate NaI. 2aq separates at ordinary temperatures. Melts at 629°; volatilises less readily than KI, but at a lower temperature than NaCl (Mohr, A. 21, 66). Deliquesces in moist air, becoming rose-coloured with separation of some I and formation of some Na₂CO₃ (Girsult, J. Ph. 27, 390).

Reactions and Combinations.—1. Heated in air some I is separated and O absorbed, and the reaction becomes alkaline (Berzelius, Lehrbuch

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[5th ed.] 3, 215).-2. Heated with charcoal in ! contact with air much Na CO is formed (Girault, l.c.). Most of the reactions of NaI are similar to those of KI (v. Potassium iodide, Reactions,

p. 304).

Combines with most iodides of less positive metals. Forms a compound with arsenious oxide NaI.As,O. (Rüdorff, B. 21, 3051). The dihydrate NaI.2H,O crystallises at the ordinary temperature from NaIAq in large monoclinic prisms; S.G. 2.448; melting at c. 65° and giving NaI; effloresces in dry air, and deliquesces in moist air.

Sodium, manganicyanide of, v. vol. ii. p.

Sodium, manganocyanide of, v. vol. ii. p. 842.

Sodium, nitride of, Na, N. A dark-grey solid; formed by heating NaNH, (v. Sodium AMIDE, p. 475) to redness in absence of O. Resembles potassium nitride (q. v., p. 304) (Gay-Lussac a. Thénard, A. Ch. 65, 325).

Sodium, nitroprusside of, v. vol. ii. p. 341. Sodium, oxides of. Two oxides have been isolated, Na₂O and Na₂O₂.

Sodium oxide Na₂O. (Sodium monoxide.) It is doubtful whether this compound has been obtained pure. Davy (T. 1808. 24) said that when Na is fused with dry soda there is 'a division of the oxygen between the alkali and the sodium.' Na does not combine with O when exposed to quite dry air at the ordinary temperature (von Bonsdorff, P. 41, 296). According to Beketoff (v. B. 12, 856; 16, 1854), NaOH and Na do not react at a red heat. Beketoff (J. R. 1883. [i.] 277 [v. B. 16, 1854]) allowed Na to drop into a red-hot copper cylinder, then passed in a mixture of 1 vol. O and 4 vols. air, and heated by a blowpipe; in this way he obtained Na,O, but always mixed with some Cu and traces of Na; considering the conditions under which Na, O, is obtained (v. infra, Sodium dioxide) it is likely that B.'s Na₂O contained Na₂O₂.

Na O is described as a greyish solid; Beketoff's preparation was rose-coloured, but it contained Cu. Na₂O dissolves in water to form NaOHAq; B. gives [Na²O,Aq] = 55,500; and from this and other data Thomsen (Th. 3, 232) calculates [Na2,O] = 99,760. According to B. (l.c.), hot Na2O reacts with H to form NaOH and Na; heated to c. 300° in CO it gives Na₂CO₃ and Na (B., lc.). Combination with CO₂, to form Na₂CO₃, occurs at c. 400°. By heating Na amalgam with HgO, B. (l.c.) obtained the compound Na₂HgO₂ = Na₂O.HgO. Comey and Jackson (B. 21, 1589; Am. 11, 145) describe various compounds of Na₂O with ZnO and H₂O.

SODIUM DIOXIDE Na₂O₂. (Sodium peroxide.) The formation of an oxide with more O than Na₂O, by heating Na in air, was noticed by Gay-Lussac a. Thénard (A. Ch. 65, 325). Pure Na₂O₂ was obtained by Vernon Harcourt (C. J. 14, 267) by heating Na, in a flask of hard glass filled with N, till the Na melted, then sending in a slow stream of dry air, and heating till the metal was changed to a yellowish-white solid, and heating this for some time in dry O. Na₂O₂ is a white solid, becoming yellowish on heating. It deliquesces gradually in air, and then is gradu-

with production of much heat; on heating O is evolved; Na,O,Aq deposits crystals of the hydrate Na₂O₂, Aq deposits crystals of the nyarate Na₂O₂, 8H₂O on standing over H₂SO₄ (v. infra, Hydrates). Na₂O₂ acts as an energetic oxidiser when heated; C, I, P, S, Sn are oxidised, more or less rapidly; heated with CO, Na₂CO₃ is formed; with N₂O the products are NaNO₂ and

N (v. Harcourt, l.c.).

Hydrates of sodium dioxide. The octohydrate, Na₂O₂8H₂O, was obtained by Harcourt (l.c.) by evaporating a solution of Na.O. in water over H_2SO_4 . Fairley (C. J. [2] 16, 125) obtained the same hydrate by adding H_2O_2Aq to NaOHAq and ppg. by alcohol. Schöne (A. 193, 241) also obtained the octohydrate by the action of H2O2Aq on NaOHAq, evaporating in vacuo, drying on a porous tile, washing with 90 p.c. alcohol, and drying between filter paper. By using a considerable excess of H,O,Aq, Schöne (l.c.) obtained crystals to which he gave the composition Na₂H₁O₈·4H₂O = Na₂O₂·2H₂O₂·4H₂O₃ on drying over H₂SO₄, Na₂O₂·2H₂O₄ remained. The dihydrate Na₂O₂·2H₂O is obtained by drying the octohydrate for some time over H2SO4.

Sodium, phosphide of. A compound of Na and P was supposed by Gay-Lussac a. Thénard, and also by Davy, to be formed by heating the elements together in N. Vigier (Bl. [2] 3, 7) recommends to place a piece of Na in rock oil, boiling at c. 120°, in a retort, to add P little by little (much heat is produced and some oil distils) till there is an excess and some crystallises on the cold parts of the retort, to distil off the oil from the black phosphide formed, to wash with CS2, and dry in a stream of CO2.

The phosphide may be kept in dry air; in moist air, water, or acids it gives off inflammable P hydride (v. also Lüpke, C. C. 1890. [ii.]

Bunsen (A. 138, 292) obtained a phosphide of Na by strongly heating a mixture of Na, HPO. and Na in a narrow glass tube.

Sodium, platinocyanide of, v. vol. ii. p. 344. Sodium, platinosulphocyanide of, v. vol. ii. p. 351.

Sodium, salts of. Compounds formed by replacing H of acids by Na. These compounds belong to the type NaX where X is a monovalent acidic radicle. The chief salts of Na derived from oxyacids are antimonate, arsenate, bromate and hypobromite, carbonates, chlorate, perchlorate, chlorite and hypochlorite, chromate and dichromate, ivdate and periodates. manganate and permanganate, molybdates, nitrate and nitrite, phosphates, phosphites and hypophosphite, selenates and selenites, silicates, sulphates, sulphites, thiosulphate and thionates. tellurates and tellurites (v. CARBONATES, NITRATES, Sulphates, &c.).

Sodium, selenides of. Two selenides have been isolated, Na₂Se and Na₂Se₂, corresponding with two of the sulphides and with the two oxides.

Sodium monoselenide Na.Se. Obtained by mixing well-cleaned Na rubbed to powder with the proper proportion of Se (Rosenfeld, B. 24, 1658). Uelsmann (A. 116, 127) says Na, Se is obtained, in large colourless crystals, by saturating NaOHAq with H₂Se, then heating in a stream of H and allowing to cool; it seems probable ally changed into solid Na, CO. Soluble water, that these crystals were a hydrate of Na, Se (v.

infral. Fabre (U. H. 102, 613) obtained Na, Se by heating 2Na,Se.9H.O (v. infra, Hydrates) in a current of N to not above 400°; F. describes Na Se as a hard, white, crystalline, deliquescent solid, becoming reddish-brown when fused; owing to its action on glass, F. did not get Na Se free from silica and alumina.

Hydrates of sodium monoselenide. By passing a rapid stream of H.Se into NaOHAq (1 part NaOH in 4 water) Fabre (l.c.) obtained Na Se.16H O, melting at 40°, giving Na₂CO₃, a little Na₂SeO₃, and Se on exposure to air. By using more conc. NaOHAq (3:1), and keeping the temperature down, F. obtained Na₂Se.9H₂O; and when very conc. NaOHAq was used, he obtained 2Na Se.9H2O.

For data regarding heats of formation of Na.Se and hydrates, v. Fabre, C. R. 102, 703.

Sodium diselenide Na2Sc2. Wöhler and Dean (A. 97, 1) obtained a selenide of K by heating K2ScO3 with charcoal; Rathke (A. 152, 211) showed that the selenide was K.Se., and Jackson (B. 7, 1277) using Na, SeO, and charcoal obtained the corresponding selenide of sodium.

Sodium, seleno-antimonate of, v. vol. i. p. 286.

Sodium, selenocyanide of, v. vol. ii. p. 348. Sodium, silicofluoride of, Na SiF . Prepared by adding H2SiF6Aq to conc. NaClAq, washing, and drying. Gelatinous when ppd., but becomes crystalline on drying. S.G. 2.7517 at 17.5° (Stolba, Fr. 11, 199). S. 65 at 17.5°; 2.46 at 100° (S., l.c.). Insol. alcohol. Melts at red heat, giving off SiF, (Berzelius).

Sodium, sulphides of. Several compounds of Na and S exist, but there is considerable doubt as to the compositions of some of the substances that are described as definite sul-

phides of Na.

Sodium monosulphide Na,S. Obtained by passing H2S over dry NaOH, the heat produced suffices to remove H₂O formed (Kircher, A. 31, 839). Rosenfeld (B. 24, 1658) says that Na₂S is formed when 1 part thoroughly clean Na is rubbed to powder and mixed with 3 parts NaCl and 7 part S; the combination is sudden, and light is produced; pressure must be avoided in mixing the substances. By heating 100 to 105 parts Na SO, with 20 parts charcoal, a fleshcoloured mass of Na,S with some C is obtained: the reduction may also be effected in H. By dissolving the product of reduction in water and crystallising, the hydrate Na₂S.9H₂O is obtained; by dissolving the crystals again, heating with Cu (to decompose polysulphides), and evaporating to dryness in a stream of H, Na₂S remains (Priwoznik, A. 164, 69).

Na,S is also obtained, fairly pure, by gently heating Na₂S.9H₂O in a stream of H (Weyl, P. 123, 362; cf. Sabatier, A. Ch. [5] 22, 5).

Na S is an amorphous, flesh-coloured, deliquescent solid, with a strongly alkaline reaction; easily sol. water, solution being colourless if polysulphides are quite absent. According to Weldon (v. Lunge's Soda-industrie, 2, 311), Na₂S is not fusible if it be quite free from polysulphides, thiosulphate, and NaOH.

Na SAq becomes yellow in moist air from formation of polysulphides (Kolb, A. Ch. [4] 10, 106); when air is blown into Na SAq, NaOH

and Na,S,O, are formed, and then Na,SO, (Lunge, l.c., p. 531). Na,S is decomposed by acids, even by CO₂, with evolution of H₂S (v. Stromeyer, A. 107, 372). Heating Na₂SAq with NaHCO₃ or NH₄.H.CO₃ produces complete decomposition to Na₂CO₃ (Lunge, *l.c.* p. 800). Boiling with AlO₃H₃, or heating Na₂S with Al₂O₃, forms Na aluminate (v. W. J. 1863. 713; 1865. 332). CaO is said not to decompose Na₂SAq (v. Kolb, A. Ch. [4] 10, 106). Several metallic oxides decompose Na SAq, forming NaOHAq, sometimes (e.g. with CuO) Na S.O. Aq is also formed. Na.S combines with various metallic sulphides (v. Schneider, P. 138, 302; 151, 446; Völcker, A. 59, 35; Berthier, A. Ch. [2] 22, 245).

Hydrates of sodium monosulphide.

The hydrates Na.S.9H.O, Na.S.10H.O, and

Na S.5H,O have been formed. The hydrate with 9H₂O is most easily obtained by saturating one half of a solution of NaOH with H.S. adding the other half, and evaporating, when large colourless crystals separate (Rammelsberg, P. 128, 172); S.G. 2471 (Filhol, A. Ch. [4] 28, The pentahydrate is formed similarly to the hydrate with 9H₂O, but using alcoholic in place of aqueous NaOH (Böttger, A. 223, 335; v. also Finger, P. 128, 635; Lemoine, C. R. 98, 45). For the preparation of Na.S.10H₂O v. Damoiscau (C. C. 1885. 36). Göttig (J. pr. [2] 34, 229) by partially saturating NaOH in alcohol

with H₂S got hydrates with 5, 5¹₂, and 6 H₂O.
Sodium disulphide Na₂S₂. This compound is supposed by Sabatier (A.Ch. [5] 22, 5) to exist in the solution obtained by heating Na SAq with solution of polysulphides formed by digesting Na₂SAq with S. Böttger (A. 223, 335) obtained the hydrate Na₂S₂.5H₂O by dissolving S in an alcoholic solution of Na,S.

Sodium Trisulphide Na2S3 is formed, according to Schöne (J. 1867. 190), mixed with Na₂SO₄, by strongly heating Na₂CO₃ with excess of S (cf. Sabatier, l.c.). For the hydrate Na₂S₈.3H₂O v. Böttger (l.c.).

Sodium Tetrasulphide Na,S, is said to be obtained by heating Na,S, (Chapman Jones, C. J. 37, 461; ef. Sabatier, l.c.). For hydrates v. Schöne (P. 131, 380) and Böttger (l.c.).

The existence of a pentasulphide is doubtful (v. Schöne, l.c.; Sabatier, l.c.; Geuther, A. 226,

232; Chapman Jones, l.c.).

Soda liver of sulphur. This name is given to the brown solid obtained by heating S with Na₂CO₃ in a closed vessel; it contains various • sulphides of Na, along with Na, S,O,, Na, SO, and generally some Na₂CO₃.

Sodium, sulphocyanide of, v. vol. ii. p. 352. Sodium, sulphydrate of, v. Sodium Hydrosulphide, p. 479.

Sodium, telluride of. According to Rosenfeld (B. 24, 1658), well-cleaned Na in powder readily combines with Te.

Sodium, thio-arsenates and thio-arsenites of, v. vol. i. pp. 316, 317. Sodium, thio-carbonate of, v. vol. i. p. 703.

M. M. P. M.

SODIUM ETHIDE NaC2H3. This compound is not known in the free state. Sodium dissolves in cold ZnEt2, separating zinc. The solution, cooled to 0°, deposits ZnEt2NaEt in trimetric tables [27°], sol. benzene, and decomposed by water. CO₃ acting on ZnEt,NaEt forms sodium propionate (Wanklyn, A. 107, 125; 108, 67). Etl attacks ZnEt, NaEt, forming ethane and C₂H₄ (Frankland, A. 110, 107). Sodium methide may be obtained in like manner

(Wanklyn, A. 111, 234).

80JA OIL. The oil from Soja hispida contains tripalmitin and tristcarin (Meisel a. Böcker, M. 4. 365).

80LANINE C₅₂H₅₃NO₁₈ (?) (Firbas, M. 10, 541); C₁₂H₃₁NO₁₈; C₁₂H₃₁NO₁₅ (Hilger, A. 195, 317); C₂₁H₃₂NO, (Kletzinsky, Z. [2] 2, 127). [244²]. Occurs in the berries of the deadly nightshade (Solanum nigrum) (Desfosses, J. Ph. 6, 374), in berries of S. verbascifolium (Payen a. Chevallier, J. Chim. Med. 1, 517), in small quantity in the tubers and green parts of the potato (S. tuberosum), in the shoots of sprouting potatoes (Baup, A. Ch. [2] 31, 109; Otto, A. 7, 150; 26, 232), to the extent of 03 p.c. in diseased potatoes (Kassner, Ar. Ph. [3] 25, 402). in the flowers, stalks, and berries of the woody nightshade (S. Dulcamara), and in the root of

Scopolia japonica (Martin, Ar. Ph. [3] 13, 336).

Preparation.—1. The berries are pressed, the juice ppd. by ammonia, and the pp. recrystallised from alcohol.—2. Fresh potato sprouts (200 kilos.) are digested with 2 p.c. acetic acid; the filtrate is ppd. by ammonia; and the pp. extracted with boiling 85 p.c. alcohol. To the hot alcoholic filtrate NH₁Aq is added until turbidity appears. On cooling, a mixture (125 g.) of solanine and solanein is de-posited. These bases are separated by fractional crystallisation from hotspirit (Firbas; cf. Reuling, A. 80, 225; Zwenger a. Kind, A. 109, 244; 118, 129; Kromayer, Ar. Ph. [2] 116, 114; Missaghi,

B. 9, 83; Gmelin, A. 110, 167). Properties.- Colourless needles, v. sol. hot 85 p.c. alcohol, insol. CHCl, and ligroin, sol. HClAq, almost insol, water and ether. The crystals are $C_{52}H_{es}NO_{16}4_{2}^{1}$ nq (Firbas). Poisonous. Not affected by alcoholic potash. Sublimes at 190° (Blyth). Gives an orange colour with I and H.SO.. On heating with 2 p.c. with I and H.SO. On heating with 2 p.c. HClAq it yields solanidine and a dextrorotatory sugar that reduces Febling's solution, [a]_D = 28.6°, yields with phenyl hydrazine an osazone [199°], and is oxidised by HNO, to mucic and saccharic acids; levulose is not present. Solanine colours a mixture of alcohol and H,SO, rose red. With ammonium selenite (1 g.) in conc. H₂SO₄ (20 c.c.) it gives a canaryyellow colour turning to brown, and, after three nours, to violet-red (Ferreira da Silva, Bl. [3] 6, 87; C. R. 112, 1267). A solution of ammonium vanadate in H2SO, is coloured brown by dry solanine, the colour becoming red, and finally disappearing on dilution (Mandelin).

Salts.—C, H, NO, HCl. Got by adding ether to an alcoholic solution of the base and HCl. Gelatinous pp. which dries up to a gummy mass.—B'₂H₂PtCl₄: yellow flocculent By H.Q.Q.7aq; crystalline crusts.

Acetyl derivative C., H., A.Q.NO,. Needles

(from ether), insol. water (Hilger).

Solane'in C₁₅H_{ss}NO₁₅ 4aq. [208°]. Obtained as above (Firbas). Amorphous. More sol. 85 p.c. alcohol than solanine. Decomposed by HClAq into the same products as solanine. Colours Mandelin's reagent red,

Solanidine C. H. NO. [191°]. Formed as above. Colourless needles (from ether). Affects Mandelin's reagent in the same way as solanin Ac.O at 140° gives a diacetyl derivative (Firbas). Converted by fuming HClAq in the cold into amorphous yellow solanioine C₂₂H₂₂NO (?), which yields B'HCl and B'₂H₂PtCl_e (Zwenger, A. 123, 341).

Salts.—B's(HCl), aq: crystalline powder.—

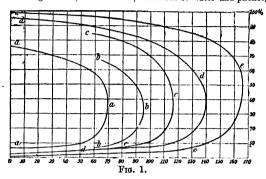
B',4H,SO,8aq: colourless plates [247°].
SOLUTIONS. Inasmuch as many of the questions connected with the state of bodies in solution are not yet fully elucidated, and inasmuch as two very different conceptions are put forward regarding the compositions of bodies present in aqueous solutions of salts, the editor of that portion of the Dictionary to which the subject of solutions belongs thought it advisable to ask the originator of the electrolytic dissociation hypothesis of saline solutions to write a short article on solutions in general, and to invite one of the leading upholders of the hydrate hypothesis of saline solutions to summarise the arguments in support of that hypothesis.

SOLUTIONS I. A solution is a homogeneous mixture of two or more bodies in the liquid state. A distinction is made between the dissolved substance and the solvent; the substance present in greater quantity is generally spoken of as the solvent. In some cases the solvent is taken to be the substance with the lower temperature of solidification. In the cases of substances miscible in all proportions—a mixture, for instance, of equal parts of alcohol and water -there is no way of determining which should be regarded as the solvent and which as the dissolved substance. There are many instances of two bodies that cannot be mixed in all and any proportions; the solubility of such bodies is said to be limited. If the 'dissolved body' in such a case is present in excess, either as gas, liquid, or solid, a condition of equilibrium is finally attained wherein the solution can take up no more of the dissolved body as long as the external conditions (temperature and pressure) remain unchanged; such a solution is said to be saturated. The attainment of saturation is hastened by shaking.

Saturated solutions of gases. When a gas is placed over a liquid, such as water or alcohol, a portion of the gas dissolves in the liquid. There is a constant relation at constant temperature between the quantity of gas remaining per unit volume and the quantity dissolved by the liquid per unit volume (Henry's law). Inasmuch as the quantity of the gas, per unit volume, is proportional to the partial pressure of the gas, the law may be stated by saying that the quantity of the gas dissolved in the liquid is proportional to the partial pressure of the gas above the liquid. As all the gases that have been examined dissolve with production of considerable quantities of heat, the solubilities of these gases decrease as temperature increases, in accordance with the second law of thermodynamics. The measurements made by Bunsen (Gasom. Methoden [Braunschweig, 1877]) show that the solubilities of some gases are independent of temperaturefor instance, the solubility of H in water and of O and CO in alcohol. Henry's law holds good, as indicated by theory, only so long as the quantity of the gas per unit volume, both undissolved

and in solution, is small, and the molecules of the dissolved and the undissolved gas are of equal magnitude. Van't Hoff has made use of the law of Henry to prove the equality of the molecules of the same gas in the gaseous state and in dilute solution (Z. P. C. 1, 489 [1877]). When NH, HCl, and SO, are dissolved in water in large quantities these gases do not follow the

temperature, which corresponds to the critical temperature for the liquids, is passed, the two liquids dissolve in all proportions. This behaviour has been more fully examined by Alexe-jeff (W. 28, 305 [1886]) and has been represented by him in curves, some of which are reproduced here (fig. 1). The curve a represents the behaviour of water and phenol, b that of water

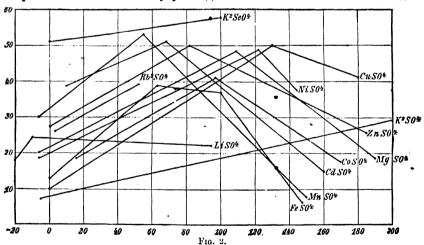


law of Henry; neither does the law hold good for solutions of acetic acid in benzene or ether in water, because the molecular magnitudes of these compounds are not the same in the gaseous state and in solution, as is proved by determinations of the boiling-points of the compounds in question (Nernst, Z. P. C. 7, 97 [1891]).

Mutual solutions of liquids. When two

liquids that are not miscible in all proportions,

and salicylic acid, c that of water and benzoic acid, d that of water and aniline phenolate, and e that of water and aniline. The abscissm represent temperature, and the ordinates percentages of the dissolved substances in the solutions. To each temperature correspond two points in the curve showing the percentage composition of the solution of the substance in water, and that of the solution of water in the molten sub-



such as other and water, are shaken together, two layers are formed, one floating on the other; one of these contains much water and little ether, while the other contains much ether and little The compositions of the two layers water. change with change of temperature. Generally speaking, the compositions become more alike as temperature rises, until a temperature is reached whereat they are identical; when this

stance; thus, for phenol and water (curve a), at 20°, the solutions are composed of 92°5 p.c. water and 7°5 p.c. phenol, and 28 p.c. water and 72 p.c. phenol respectively. The two liquids are miscible in all proportions above 69°

It happens sometimes that two liquids are miscible in all proportions below a certain temperature, but form two layers above this temperature; in such cases—for example, in the solution of di-ethylamine in water-the convexity | add a tl of the curve is turned to the left.

Saturated solutions of solids. Most of the measurements that have been made deal with solutions of salts in water. The example of Gay-Lussac has generally been followed, and the solubility of the salt has been taken as the weight thereof dissolved by 100 parts by weight of the solvent. Etard and Engel have given solubility-curves for very large variations of temperature (C. R. 98, 993, 1276, 1432; 104, 1614; 106, 206, 740 [1884-88]). Some of these results are shown in fig. 2, p. 485; the abscissæ represent temperature and the ordinates parts by weight of the salts in 100 parts of the solution (not in 100 parts of the solvent). The change of solubility with change of temperature depends on whether the process of solution is accompanied by disappearance or production of heat; in the former case solubility increases, in the latter case it decreases, as temperature rises. Inasmuch as different hydrates of the same salt are dissolved with the production of different quantities of heat, these hydrates give different solubility-curves. Sodium sulphate is the salt that has been most carefully examined in this respect. The hydrate Na₂SO₄.10H₂O, that exists up to 33°, dissolves in water with disappearance of heat; hence the solubility of this hydrate increases as temperature increases. On the other hand, Na₂SO₄, stable above 33°, dissolves with production of heat, and its solubility decreases with increasing temperature. The so-called curve of the solubility of sodium sulphate consists, therefore, of two parts, one rising till the temperature reaches 33°, and one falling above that temperature. Looked at accurately, the first part of the solubility-curve holds good only for Na₂SO₄.10H₂O₅ and the second part only for Na SO. For the solubility of a chemical compound is determined only when the composition of the solid compound that is in contact with the solution is definitely stated. The compound CaSO, is considerably more soluble than the crystalline hydrate CaSO, 2H,O. The measurements made by Etard show that many other sulphates -MnSO. and CdSO, for instance-behave similarly to Na₂SO, (see fig. 2).

The solubilities of most salts increase as temperature rises; the solubility of NaCl varies very little with temperature. The solubilities of many compounds of calcium decrease with increasing temperature, e.q. hydroxide, acetate, isovalerate, isobutyrate, succinate, and iso-succinate of calcium. Barium succinate and SrSO, behave similarly, but not the other corresponding salts of Ba and Sr. Some calcium salts show maximum solubilities at certain temperatures-e.g. CaSO, 2H,O at 35°; others show minimum solubilities -e.g. propionate at c. 55°, isobutyrate at 65°, also normal butyrate, valerate, iso-octoate, citrate, and benzoate (Allen, C. N. 57, 236 [1888]). Attempts have been made to express the connection between the solubilities of salts and temperature by a formula. The following expression holds good in many cases: S = a + bt (t =temperature, and a and b are constants); i.e. solubility changes linearly with temperature-for instance, for KCl, BaCl, NaNO, and several sulphates, especially at high temperation absence of these (Barus a. Schneider, Z. P. C. tures (Étard). In other cases it is necessary to 8, 291 [1891].) Colloidal substances having

a serm, and so scops the formula $S=a+bt+ct^2+dt^2$ (c and d are constants as well as a and b). The formula log. $S = a + bt + \dots + \dots$ often gives a better representation with a smaller number of coefficients.

Supersaturated solutions. When a salt whose solubility increases with temperature is dissolved at a high temperature in water (or other solvent), and the solution is cooled, a temperature is reached whereat the solution is saturated with reference to a definite hydrate of the solid salt: but if the solution is further cooled salt does not separate, provided there is no crystal of the hydrate in question in contact with the solution. Such a solution is said to be supersaturated. A solution may be supersaturated with reference to one hydrate, but not supersaturated with reference to another hydrate. For example, Na₂SO₄.7H₂O is more soluble in water than Na, SO, 10H,O, and so a solution may be obtained, by dissolving Na.SO,, that is supersaturated as regards the decahydrate but not as regards the heptahydrate; that is to say, if a crystal of Na₂SO₄.10H₂O is brought into the solution, at a certain temperature, the decahydrate crystallises out, but at the same time the solution is able to dissolve the hydrate with 7H,O. If temperature falls again the solution, of course, becomes supersaturated with reference to both the hydrates.

At one time the supposition was often held that the dissolved substances were present in supersaturated solutions in a state different from that in which they existed in ordinary solutions. More accurate investigations of the physical properties on both sides of the point of saturation have shown that there is no essential difference between the solution before and after saturation, but that the relation of a supersaturated to a saturated solution is exactly the same as that of a saturated solution to the solution before saturation.

Colloidal solutions. Certain substances, such as gelatin, absorb unlimited quantities of water and become swollen thereby; when much water has been taken up, liquids are formed which do not part with the dissolved body on cooling, as ordinary solutions do, but set to jellylike substances. All compounds that form colloidal solutions have very large molecular weights; such compounds are acids of Mo, Si, Sn, Ti, and W; oxides of Sb, Fe, and Mn; sulphides of Sb, As, Bi, Cd, Co, Au, Fe, Pb, Hg, Ni, Pd, Pt, Ag, Tl, and W; many organic substances, such as caramel, dextrin, eggalbumen, tannin, &c.; and also some elements, such as Se and Ag. Some of these solutions are characterised by the fact that the addition of small quantities of foreign substances-as salts, acids, and bases-causes coagulation, whereupon the bodies in the colloidal solutions become insoluble. For that reason it is generally supposed that colloidal solutions are intermediate between emulsions and true solutions. Emulsions -e.q. a fine deposit of alumina-possess the special property that the emulsionised bodies are thrown down much more quickly in presence of electrolytes, and also of other foreign substances, than

molecular weights under 30,000—gelatin or gum, for instance—are characterised by the fact that if their solutions are solidified by cooling they again become liquid and transparent when heated. Colloids having molecular weights greater than 30,000 do not share in this property, but behave, in this respect, like very supersaturated solutions (Sabanejeff, J. R. 1891. [1] 80; Z. P. C. 9, 89 [1892]). When colloids take up water, and swell but do not dissolve, heat is produced; when they dissolve heat disappears (Wiedemann a. Lüdeking, W. 25, 145 [1885]).

Reasons for assuming the existence of hydrates in solutions. When a dissolved substance is isolated, by various methods, from its solvent the solid generally separates in combination with water of crystallisation. It has, therefore, been generally supposed that a pre-ponderating quantity of this hydrate must be present in the solution. This conclusion is not, however, tenable; for if only a minimum quantity of the compound that separates out were present in the solution this might suffice to cause the separation. The following consideration has been brought forward as an argument in favour of the existence of hydrates in solutions. A solution of 57 parts by weight HI and 43 parts water boils at 127°, and the distillate has the same composition as the residue; this lends some countenance to the view that this mixture behaves like a definite chemical compound. On adding water to this solution and distilling a more dilute acid at first passes over, and at last the acid with 57 p.c. HI distils off. If the solution contains more than 57 p.c. HI to begin with, the distillate at first contains a more conc. acid, and, later, acid of 57 p.c. This behaviour is simply explained in the following way. A solution of 57 p.c. HI possesses a minimum vapourpressure, so that both less dilute and more dilute solutions at the same temperature have larger VADOUR-PRESSURES. Speaking generally, the vapour from a solution does not contain both components in the same proportion as the solution itself. In the case under consideration the vapours from the more dilute solutions contain more water (in proportion to HI) than the solutions, and the vapours from the less dilute solutions contain, relatively, more HI. The dilute solutions increase in concentration as distillation proceeds, the boiling-point rises, and there is at last produced the 57 p.c. solution which possesses the lowest vapour-pressure at an equal temperature—i.e. the highest b.p. (127°) at an equal pressure. If, on the other hand, distillation is commenced with a more concentrated solution proportionally more HI passes over, and an approach is gradually made, from the other side, to the solution with highest b.p. There is, therefore, no binding reason for regarding this solution as a definite chemical compound. For, indeed, the composition of the solution changes according to the pressure under which the distillation is conducted; and this could not well be the case were the solution really a definite chemical compound.

In investigating the freezing-points and vapour-pressures of solutions it was found that in many cases the deviation from the freezing-point and vapour-prossure of the pure solvent

was proportional to the quantity of substance (salt) in solution. But in other cases this proportionality seemed not to be maintained unless the supposition were made that a portion of the water had combined with the dissolved substance (Wüllner, P. 103, 529; 105, 85; 110, 564 [1858, 1860]; de Coppet, A. Ch. [4] 23, 366; 25, 502; 26, 98 [1871-2]; Rüdorff, P. 114, 63; 116, 59 [1861-2]; 145, 599 [1870]). It was, therefore, supposed that such compounds as HI, HCl, BaCl, CaCl, NaBr, &c., were combined in aqueous solutions with definite quantities of water of crystallisation. But the recently-discovered laws which express these phenomena lead to very different methods of explanation, so that the conclusion that these compounds exist as hydrates in solutions seems, in this respect, to be entirely without foundation.

Mendeléeff not long ago examined the changes in the S.G., accompanying changes in the composition, of aqueous solutions of alcohol and of sulphuric acid (Z. P. C. 1, 273 [1887]); he thought he had found abrupt irregularities in the changes of S.G. He supposed, without any theoretical foundation, that at the concentrations whereat these occurred the solutions corresponded to perfectly definite hydrates. Pickering (Z. P. C. 6, 10 [1890]) showed, as the result of more accurate investigations, that Mendeléeff's conclusions rested on inaccurate observations. Pickering, however, accepted Mendeléeff's idea, and supposed that the higher derivatives of the S.G. in reference to percentage composition showed similar irregularities. He treated the freezing-points and the electrical conductivities of solutions in the same way, and he supposed that in all these cases he had discovered such irregularities as indicated the existence of definite hydrates. It is absolutely impossible to reconcile the numbers for the electrical conductivities of dilute solutions of acids and bases (e.g. for acetic acid) with Pickering's views; nor do the most recent investigations on the freezing-points of very dilute saline solutions (Jones, Z. P. C. 11, 534; 12, 623 [1893]) in any way agree with these views. Moreover, the method used by Pickering is not free from objection under any conditions.

From an extended and systematic investigation recently made into the constitution of ammoniacal metallic compounds, and compounds analogous therewith, Werner (Zeit. f. anorg. Chem. 3, 267 [1893]) concluded that in electrolytically conducting salt solutions the metallic atoms of the salts might be expected to be generally accompanied by six molecules of water, and that those salts which readily combine with water of crystallisation would be the best conductors. This statement is not, however, in any way in keeping with the experimental results. The salts of ammonium, K, Rb, and Cs conduct better than any others that have been examined; after these come the salts of Na. Li, and the metals of the earths; and then, much behind these, come the salts of the heavy metals; but water of crystallisation combines most readily with the salts last mentioned. and least readily with those mentioned first.

Conclusions regarding the existence of hydrates of substances in solution have also been drawn from the results of investigations of other u properties, such as contraction or , or production of heat, during solution,

osity, &c. general, it has been supposed that where

properties exhibited a maximum or minior other purely mathematical characterhere existed a definite hydrate of corresponding composition. Attention may, however, be called to the fact that these points generally shift with changes of temperature, so that the hypothetical hydrate must have a different, and constantly changing, composition at different temperatures—a conclusion which is not in keeping with the representation of the hydrate as a

definite chemical compound.

It is, indeed, in the highest degree likely that when definite hydrates separate from a solution the same hydrates were previously present in the solution, perhaps only in small quantity; but we have as yet no accurate knowledge as to the magnitude of the quantity. The methods that have been used in investigating this most interesting question have scarcely brought to light a single new result, although many and renowned investigators have carried out a very large amount of work in this direction.

The solubility of a salt, at constant temperature, is to a small extent dependent on pressure. Sorby was the first to carry out detailed investigations on this subject (Pr. 12, 538 [1863]). The following statement may be demonstrated by the use of the dynamical theory of heat. When the total volume of salt and solution is diminished (or increased) by the taking up of salt into the solution, then the solubility increases (or diminishes) with increased pressure. The researches of Braun (W. 30, 272 [1887]) have confirmed the

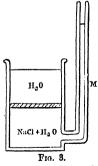
theoretical conclusions.

Dilute solutions. Osmotic pressure.-If a quantity of the pure solvent is floated on a solution, a movement of the dissolved substance takes place and the substance strives to distribute itself throughout the whole of the solvent. This occurrence is completely analogous with another; if a cylinder is filled with CO, and the mouth is covered with a membrane, another cylinder is filled with H and placed mouthdownwards on the first, and the membrane is withdrawn, the two gases begin to diffuse into each other (notwithstanding the action of gravi-'tation). The H is driven downwards by its partial pressure, and the CO, is driven upwards. The velocity of diffusion is proportional to this propelling force, otherwise it is dependent only on the freedom of motion of the molecules among each other. The inverse value of this freedom of motion is called molecular friction. The following statement expresses the results of experiment: the velocity of diffusion is proportional to the difference between the partial pressure of one of the two gases in the upper and lower parts, and is inversely proportional to the friction of the molecules. Solutions behave in a similar way. The substance in solution in the under layer strives to distribute itself into the upper layer; this striving corresponds to the pressure of a gas, and, as will be shown immediately, it is equal to the so-called osmotic pressure. solvent is driven downwards by the same force. In this case also the velocity of diffusion is proportional to the osmotic pressure, and is inversely proportional to the friction of the molecules of the dissolved substance against the solvent. The only difference between this case and that of gases is that molecular friction is very much larger in liquids, a fact that is explained by the great number of molecules against which a molecule of the dissolved substance collides during its movements.

The amount of molecular friction is known in certain cases, viz. for electrolytes. Let a cubical trough (sides 1 cm.) be filled with the solution of an electrolyte (e.g. NaCl), and let an electric current be passed through the trough by the help of two electrodes A and B. The positive electricity is carried by the metallic parts (Na) of the electrolyte in the direction of the current (towards B); the negative electricity travels with the negative radicle (Cl) of the electrolyte towards A. the Na and Cl atoms-or ions, as they are called in this case-are impelled by unit electrical force, the Na ions will move with a velocity vi and the Cl ions with the velocity v2 velocities can be determined, partly indirectly from the conductivity and the migration num-bers of Hittorff, partly directly by chemical analysis. Putting the corresponding frictions as r_1 and r_2 , then $v_1 = \frac{1}{r_1}$ and $v_2 = \frac{1}{r_2}$. The frictions of a large number of ions have been determined in this way. If we now have a layer of pure water floated on a solution of NaCl, in a vessel, then the velocity of diffusion, D, is equal to the quotient of osmotic pressure, O, and the frictions $r_1 + r_2$ of the salt. We have, therefore, $D = \frac{O}{r_1 + r_2}$. Nernst (Z. P. C. 2, 613 [1888]) has completely established the accuracy of this

formula.

Osmotic pressure can be measured directly. Let us suppose that in the foregoing example we had a division separating the solution of NaCl from the water, and that the division allowed water, but not NaClAq, to pass through it (a so-called semipermeable membrane); v. fig. 3. Such a membrane is obtained by impreg-



nating a plate of porous burnt clay with ppd Cu.Fe(CN). The water will then be driver downwards, and will be compressed in the lower part of the apparatus; the pressure in this division will increase; this may be confirmed by using a manometer (M, fig. 3). Equilibrium is attained after a time, and the manometer then indicates a certain pressure, which is called the

senctic pressure of the solution. When no more water is driven downwards, then, in the case in point, the partial pressures of the water in the apper and lower parts of the apparatus are equal. The excess of pressure in the lower part that is, the osmotic pressure -is then equal to the partial pressure of the NaCl molecules. Measurements of this kind have been made by Pfeffer, Tammann, and Adie (Osmotische Untersuchungen, Leipzig, 1877; W. 34, 229 [1888]; C. J. 59, 344 [1891]).

Semipermeable membranes are found in the lining of living cells which incloses the con-tents of the cell. De Vries made observations with cells of Tradescantia discolor and Begonia manicata; Donders and Hamburger used bloodcells. If a cell is immersed in water the cell swells, because of the entrance of water; if a soluble substance is added to the water, in constantly increasing quantity, the water will at last be driven equally inwards and outwards; if this limit is overpassed, the water passes out of the cell and the protoplasmic contents of the cell shrink together. The whole process may be followed by the help of the microscope. The limit reached immediately before shrinkage begins is characterised by the attainment of equality between the osmotic pressure of the cell-contents and that of the surrounding solution. By bringing similar cells into solutions of different substances it is possible, in this way, to determine the concentration that must be attained by two solutions in order that they may possess equal osmotic pressures. Using the results of Pfeffer and de Vries, van't Hoff made an examination of the magnitude of osmotic pressures. He found that the osmotic pressures exerted in their solutions by non-conductors of electricity—such as cane sugar, urea, glycerin, &c .- were exactly the same as the pressures which these substances would exert, in accordance with Avogadro's law, were they present as gases in the same volume as the volume occupied by the solutions. The osmotic pressure is therefore proportional to the concentration and the absolute temperature (law of Boyle and Gay-Lussac); this was confirmed by Pfeffer's investigations (van't Hoff, Handingar der Stockh. Ak. 21 [1886]; Ar. N. **20** [1885]; Z. P. C. 1, 481 [1887]).

An explanation of gaseous pressure is found in representing it as the result of the bombardment of the walls of the vessel by the gaseous molecules. Similarly, osmotic pressure is thought of as resulting from the knocking of the molecules of the dissolved substance against the walls of the containing vessel. The gaseous laws hold good in all respects for osmotic The gaseous

Vapour-pressures of solutions. Let there be a solution, say of cane sugar, in a trough, separated by a vertical semipermeable membrane from pure water, and let the membrane extend above the solution; the air above the liquid behaves exactly like the semipermeable membrane, inasmuch as it allows the water to pass through (as water-vapour), but it does not allow the cane sugar to pass through (because of the non-volatility of the sugar). The water has, therefore, a tendency to pass across through the air as well as through the semipermeable membrane from the water in the solution. This circumstance may be expressed by saying that the pressure of the water-vapour is greater over the water than over the solution. In like manner it follows that solutions which have equal osmotic pressures have also equal vapour-pressures. By making use of the second law of thermodynamics it can be shown (van't Hoff, l.c.) that a solution containing n molecules of dissolved substance to N molecules of solvent has a vapourpressure, P, which is given by the formula

$$P = \left(1 - \frac{n}{N}\right)p,$$

where p = the vapour-pressure of the pure sol-(The molecular weight of the solvent must be taken as that of the substance in the gaseous state at the same temperature.) This formula was originally experimentally established by Raoult; it agrees well with experience (C. R. 103, 1125 [1886]).

Boiling-points of solutions. According as the vapour-pressure of a solution is less than that of the solvent (assuming that the dissolved substance possesses no marked vapour-pressure), so the solution begins to boil, under a definite external pressure, at a higher te aperature than the pure solvent. The following formula may be deduced from the dynamical theory of heat: $E = \frac{0\cdot 2}{L} \cdot n,$

$$\mathbf{E} = \frac{0.2 \, \tau^2}{\Gamma_1} \cdot n,$$

where E is the increase in the boiling-point of the solvent brought about by dissolving n molecules of the substance in 100 grms. thereof, risthe absolute boiling temperature, and L is the latent heat of vapourisation of 1 grm. of the solvent. Beckmann has contrived an apparatus for determining E, and therefore for finding n-that is, for determining the molecular weight of the dissolved substance when the quantity thereof in 100 grms. of solvent is known. He has shown that the formula gives results which agree closely with experience (Z. P. C. 5, 76 [1890]).

Freezing points of solutions. When a solution is caused to freeze, in most cases only the pure solvent separates as a solid. The solid substance is in equilibrium with the solution at the freezing-point; hence, the vapour-pressures of the solvent over the solid and over the solution must be equal, as otherwise distillation would take place from the one to the other, and equilibrium would not be attained. For the sake of simplicity let us take water as the solvent. Ice and water have, therefore, the same vapour pressure at the freezing-point of the latter (0°); but an aqueous solution has a smaller vapour pressure at 0°; hence at 0° ice cannot have the same vapour pressure as an aqueous solution, but this equality occurs only at a lower temperature. In other words, the freezing-point of a solution is lower than that of the solvent. Van't Hoff (l.c.) has deduced the following expression from the dynamical theory of heat, $E = \frac{02 \tau^2}{W}$. n, where E is the difference

between the freezing-points of the pure solvent and a solution therein, which solution contains n gram-molecules of the dissolved substance in 100 grms. of the solvent, 7 is the absolute temperature, and W is the latent heat of fusion of 1 grm. of the solvent. This formula is of much importance, for the molecular weights of very many substances have been determined by its help. It is immaterial in this case whether the dissolved substance exerts a considerable vapour-pressure or not, for only the pure solvent freezes out. The following table gives some values calculated by the formula placed side by side with the values obtained by experiment, for the case where n = 1:

	E observed	E calculate
Water	18.9	18.9
Acetic acid .	38.6	38.8
Formic acid	27.7	28.4
Benzene .	50.0	53.0
Nitrobenzene	70.7	69.5

Electrolytic dissociation. When determinations of molecular weights are made, by the foregoing methods, based on osmotic pressures (de Vries), freezing-points (van't Hoff, Raoult), depressions of vapour-pressures (Raoult), or increments of boiling-points (Beckmann), the values obtained for all those substances whose solutions conduct electricity are much smaller than would be expected. For instance, the results obtained by working with a half-normal solution of NaCl lead to the value 31-6 for the molecular weight of the salt, a number which is 1.85 times smaller than the calculated value, 58.5 (NaCl). From this and many other considerations Arrhenius drew the conclusion that the molecules of electrolytes are largely dissociated in aqueous solutions; about 85 p.c. of the NaCl, for instance, in an aqueous solution of this salt is regarded as dissociated into Na and Cl. This conclusion is completely analogous with those which are drawn regarding the dissociation of the molecules of ammonium salts and other substances, in the gaseous state, from observations of the abnormal vapour densities of these substances. The development of the theory of electrolytic dissociation, based on these considerations, and confirmed in the fullest way by experience, has lent much support to the theory of solutions which has already been sketched. This part of the subject is treated by Ostwald in the article ELECTRICAL METHODS, to which reference should be made (this vol., pp. 187-221).

Some of the deductions regarding diffusion, solubility, and affinity must, however, be mentioned here.

Diffusion of mixtures. When a solution of HCl is placed in contact with pure water, the HCl gradually diffuses into the water. Inasmuch as most (almost all) of the HCl molecules are dissociated, one would expect the diffusion to result in a separation of the H and Cl from each other, just as the alums and the double salts of the sulphates of the alkalis and the magnesium metals, which are partially decomposed in aqueous solution, can be separated into their constituent salts in this way (Graham, T. 1850. 1, 805; Marignac, A. Ch. [5] 2, 546 [1874]). But this separation does not occur. The H moves into the water more quickly than the Cl, and, because of the positive electrical charge of the H ions, the water becomes positively and the solution negatively charged. If this charging is not carried off by metallically connected un-polarisable electrodes placed in the solution and in the water (v. this vol. p. 212), it prevents the separate diffusion of the H and the Cl. But there is another way whereby the restrain- | p. 81).

ing force of the electrical charge on the diffusion of the H may be diminished—namely, by addition of chlorides. For instance, the velocity of diffusion of HCl (properly speaking, of H) is increased in the ratio of 1:224 by adding 25 times the quantity of NH, Cl (Arrhenius, Z. P. C. 10, 51 [1892]). Similar, although not so strongly marked, characteristic phenomena, which find an explanation in the dissociation theory, have been observed by Graham and Marignae.

Decrease of solubility by addition of foreign salts. Nernst (Z. P. C. 4, 372 [1889]) was the first to draw attention to the conclusion from the theory that a slightly soluble salt, e.g. silver acetate, must be more soluble in pure water than in a solution that contains other silver ions (e.g. AgNO₂) or acetate ions (e.g. NaC,H₂O₂). Similar relations are shown by gases which partially decompose (e.g. NH,SH); these exhibit smaller vapour-pressures when one of the two components (NH, or H,S) is added. This lowering of solubility can be calculated from the laws of mass-action, with results which agree well with experience (Noyes, Z. P. C. 9, 603 [1892]).

Division of a dissolved substance between two solvents. Berthelot and Jungfleisch examined the distribution of succinic acid between ether and water, and found that the concentrations of the acid in the aqueous and in the ethereal solution were in a constant proportion, which appeared to be independent of the absolute concentration. Many other substances were found to behave in the same way (A. Ch. [4] 26, 396, 408 [1872]). This result corresponds completely with Henry's law for gases. It is readily deduced from the theory; but in doing this it is assumed that the dissolved substance has the same molecular weight in both solutions. If this is not the case—as, for example, in the distribution of benzoic acid between benzene and water-altogether different laws express the phenomena (these laws, also, are in keeping with experimental results; Nernst, Z. P. C. 8, 110 [1891]).

Reaction velocities. There are many so-

Reaction velocities. There are many socalled catalytic processes that are brought about by the H ions of acids—for instance, the inversion of cane-sugar, saponification of esters, &c. According to the theory, the velocity with which these reactions take place must depend only on the number of H ions that are present, and not on the nature of the reacting acid. This conclusion is confirmed by experience (Arrhenius, Z. P. C. 4, 226 [1889]; cf. Affinity, vol. i., especially pp. 77-81).

Division of a base between two acids present in equivalent quantities. Thomsen made investigations regarding the quantity of a base (NaOH) that reacts to form salts with two acids (e.g. HCl and HF) added in equivalent quantities. He found that, in the case quoted, 95 p.c. NaCl and only 5 p.c. NaF were formed in dilute aqueous solution. It may be deduced from the theory that the quantities of NaOH combining with the two acids (HCl and HF) are in the same ratio as the extents of dissociation of the acids at the same dilution. The observations of Thomsen and of Ostwald agree extremely well with this deduction from the theory (Arrhenius, Z. P. O. 5, 14 [1890]; cf. APPINITY, vol. 1, n. 81).

Influence of temperature on rate of solution. If a finely and equally powdered substance is shaken with a solvent at two different temperatures, for a very short time, the rapidity of solution is found to increase rapidly with the temperature. For instance, the rates of solubility in water of cream of tartar and benzoic acid increase between 0° and 17° in the ratios 1:38 and 1:31.

So-called solid solutions. Palladium is able to take up much H, but the mixture retains the solid form. There is, therefore, here no proper solution; nevertheless, van't Hoft has shown that the laws which hold good for solutions are valid for this phenomenon also (Z. P. C. 5, 322 [1890]). There is formed at first an alloy, Pd.H, which possesses a definite dissociation pressure. If the pressure of the H is increased more H is absorbed, and the quantity absorbed is in direct proportion to the excess of pressure of the H. Henry's law, therefore, holds good. On this ground van't Hoff called mixtures similar to this 'solid solutions.' Solid solutions of thiophene and benzene have been examined by van Bijlert (Z. P. C. 8, 343 [1891]).

Heats of solution. A considerable quantity of heat is generally produced during the solution of a substance in a solvent. The heat of solution of a substance is defined to be the quantity of heat that appears during the solution of a gram-molecule of the body in much water. The following table gives the heats of solution of some of the commoner substances. Most of the numbers are taken from Thomsen

(Th. 3, 195).

Gases.	
Chlorine Cl ₂	4870
Carbon dioxide CO ₂	5882
Ammonia NH.	8430
Hydrogen fluoride HF	1 1800
" chloride HCl	17310
" bromide HBr	19940
, iodide HI	19210
" sulphide H ₂ S	4560 '
Sulphur dioxide SO ₂	7700
Liquids.	
-	0000
Methyl alcohol CH ₃ .OH	2000 2540
Ethyl , C ₂ H ₃ .OII.	
Propyl , C ₃ H ₇ .OH	3050
Ether (C ₂ H ₃) ₂ O	5910
Acetic acid C ₂ H ₃ O.OH	420
Sulphuric acid H ₂ SO	17850
Solids.	
Caustic potash KOH	. 12500
" hydrate KOH.2H,O	30
Lithium chloride LiCl	. 8440
Sodium , NaCl	1180
Potassium , KCl	-4440
Sodium bromide NaBr	190
" hydrate NaBr.2H ₂ O	4710
Potassium sulphate K ₂ SO ₄	6380
Mercuric chloride HgCl,	8300
Sodium acetate NaC ₂ H ₃ O ₂	. 4200
Sodium benzoate NaC, H,O,	. 800
Benzoic acid C.H., CO.H	6700
Silver chloride AgCl	15800
. bromide AgBr	20200
iodide AgI	26600
Cane sugar CaHaOn	800

Volume changes accompanying solution. In most cases the solution of a substance in water is accompanied by a considerable amount of contraction. For instance, a mixture of 100 c.c. alcohol with 100 c.c. water measures only 192-8 c.c. at 18°. The contraction may be so great that the volume of the solution is less than the volume of the water used as solvent: for instance, when Na₂CO₃, NaOH, or LiOH is dissolved in much water. The following table shows the volume change, in c.c., that takes place when one gram-equivalent of some of the most important compounds is dissolved in much water—e.g. in 10 litres:—

		п	Na.	K	NH.
\mathbf{oH}		18	- 5.8	8.6	
Cl.		18.3	16.6	26.9	87.4
NO.	•	29.0	28.0	38.5	48.2
³ So⁴		16.2	6.4	15.7	24.2

A mixture of 40 grms. NaOH with 10 litres water occupies, therefore, a volume of 9994.2 c.c.

When the solvent is other than water an increase of volume sometimes takes place; for instance, a mixture of 100 c.c. alcohol with 100 c.c. CS₂ occupies about 202 c.c.

Specific heats of solutions. The water value of a solution of a salt in water is not equal to, but is generally less than, the sum of the water values of the water and the salt. In a few cases this decrease is so great that the water value of the solution becomes less than that of the water used as solvent. The following data show the water values of one gram-equivalent of the chief salts in extremely dilute solutions (according to the determinations of Thomsen):—

The water value of a solution of 40 grms. NaOH in 10 litres water, for instance, is not only not greater than that of the water alone (10,000), but is distinctly smaller (9,973).

Deviations shown by concentrated solutions. The laws that have been stated for the osmotic pressure, the lowering of freezing-point, the raising of boiling-point, and the lowering of vapour-pressure, brought about by substances in solution, are valid, strictly speaking, only for very dilute solutions. Deviations from these laws occur when the solutions are more concentrated. Sometimes the observed values are smaller than those theoretically deduced. In such cases it is supposed that molecular aggregates are formed. This occurs, for instance, gates are formed. with solutions in benzene of oxims, alcohols, phenols, and fatty acids, and also with fairly concentrated aqueous solutions of the sulphates of Mg, Cu, Zn, and Cd, and CdI2 (Beckmann, Z. P. C. 2, 737 [1888]; Arrhenius, Z. P. C. 2, 496 [1888]). On the other hand, most concentrated aqueous solutions give values greater than the calculated values; this is made especially evident by Tammann's investigations into the vapour-pressures of salt solutions at 100° (Mem. de l'Acad. de St. Pétersbourg [7] 1, 85 [No. 9, 1887]). An explanation of this behaviour has been sought for in the attraction between the

solvent and the dissolved substance (Arrhenius, Z. P. C. 10, 40 [1892]). S. A.

SOLUTIONS II. The view that hydrates exist in aqueous solutions, and analogous compounds in non-aqueous solutions, is one which has long been held by many chemists; it is only in the last few years, however, that the hydrate or association theory has assumed a precise form, and that definite experimental evidence in support of it has been accumulated. In giving some account of the present position of this theory it will be convenient to collect the evidence on which it depends under the headings 'general' and 'special,' and to discuss separately the bearing which recent work on dilute solutions has upon it. Aqueous solutions have naturally been more studied than solutions in other solvents. but these other solutions have been investigated sufficiently to show that they are similar to aqueous solutions in every respect, except as regards electric conductivity. Although, therefore, to simplify matters in the present article, in most instances aqueous solutions alone are mentioned. it must not be understood that the arguments do not apply equally to other cases.

General. The changes accompanying dissolution seem to be in every respect similar to the recognised accompaniments of chemical combination: evolution of heat, a more or less profound alteration in the nature of the reagents, and an irregular variation in the properties of the resulting solution with regular variations in the proportions of dissolved substance and solvent. For reasons which will be mentioned below, these irregularities may often not be very pronounced, but it may safely be stated that every attempt which has been made to express the properties of any series of solutions by a simple expression agreeing, within the limits of experimental error, with the observed values throughout a wide range of concentration has been unsuccessful.

The affinity which a large number of substances possess for water, as evidenced by the many solid compounds which they form with it, and by the heat evolved in their formation, renders it prima facie extremely improbable that these substances should exist in presence of excess of water without combining with it. It is, moreover, those very substances which exhibit the greatest tendency to form solid hydrates which are generally most soluble. more careful study of the thermal phenomena of solutions places this argument beyond the range of mere speculation. From the known heat of fusion of water and of a few anhydrous salts we can obtain a very close estimate of what the heat of fusion of any hydrated salt would be, if no change beyond the mere passage from the solid to the liquid condition occurred; with hexahydrated calcium chloride, for instance, the heat of fusion under such circumstances would be 11,000 to 12,000 cal., and on the most exaggerated estimate could not exceed 14,000 cal., whereas if decomposition as well as mere liquefaction occurred the heat absorbed would be at least 25,000 cal., since the heat of fusion of the 6H2O alone is 9,500 cal., and the heat of combination of CaCl₂ with 6H₂O (both solid) is 14,500 cal. The observed heat of fusion, however, is only 11,417 sal, a value which disproves that any consider-

white change beyond mere liquefaction has occurred during the fusion—i.e. the combination which existed in the solid must exist also in the liquid. The data in the case of sulphuric acid afford more striking evidence of a similar character. The heat of combination of solid water with the solid acid to form the solid monohydrate is 6,550 cal., and if, when the reagents are mixed in the liquid condition, they do not combine chemically, far less than this amount of heat would be evolved; whereas the heat actually evolved is found to be almost identical with the above, namely 6,667 cal.

The separation of a crystalline hydrate from a solution is an argument to which due weight has hardly yet been attributed in favour of the existence of that hydrate in the solution, although not necessarily in large quantity. If there are no molecules of the hydrate existing as such in the liquid, these must have been deposited in the solid form at the moment of their formation, whereas we know that whenever deposition occurs simultaneously with formation, as in the precipitation of an insoluble salt, the substance is deposited in the amorphous and not in the crystalline condition.

If, as would appear to be the case, it is necessary to admit the existence of hydrates in concentrated solutions, it is necessary to admit their existence in dilute solutions also. The mass action of an excess of one or other of the constituents of any composite fluid is well known, and is universally accepted: it must operate with hydrates as much as with other substances, and must do one of three things: either (1) it must increase the stability or amount of the particular hydrate present, or (2) it must combine with it to form a higher hydrate (if it is the water of which excess is added), or (3) it may decompose the hydrate by reacting with the non-aqueous constituent of it to form new compounds, as when free alkali and acid are produced (a decomposition, however, which can be proved in many cases to occur to but a negligible extent), but in no case could excess of water decompose the hydrate taken so as to liberate the dissolved substance in the anhydrous condition. The thermal phenomena of solution afford important evidence in this case also; to interpret them properly, however, it must be remembered that the dissolution of a substance in excess of solvent entails the separation of the particles of that substance from each other to the same extent as if it were vapourised, and that to effect this separation the same amount of heat must be absorbed in either case. The heat evolved due to the reaction of a liquid with excess of solvent is, therefore, the observed heat of dissolution minus the heat absorbed in vapourisation, and, in the case of a solid, the heat of fusion as well as that of vapourisation will have to be subtracted. Making allowance for these so-called physical changes, we find that the formation of every concentrated solution—that is, a solution which contains hydrates -is accompanied by the evolution of heat, and inasmuch as, with the same allowance, dilution is always accompanied by a further evolution of heat, the action of the diluent cannot be regarded as a reversal of the initial reaction, but rather as an extension and completion of it, the hydrates present in the concentrated solutions soing increased in amount or in complexity thereby. When matters are simplified by dissolving a gas, instead of a liquid or solid, and adjusting the pressure of the gas or the quantity of solvent so that the former occupies the same volume after as before dissolution, we still find that a very considerable evolution of heat occurs; with the haloid acids this is as much as 17,000 cal., and though this may be glossed over by some of the advocates of the physical theory by stating that the decomposition of the acids into their ions, which they consider occurs, evolves a very large amount of heat, no such explanation can be offered in cases where no such decomposition is imagined, and it has been proved that the dissolution of gaseous non-electrolytes both in water and in other solvents is accompanied by the evolution of as much as 5,000 to 14,000 cal. In the face of such a considerable loss of potential energy, it is impossible to maintain that the substances losing it remain unchanged, and that the dissolved substance can, in any true sense, be still gaseous and uncombined with the solvent. It is important to note that van der Waals, through a different line of reasoning, has arrived at the same conclusion as to the necessity of recognising some action evolving heat between the substance and solvent, even when the former is in the so-called dissociated condition.

Amongst the general considerations favouring the view that dissolution consists in the formation of liquid compounds, not the least important is that this gives us some intelligible reason for dissolution occurring at all, whereas if the solvent is regarded as being inert and only playing the part of so much empty space (as some of the advocates of the physical theory have maintained), we have no explanation of why dissolutions occur; the presentation of empty space to a stable solid does not make the latter fill the empty space, and even attributing dissolution to the possession of a certain 'solution pressure' by the dissolving substance would appear to amount to no more than stating that a substance dissolves because it does do so.

Special. Berthelot determined the heats of dissolution of various series of solutions of different concentrations, and concluded that his results when plotted out showed the presence of changes of curvature or inflections at certain points, indicative of the existence of hydrates in the solutions. In many cases he adduced various special considerations in support of the existence of the hydrates thus indicated, but his determinations were not sufficiently numerous or accurate, nor were his methods of examining them sufficiently precise, to lead to more than vague conclusions Thomsen's investigations on the same subject were equally unsatisfactory; he sought to disprove the existence of any such changes of curvature by finding empirical equations to represent each series of results, but in the four cases which he thus investigated the equations deduced express but a small portion of the whole series, leaving in the remainder errors ten and a hundred times greater than the experimental error. Mendeleeff next took up the question from a different point of view. Theoretical considerations led him to conclude that solutions consisted of different hydrates according to the

amount of water present, and that, if not more than two hydrates were ever present together in the same solution, there would be definite changes of curvature in the figures representing the properties of the solutions at the concentrations corresponding to these hydrates; that is, that the rate of change in the property with change of concentration would be different when the solutions consisted of the hydrates A and B from what it would be when they consisted of B and C, so that there would be a change at a concentration corresponding to the composition of B, and further, he concluded that these rates of change (first differential co-efficients) in the case of the densities would be rectilinear functions of the percentage composition between the points A and B. B and C, &c. (It should be noticed in passing that the idea which lies at the root of Mendeléeff s conception-and, to a certain extent, of Berthelot's also-is that the water in any solution is nearly entirely combined with the dissolved substance, and not merely that the solution consists of a simple hydrate mixed with excess of free water.) That the concentration-rate of change of the densities is representable within experimental error by a series of straight lines is probably true in many cases, but in the two cases on which Mendeleeff chiefly relied for proof these first differences are conspicuously curvilinear throughout. The reason of this, doubtless, is that solutions of a given concentration generally contain more than the two hydrates which he postulated. Roozeboom's work on ferric chloride, and Pickering's on sodium hydroxide, render it probable that five or six hydrates may co-exist in the same solution; at any rate, as many as four have actually been obtained from certain solutions. Pickering next attacked the subject from a purely experimental point of view. The distinctive feature of his work is the search for changes of curvature (breaks) by the application of a flexible lath to his plotted results. A lath bent by the application of two couples near its extremities forms, for all practical purposes, a curve of a very simple nature; and it has been proved that the use of such a lath is tantamount to, and leads to precisely the same conclusions as, the application of ordinary parabolas with three or four constants deduced mathematically from the experimental values; and in several respects, besides expeditiousness of application, this method is superior to the mathematical method. The mere fact that a certain figure may be represented accurately by a series of parabolas is by itself no proof that it really consists of these independent curves, any more than the existence of breaks can be disproved by finding an artificial equation which will bridge them over; the correctness of any particular form of representation can be measured only by the results to which it leads, and in this respect the discontinuous expressions would appear to be highly satisfactory. The positions of the breaks are not dependent on the taste of the draughtsman: the figures examined seem to split up naturally into certain sections only, and when drawn in these sections it was found, in some dozens of series of experiments, that the apparent error of the points agreed within 5 or 10 per cent. with the known experimental error (though in a great number of the cases the true

magnitude of the latter was not as after the drawings were made), whereas drawings of a similar character, but placing the breaks at other points, or drawings obliterating the breaks altogether, represented the error of the points to be far larger, often 10 or 100 times larger, than the known experimental error. It must be remarked that, once the magnitude of the experimental error is known with certainty, no drawing can be accepted unless it agrees closely with it. and Pickering has devised a method by which the experimental error can be accurately determined independently of any considerations other than the examination of the final results themselves; he has also devised a means of obtaining a numerical estimate of the acceptability of any drawing, by combining together the various factors which are usually taken as affording a criterion of acceptability. Again, when sections of increasing lengths are taken, and these are represented by single parabolas, or bent-lath curves, there is little or no increase in the apparent error of the points till the sections extend beyond a point where one of the supposed breaks exists, but as soon as they do so there is a large and sudden increase, indicating that some real change at the point in question exists. Moreover, it has been shown that in a case where two parabolas will represent a series of results perfectly, a single parabola will not do so, even if it contain as many constants as the two parabolas together contain. The strongest argument, however, in favour of the reality of these breaks is that the various properties of any series of solutions, although they form figures differing from each other widely in general form, are yet all thoroughly concordant as to the positions at which the breaks occur. The properties of sulphuric acid which were investigated were the densities at four temperatures and the contraction on mixing deduced from them, the heat of dissolution, the thermal expansion, the electric conductivity (Kohlrausch's values), and the thermal capacity; subsequently also the freezing-points and van der Willigen's values for the refractive indices were investigated. Perkin also found indications of two of the breaks in his determinations of the magnetic rotations, and still more recently Féry has recognised some other of the breaks in his own measurements of refractive indices. Three different properties were also examined by Pickering in the case of calcium chloride and nitrate, and were found to show a similar concordance.

That the breaks are really due to, and indicate the presence of, compounds in solution is shown by the fact that, not only in the cases above mentioned, but also in many others where other solvents besides water were used, they always occur at points which correspond within small limits with definite molecular proportions -wherever, that is to say, the proportion of substance to solvent is sufficiently simple to permit of any conclusions at all being drawn in the matter. Further evidence on this point was also afforded from a study of the freezing-points of fourteen of the alkyl amines, where, with one exception, hydrates of the very compositions indicated by breaks in the case of some of the amines were isolated in the crystalline condition in the case of the others. Finally, as a more striking, though perhaps not more cogent, argument, we

no less than six new hydrates, the existence of which had been foreshadowed in the properties (chiefly densities) of the solutions—namely, H₂SO₄4H₂O, HBr.3H₂O, HBr.4H₂O, HCl.3H₂O, HNO₄.H₂O, and HNO₂.3H₂O—the last three being especially conspicuous examples, for the only marked breaks which the densities showed coincided with the only hydrates which were subsequently isolated.

Two important features of the conclusions drawn from the above-mentioned work on sulphuric acid should be mentioned; firstly, the large number (18-20) of hydrates of which indications were obtained; secondly, the complex nature of hydrates in very dilute solutions. Any improbability which might be considered to attach to the former conclusion (though, in reality, no data exist on which to found any estimate of the probabilities in such a case) is removed by the fact that a still larger number of hydrates (when equal ranges of concentration are compared) have been isolated in the crystalline condition from solutions of sodium hydroxide. The complexity of the hydrates indicated extends up to compounds with hundreds and even thousands of molecules of the solvent, but, with the explanation to be mentioned below as to their possible constitution, these hydrates can scarcely be branded as improbable; at any rate. the breaks which indicate their existence appear to be precisely similar in nature to those which indicate the presence of the simpler hydrates. Pickering has investigated the freezing-points of many dilute solutions besides those of sulphuric acid, and has found that nearly all of them show indications of similar changes, and those recognised in the cases of sodium chloride and sulphuric acid have received further confirmation from a series of results made by H. Jones; a confirmation of special importance, since Jones's determinations were made with the view of disproving the existence of breaks. Complex hydrates, though of a comparatively small degree of complexity, would appear to exist in regions other than those of very dilute solutions; two such were indicated in the neighbourhood of the monohydrate of sulphuric acid, and a similar one, perhaps another also, has been isolated in the case of soda. These are probably compounds of two different hydrates.

It is important to note that the changes of curvature here described need not necessarily be absolutely abrupt. On the strength of experimental evidence only, where experimental error necessarily exists, it is obviously impossible to prove or disprove the abruptness of any change, and no satisfactory mathematical theory has yet been formulated to lead to any views on the subject. It is sufficient for the purpose that comparatively abrupt changes exist. Nor should it be expected that these changes would necessarily be of a very marked character, for a large proportion of the factors determining the properties of solutions must be of a purely physical or even mechanical character; the densities of sulphuric acid solutions, for instance, must rise more or less gradually from 1 to 1.85, and it is only in

It should be noted that Jones himself asserts that his results entirely disprove Pickering's 'breaks' (c. B. 26, 547, 1633).—M. M. P. M

the variations from the 'more to the 'less' that we can expect to find evidence of inter-

mediate compounds.

Application of the hydrate theory to explain the properties of dilute solutions. Diversity and irregularity are some of the most marked features of the properties of concentrated solutions, and though in dilute solutions these irregularities are much less conspicuous (as, indeed, we should expect them to be when the hydrates present become excessively complex and, consequently, excessively unstable), they are still recognisable, and it is only in the most extreme dilution, where the experimental error amounts to a large fraction of the total quantities measured, that the results can be expressed within the limits of this error as an apparently regular function of the concentration. It may safely be stated that any purely physical theory which confines itself to regions of extreme dilution, and which ignores some of the most marked features of dissolution. as well as the mass of direct evidence showing the existence of compounds in solution, cannot be accepted as a complete theory; nor, on the other hand, can the hydrate theory of solutions be accepted as satisfactory unless it can be shown to be consistent with the two main characteristics of weak solutions—the apparent quasi-gascous independence of the dissolved substance in dilute solutions, and the approximately accurate results which are obtained when calculations are based on the assumption that electrolytes in dilute solutions are dissociated into their ions. However important the service rendered to science by the gaseous and dissociation theories of solution, there are many fundamental objections which militate against their universal acceptation. They offer no satisfactory explanation of why substances dissolve at all, and still less why water alone, of all ordinary solvents, should resolve salts, &c. into their ions. These ions are represented to be atoms charged with enormous electric charges, but no explanation is given of the origin of these charges, or of the peculiarities which they are supposed to exhibit; two atoms oppositely electrified are represented as being less combined than when not charged at all; the charged atoms are represented as swimming about in the water without decomposing it, and without giving up their charges to their oppositely electri-fied companions, although they can part readily with them to an electrode; and to explain the thermal phenomena of solution, it has to be boldly assumed that the decomposition of molecules (elementary or composite) into charged atoms often evolves a considerable amount of heat, and consequently that the charging of an ordinary atom must be a process which evolves heat also. The only crucial experiment which has so far not been susceptible of an opposite interpretation seems to disprove any real dissociation of electrolytes. The lowering of the freezing-point of a solvent is accepted as affording a measure of the number of acting units (molecules or ions) in any substance added to it, and when, for instance, to some acetic acid a weak solution of sulphuric acid is added, the depression produced proves that the latter con-tains fewer acting units than the water and sulphuric acid do separately, instead of more, as

would be the case if the sulphuric acid molecules had to be split up into independent ions.

In a paper in the Berichte, Pickering has offered an explanation of the behaviour of dilute solutions based on the hydrate theory and on the views held by him as to residual affinity. The explanation may be rendered more intelligible by representing chemical attraction, as we represent electrical attraction, to be due to 'charges' on the surfaces of the attracting matter, but inalienable from the matter, owing to a repulsive force between the atoms similar to that which produces elasticity preventing the atoms ever coming close enough together to allow of the charges combining. The charges are represented as being always self-attracting. Each atom possesses one or more unit affinity. charge according as it is a monad or a polyad: with a free atom the charge would be uniformly distributed over its surface, whereas when two atoms are combined the greater part of the charges would be drawn to those sides of the atoms facing each other; but, as in the case of electric charges, a certain amount would still be left on the further sides capable of acting on, and being acted on by, other atoms or molecules in like condition, this residue, or unbound charge, forming what appears as residual affinity. As in the case of electrical charges, the nature of the matter composing different atoms will cause different degrees of mobility in the charges on their surfaces, and hence different pairs of atoms will be held together with different degrees of firmness, and different molecules will exhibit different amounts of residual affinity. When a molecule A B, possessing a certain amount of residual affinity, is surrounded by a number of other molecules CD possessing residual affinity also, the two residual charges will react on each other and increase the amount of the charges on the external portions of the molecules, leaving a smaller amount of charge on the portions of A and B which face each other; in the same way the charge on C will be partially withdrawn from the surface facing D, and will be able to retain a smaller amount of D's charge on the portion of D which is next to it, so that D will exhibit more residual affinity than formerly, and will be able to react in a similar manner on its neighbours, C' D'. Thus, by a process precisely analogous to electric induction, the number of molecules of C D which are acted on by, and are more or less combined with, A B may be very large, and far greater than the number which are capable of coming into its immediate vicinity. The existence of the very complex hydrates which have been recognised in dilute solutions is thus easily explicable. It is evident that a molecule when thus surrounded by, and combined with, a large number of solvent molecules will be attracted equally in every direction, and as the magnitude of the force exerted on it by each individual solvent molecule must be very small, it will be able to move easily in any direction, especially as any of the solvent molecules from which it parts during the process will have their places supplied at once by other similar molecules, of which, owing to continuous dissociation and recombination, there is an abundant supply in the liquid. Thus, into whatever new position the sentral morecure moves, the status quo ante is immediately reproduced, and, consequently, the molecule will move almost unfettered by the presence of the solvent, and will act almost as if it were in the gaseous state. We thus obtain at once an explanation of why the application of the ordinary gaseous laws to dilute solutions yields very nearly true results; we should, indeed, expect that they would not be absolutely true, for certain definite numbers of solvent molecules would be capable of a more symmetrical arrangement about the central molecule than others, and such arrangements (definite hydrates) would be more stable than others, and the tendency to form them might have an appreciable effect on the regularity of the results: small irregularities of this sort are exactly what we find in the case of those dilute solutions which have been fully examined.

It is obvious that as the quasi-gaseous freedom of the molecule is dependent on its being combined with the solvent, this freedom obtains only so long as the molecule remains within the solvent, and would not admit of the possibility of its leaving the liquid, or of exerting an external gaseous pressure; for the same reason it would be impossible for it to pass through any crevice so small as not to allow it to retain as many solvent molecules as it was combined with in the solution. This gives us an explanation of the action of semipermeable diaphragms and all the phenomena of osmotic pressure; it, moreover, removes a difficulty which must be experienced in accepting the explana-tion given by the supporters of the physical theory of the action of these diaphragms—why it is that the water molecules (which are admittedly combined in great part into complex aggregates) can so easily pass through interstices which are impervious to what are held to be the single free molecules and ions of the dissolved substance. Direct experiment would seem to decide conclusively in favour of the explanation of osmotic pressure given above, for, when a suitable solution in a porous pot is immersed in either of the substances which compose the solution, osmosis through the pot towards the solution occurs in both cases, showing that osmotic pressure is not due to the impermeability of the pot to either of the constituents of the solution, but to its impermeability to the solution as a whole.

In a case where the atoms of the dissolved molecule possessed a considerable amount of residual affinity, the action and reaction between them and the solvent molecules would, in every respect, be proportionally great, and, con-sequently, those portions of the whole charges which are utilised in uniting the component atoms of the dissolved substance would be reduced, and, in extreme cases, might be reduced to the lowest possible limits-that is, till the amount of affinity utilised in holding them together was equal to that utilised in attaching them to the solvent molecules, in which case there would be an equal distribution of the affinity charges over the atoms. The atoms composing a molecule in such a condition would have a great amount of freedom of motion within the molecule; being attracted equally in all directions, they would be at liberty to start to

move in any direction, and their movements might attain considerable amplitude under suitable conditions as to the rate at which the forces between them varied with the distance; for to explain the apparent independence of the atoms, and therefore the abnormal osmotic pressure of a salt molecule, 'it only requires.' according to Fitzgerald, 'the space within which [the atoms] are bombarding about to be small compared with the space rate of variation of the force between [them].' The atoms of the two molecules in such a condition would obviously change partners very readily during collision, and this gives us an explanation of why such an interchange does take place when two different salts, &c., are mixed. This ready exchange, moreover, would take place continuously, and in a definite direction, under the influence of any external force, such as a charged electrode, a Grothüss' chain being formed, and we should consequently expect to find that substances in this condition—i.e. those which give abnormally large osmotic pressures—were electrolytes; this is so: and since, moreover, the amount of electrolysis occurring in a given time under a given force would be proportional to the number of molecules in the condition postulated, it follows that this number-and, therefore, the osmotic pressure-could be calculated, at any rate approximately, from the conductivity. In short, whatever calculations hold good on the assumption that the atoms in the molecules are absolutely independent will also hold good if they are assumed to be in the peculiar condition of combination here described—a condition which is brought about by their great tendency to combine with the solvent, and not by a tendency to part company for no assignable reason. On the present view also it is possible to understand why it is that salts and acids are generally electrolytes, and why water is the solvent which makes them electrolytes, for both salts and water are composed of elements which have a strong attraction for elements of an opposite character, and in such a case the residual affinity of both the elements (basylous and chlorous) constituting the salt would be acted on by that of the two opposite elements constituting the water, and we would get an amount of mutual reaction which would be impossible in the case of other anhstances.

The memoirs referred to in this article are: Berthelot, Méc. Chim. 1, 394; 2, 142; Thomsen, Thermochem. Untersuch. 3, 1-216; Mendeléeff, The Investigation of Aqueous Solutions according to their Specific Gravities (1887); also The Principles of Chemistry; and C. J. 52, 779; Roozeboom, Z. P. C. 10, 477; Féry, C. R. 115, 1309; Van der Waals, Z. P. C. 8, 214; Perkin, C. J. 63, 70; Jones, Z. P. C. 11, 112, 536; 12, 623; Pickering, C. J. 53, 865; 55, 14; 57, 16, 331; 63, 99, 141, 436, 890, 998; P. M. [5] 29, 427; 30, 400; 32, 20, 90, 478; 33, 132, 436; 34, 36; 35, 127; 86, 11; Z. P. C. 6, 10; B. 24, 277, 1579, 3317, 3328, 3629; 25, 1099, 1814, 1589, 1854, 2011, 2518, 3434; 26, 277, 1221, 1977, 2307, 2766; 27, 80, 67; C. N. 57, 116; 63, 260, 305; 64, 1, 311. B. U. P.

SONNENSCHEIN'S REAGENT. Prepared by adding phosphoric acid to a warm solution of ammonium molybdate in nitric acid, boiling the pp. with aqua regia to destroy NH₂, evaporating to dryness, and dissolving in 10 p.c. nitric soid (A. 104, 45). This reagent gives yellow

pps. with alkaloids.

SOPHORIN. S. . 009 in the cold; .5 at 100°. S. (alcohol) ·8 in the cold; 7 at 78°. Obtained from Chinese yellow berries, the undeveloped flower buds of Sophora japonica (Stein, J. pr. 58, 899; 85, 351; 88, 280; Spiess a. Sostmann, J. 1865, 587; Förster, B. 15, 216). Decomposed by boiling dilute H.SO, into isodulcite and

yellow sophoretin, which resembles quercetin.
SOPHORINE. An alkaloid obtained from the pods of Sophora speciosa (Wood, Ph. [3] 8, 1047). Liquid, forming a crystalline hydro-chloride, which gives a deep-red colour with FeCl. Poisonous. A poisonous alkaloid may also be obtained from the seeds of Sophora tomentosa (Greshoff, B. 23, 3539).

SORBIC ACID C.H.O. i.e. CH₃.CH:CH:CH:CH.CO,H. Mol. w. 112. [134.5°]. (228°). H.O. 730,000 (Ossipoff, J. R. 20, 650). Heat of neutralisation: Gal a. Werner, Bl. [2] 46, 802). Occurs in the juice of unripe mountain ash berries (Hofmann, C. J. 12, 43; A. 110, 129). The juice is partially neutralised with milk of lime, decanted from acid calcium malate, and distilled after addition of H2SO4. Needles (from dilute alcohol), v. sol. alcohol and ether, in. sol. hot water, volatile with steam. Partially decomposed on distillation (Barringer a. Fittig, A. 161, 307). Has no odour. Br in CS2 forms tetra-bromo-hexoic acid [179°] and di-bromo-hexenoic acid [90°-95° Fuming HBr forms di-bromo-hexoic acid [68°] (Stahl, B. 9, 120). Very dilute alkaline KMnO. at 4° gives aldehyde, racemic acid, oxalic acid, and CO2 (Doebner, B. 23, 2376). Sodium-amalgam forms hydrosorbic acid.

Salts. BaA'2. - CaA'2: silvery scales.

AgA': white crystalline pp.

Ethyl ether EtA'. (195.5°). Liquid. Chloride C.H,OCl. Converted by NH, and aniline into crystalline C₆H₇O.NH₂ and C.H.O.NHPh respectively.

Hydrosorbic acid v. HEXENOIC ACID. Isosorbic acid v. HEXINGIC ACID. Reference .- Oxy-sorbic acid.

SORBINOSE G_1, Q_0 i.e. $CH_2(OH)$. (CH.OH), CO.CH₂(OH). (CH.OH), CO.CH₂(OH). An unfermentable sugar obtained from the fermented juice of mountain-ash berries (Pelouze, A. Ch. [3] 35, 292; Byschl, J. 1854, 664; Delffs, C. N. 24, 75). The juice is left to stand for a year, and then filtered and evaporated. Trimetric crystals, as sweet as cane sugar. Lavorotatory. V. e. sol. water, sl. sol. hot alcohol. Forms with NaCl a compound crystallising in cubes. Its aqueous solution dissolves CaO, PbO, and Cu(Oh)₂. Not attacked by Br. Yields tri-oxy-glutaric acid on oxidation by HNO₃ (Kiliani a. Scheibler, B. 21, 8276), but no mucic or saccharic acid (Tollens, A. 249, 222). HIAq and P yield hexyl iodide. Reduced by sodium amalgam to sorbite (Vincent a. Delachanal, C. R. 111, 52). Not turned brown by hot alkalis. Reduces Fehling's solu-Bromine water yields glycollic acid (Hlasiwetz a. Habermann, A. 155, 120). On heating sorbinose (1 pt.) on the water-bath with a solution of phenyl-hydrazine hydrochloride (2 pts.) and NaOAc (3 pts.) in water (10 pts.) it phous.—B"H_PtCl, 2aq. Decomposed by boiling Vot. IV.

yields the osazone $C_{10}H_{22}N_4O_4$ [164°], which crystallises in yellow needles, sl. sol. hot water, v. sol. alcohol, v. sl. sol. ether (Fischer, B. 17. 582; 20, 827).

SORBITANNIC ACID. Obtained from the berries of Sorbus aucuparia (Vincent a. Delachanal, Bl. [2] 47, 492). Gives a yellow colour with alkalis; reduces silver salts in the cold; is not ppd. by alum or gelatin. Potash-fusion forms protocatechuic acid and phloroglucin.

SORBITE $C_6H_{14}O_6$. Mol. w. 182. [1117]. $[\alpha]_D = -1.73^\circ$. Occurs in mountain-ash berries (Boussingault, A. Ch. [4] 26, 376); in plums, cherries, and the fruits of nearly all the Rosacea (Vincent a. Delachanal, C. R. 108, 147; 109, 678; 111, 52). Formed on reduction of sorbin and of l-gulose (Fischer a. Stahel, B. 24, 2144). Formed also, as well as mannite, by reducing glucose (dextrose) with sodium-amalgam in the cold (E. Fischer, B. 23, 3684; Meunier, C. R. 111, 49). Pearly crystals (containing and). Melts at 75° when hydrated. V. sol. water and hot alcohol. Neither ferments with yeast nor reduces Fehling's solution. Levorotatory, becomes dextrorotatory on addition of sodium borate (Vincent a. Delachanal, C. R. 108, 354). HIAq yields (β)-hexyl iodide (Hitzemann a. Tollens, B. 22, 1048). Boiling with Ac₂O and some ZnCl₂ forms a hexa-acetyl derivative. Benzoic aldehyde and a little hydrogen chloride give C₆H₁₃O₅(C,H₅O), crystallising in rectangular prisms [c. 175°]; if more acid is present the insoluble compound C,H,2O,(C,H,O), [162°] is formed (Meunier, C. R. 108, 148; 110, 577; A. Ch. [6] 22, 423). In like manner valerio and HClAq form, on shaking, CoH12O4(CbH2O)2, crystallising in prisms, sol. alcohol and ether. Sorbite may be exidised to glucose by heating in sealed tubes with brominewater at 60° and treating the product with Pb and PbO (Vincent a. Delachanal, C. R. 111, 53).

SORDIDIN C16H18O7. [180°]. A neutral crystallisable substance occurring in the lichen Zcora sordida (Paterno, J. 1875, 863). Insol.

water, v. sol. alcohol and ether.

SPARTEINE C₁₃H₂₈N₂. Mol. w. 234. (811° at 723 mm.) (Bamberger, A. 235, 368). [a]_D = -14·6° at 26° (Bernheimer, G. 13, 451). Occurs in the common broom, Spartium scoparium (Stenhouse, A. 78, 1; Mills, C. J. 15, 1). Prepared by extracting the plant with water acidulated with H₂SO₄, evaporating, and distilling with NaOHAq. The distillate is acidified by HCl; evaporated to dryness; and the residue distilled with solid KOH. The base is finally rectified over sodium. Heavy oil, with peculiar odour and bitter taste, sol. alcohol and ether, insol. benzene and ligroin (Houdé, Fr. 25, 568). Lævorotatory. Turns brown in air. Alkaline in reaction. Narcotic poison.

Reactions.—1. Yields (γ)-methyl-pyridine on distillation with lime (Ahrens, B. 21, 826).—2 HIAq at 200° yields MeI and C₁,H₂₄N₂ (276°), which forms a platinochloride [280°], an aurochloride [157°], and a nitrosamine. -3. On passing the vapour through a red-hot tube it gives pyridine, (γ)-methyl-pyridine, C₂H₄, propylene, NH₄, HCy, and other bodies.—4. H₂O₂ forms a

base O₁H₂₆N₂O₂.
Salts.—The hydrochloride is amor-

water (Oechsner De Coninck, Bl. [2] 45, 181) .-B"2HAuCl. Decomposed by boiling water.-B"HI: tables, m. sol. cold water.-B"H₂ZnI₄. B"Ia: green needles (from alcohol), insol. cold water.—B"H₂SO₄: prisms.—B"2C₆H₃N₃O₇.

Methylo-iodide B"Mel. Trimetric plates;

a:b:c = .899:1:1.601.

water), v. e. sol. water and alcohol, insol. Nachaq.—B'EtiHi. Got by heating sparteine with Eti and alcohol at 1000 with Etl and alcohol at 100°. Prisms (from cold alcohol). Not coloured by alcoholic potash (De Coninck, C. R. 104, 513). B"EtClHClPtCl.

Dihydride C₁₅H₂₈N₂. (283°). Got by reducing sparteine with tin and HCl (Ahrens, B. ducing sparteine with tin and HCl (Ahrens, B. 20, 2219). Colourless oil.—B"HCl: very deliquescent needles.—B"H₂PtCl₄. Blackens at 239°.—B"HAuCl., Blackens at 130°.—Piorate. [125°]. Needles, decomposing at 215°.—B"HgCl₂. Oxysparteine C₁₃H₂₁N₂O. [84°]. Formed by oxidising sparteine, and extracting the solution with chloroform (Abrang, B. 24, 1005.—\$28, 2607.)

with chloroform (Ahrens, B. 24, 1095; 25, 3607). White hygroscopic needles, v. sol. water, alcohol, and ether. "Its solution is strongly alkaline. Reduces hot Fehling's solution.—B"H,Cl,4aq. Needles,v.sol.water.—B'HClaq.—B"₂H,P'tCl,4aq. Decomposed at 203°.—B"H.P'tCl,4aq. Needles; decomposed at 223°.—B"HA'uCl,.— Mercury double chloride [58°].—B'HBr 2\frac{1}{2}aq.—P'HBr 3\frac{1}{2}aq.—P'HBr 3\frac{1}{2}aq.—P'errate B'HBr 31 aq. -B'HI aq. -B'HNO, aq. - Picrate

Methyl-iodide of oxysparterne B'MeI. [193°].—B'McCl.—B'MeClHClPtCl, aq. [229°]. POCl, at 150° converts oxysparteme into an oily base C15H22N2 which yields C15H22N22HAuGl

Di-oxy-sparteine $C_{15}H_{26}N_2O_2$. [129°]. Formed by dissolving sparteine in aqueous H2O2 (Ahrens, B. 20, 2220; 25, 3609). Prisms, v. e. sol. water and alcohol, sl. sol. benzene, insol. ether. Alkaine in reaction.—B"H_PtCl_e. Blackens about 285°.—B"HAuCl_e. [c. 146°]. Necdles.—B"HI. [137°].—B'HBr. [147°].—B'H_HgCl_e. [193°].

Tri-oxy-sparteine C₁₅H₂₁N₂O₃. Formed by action of H₂O₂ on oxy-sparteine. Crystalline,

7. sol. water and alcohol.—B'2H2PtClaStaq. B'HAuCl. [137°]. SPECIFIC GRAVITY v. Densities, Relative,

vol. ii. p. 370.

VOLUMES. SPECIFIC The molecular weights of substances when divided by their respective specific gravities, taken under comparable conditions, furnish values which have been termed atomic, molecular, or specific volumes. The specific volume is, therefore, the space occupied by aggregates of atoms, including the interstitial spaces, whose weights are proportional to the molecular weights of the substances.

Objection has been raised against the term 'specific volume' on the ground that, as specific gravity is the weight of unit volume, specific volume should by analogy be the volume of unitweight; hence of late years the term 'molecular volume' has been preferred. The term 'specific volume ' has, however, acquired by definition and use a distinctive meaning. The adoption of the term 'molecular volume' is almost certain to be attended with confusion, owing to the different sense in which it is frequently employed by

physicists and chemists. The specific gravity of solids and liquids, referred to water at 4°, is the weight in grams of the unit volume. If, then, the molecular weight be expressed in grams, we may define the specific volume of a solid or liquid substance as the number of cubic centimetres occupied by this mass.

The specific gravity of a gas is usually referred to hydrogen as unity. It follows, then, from the law of Avogadro that all gases should have the same specific volume. There are a few exceptions to the universal truth of this statement arising from so-called abnormal vapour densities, but the specific volumes of the exceptional substances stand in the same simple relation to the normal value that their molecular weights stand to what analogy would indicate as the normal molecular weight.

Inasmuch as the specific gravity of a substance is affected to a greater or less extent by heat, it is obviously necessary to determine this constant under comparable conditions of temperature-that is, at temperatures at which heat may be supposed to exercise the same effect on the substance. In the case of liquids Schröder suggested that temperatures at which the vapour pressures of the various liquids are the same-as, for example, their boiling-points under a standard atmosphere - should be regarded as comparable.

In the case of solids the effect of temperature is of course much less marked, and hence the specific gravity of these substances is usually taken at the ordinary temperature of the air.

Specific volumes of solids.

The first attempt to trace relationships between the chemical nature of substances and their equivalent volumes appears to have been made by Le Royer and Dumas in 1821 (J. Ph. 92, 408). They sought to determine the equivalent volumes of the elements by dividing their atomic weights by their respective specific gravities, the values so obtained being termed by them atomic volumes. They were led to infer that these volumes formed an arithmetical seriesa supposition which was hardly warranted by the facts then known, and which has since been completely disproved by more accurate observations. This idea of combination among solids in definite volumetric proportion was further developed in 1824 by W. Herapath (P. M., Nov. 1824), who sought to prove that the volume of the oxygen in a metallic oxide bears a simple ratio to that of the metal with which it is combined. Almost simultaneously the same problem was attacked by Karsten (S. 65, 394), and subsequently, in 1830, by Boullay, but with no definite general result.

Ammermüller, however, in 1840, concluded (P. 49, 341; 50, 406) that the specific volumes of compounds containing the same elements in different proportions are either identical or stand to one another in rational proportions. Persoz in his 'Introduction to the Study of Molecular Chemistry,' recognised that equivalent amounts of many bodies of analogous composition occupy the same volume, and he inferred that the specific volumes of all substances are multiples of one and the same number, a conclusion also drawn by Le Royer and Dumas, but which is not supported by facts.

Kopp (P. 47, 188), in 1889, first attempted to

educe general formulæ from which he was able o calculate the specific gravities of certain oxides ind haloid salts, with results which showed, in eneral, a fair agreement with the observed values. In the same manner he calculated formulæ for other anhydrous salts-such as sulphates, carbonates, and nitrates—on the supposition that such salts consist of combinations of oxides and acids, or that they are made up of a radicle, acid plus oxygen. By means of these formulæ he inferred that it is possible to draw conclusions concerning the specific gravity of metals for which this constant is unknown. Kopp, in this memoir, used the term specific volume for the first time, and he defined it as the nolecular weight (Mischungsgewicht) of a substance divided by its specific gravity. He found that the specific volumes of similarly reactive elements -as, for example, chlorine, bromine, and iodine; tungsten, molybdenum, chromium, ron, manganese, nickel, cobalt, &c.—are equal or nearly equal. In other cases—as silver and gold, potassium and sodium—the specific volumes stand to each other in simple relations. Elements which, like barium and strontium, form isomorphous compounds have the same specific volume. Strictly speaking, this law can hold only for those substances which are perperfectly isomorphous. The more nearly the crystalline forms of isomorphous substances are identical, the more nearly will their specific volumes be the same. This is made evident by a comparison of the axial ratios of witherite, strontianite, arragonite, and cerussite; and also of the carbonates of zinc and magnesium (mesitene), the carbonates of iron and manganese, and dolomite and calc-spar. It is seen that there is a direct comparison in the case of the latter compounds between the length of the principal axis a and the specific volume V, such that a 4.789 =0.0127671V, from which it is possible, of course, to deduce the specific gravity of the substance from its crystalline form. It also follows that an increase of specific volume is occasioned by an increase in the length of the axis a. If we heat one of these crystals the density decreases; the axis a must therefore increase in length, while the angle R becomes less obtuse. This fact, indeed, was discovered by Mitscherlich, who found that the specific gravity of calc-

spar decreased in the ratio of 1 to $\frac{1}{1.001961}$ when

calc-spar was heated through 100° . The specific gravity of calc-spar is 2.7220, when a=0.8544 and $R=105^\circ$ of. By heating calc-spar through 100° , the specific gravity becomes 2.7167, or the specific volume changes from 36.73 to 36.80. If we determine the length of the axis a by means of the above formula, we find it to be 0.85672, corresponding to an angle R of 104° 57', or a difference of 3', which closely agrees with that actually observed by Mitscherlich $(P.\ M.\ [3]\ 18, 255)$. Schröder $(P.\ 1840.\ 553)$, starting from the observation of Ammermüller, that equal volumes of the two oxides of copper contain the same amounts of copper and multiple amounts of oxygen, assumed that the volume of the copper, as of the oxygen, is equal in the two substances, but that the amount of the oxygen in the cuprous oxide stands to that in the cupric oxide as 1 to 2.

Hence Schröder drew the general conclusion that the same element can have different specific volumes in different compounds, but that the several values for the specific volumes stand in simple relations to each other. He saw in this hypothesis not only an explanation of the condensation which accompanies chemical union, but also a rational basis for the belief that the specific volume of a compound is equal to the sum of the specific volumes of its components.

Schröder found that if in a series of analogous bodies, AO, BO, CO, the specific volumes of which are known, we subtract from these values the primitive atomic volumes of A, B, and C respectively, we obtain a constant remainder. This he found to be the case with the oxides of lead, cadmium, and zinc, and hence he inferred that the metal in these oxides retains its primitive atomic volume. Kopp assumed that this is equally true of the salts of the heavy metals, but with the salts of the metals of the alkalis and alkaline earths this is impossible, as the specific volumes of the salts are, as a rule, smaller than the primitive atomic volumes of the component metals. He had consequently to assume for these metals a special atomic volume, which however, remains the same in all the salts. He determined these values as follows: Suppose M+R to be a compound of a heavy metal, and m+R the analogous compound of a light one; suppose A to be the known specific volume of M+R, and a that of m+R, B the primitive atomic volume of M, and b that of m.

Then, M + R = A,

and M=B.

Therefore the atomic volume with which R is contained in the compound is A-B, say x.

It is assumed that R retains its value in m+R.

and since m + R = a, and R = x;

therefore b. i.e. the atomic volume of m = a - x. Kopp also showed that the densities of the hydrated oxides, and of a number of hydrated salts, may be calculated with considerable accuracy by assuming certain definite values for water in a state of combination. It ought to be stated, however, in this connexion, that subsequent researches have indicated that Kopp's conclusions respecting the specific volume of water of crystallisation must be slightly modified. Schiff, many years ago, showed that the members of certain classes of hydrated salts have practically the same specific volume. Thus, all the alums have a specific volume of about 277; double sulphates of the form M₂M"(SO₄)₂.6H₁O have a common volume of 207; and all the vitriols-that is, salts of the form M"SO4.7H2Owhether isomorphous or not, have the specific volume 146.

Thorpe a. Watts (C. J. 37, 102, [1880]) have shown that the volumes occupied by the several molecules of water vary with the degree of hydration of the salt. In the case of the so-called magnesian sulphates, the first molecule of water, the constitutional water, or 'water of halhydration' of Graham, occupies considerably less bulk than the remaining molecules; its mean relative value is 10.7. Each additional molecule appears to occupy a gradually increasing volumes. The difference between the specific volumes of

the monohydrate and dihydrate is 18.3; between the volumes of the dihydrate and trihydrate the difference is 14.5; between the trihydrate and the tetrahydrate it is 15.4; and between the hexhydrate and heptahydrate it is 16.2. These observations are so far in harmony with Kopp's general conclusions that in the compounds containing only a small number of water molecules (1 to 3) the specific volume of the water is 12.4; in others containing a larger number of molecules of water (2 to 7) it is 13.4; whereas, in a third class, containing the largest number of molecules of water (from 3 to 10), its mean value is 15.3.

Specific volumes of liquids.

Methods. The specific gravity of the liquid at its boiling-point may be determined either directly or indirectly. Ramsay (C. J. 35, 463 [1879]) devised a simple method by which the weight of a known volume of liquid at its boiling-point may be directly ascertained with approximate accuracy. The vessel containing the liquid consists of a thin glass lemon-shaped bulb of about 10 c.c. capacity. At the upper end of the bulb is a capillary tube, bent into the form of a hook; the lower end is provided with a similar hook of solid glass. The capacity of the bulb is ascertained by weighing it full of water at a known temperature. The bulb is filled with the liquid to be examined, in the usual way, by warming and dipping the capillary neck of the bulb beneath the surface of the liquid. It is not necessary to fill the bulb completely; two or three c.c. of the same liquid are then introduced into the wide tube, and the bulb is suspended within it by thin platinum wire attached to a piece of glass rod passing through a hole in the cork. The wide tube is then heated until the liquid within it boils violently, and it is kept in ebullition so long as liquid drops from the end of the capillary neck of the bulb. The lamp is now removed, and the whole allowed to cool. When cold the bulb is dried and weighed. The specific gravity of the liquid is given by the formula

Sp. gr. =
$$\frac{W'}{1 + (0.00015 \times TW)}$$

in which W' is the weight of the liquid; W, that of the water filling the bulb at 0°; and T the temperature at which the liquid boils; 0.00015 is an empirically-determined, co-efficient required in order to make the volume correspond with the real volume at T.

A somewhat similar method of determining the specific gravity of a liquid at its boiling-point is described by R. Schiff (A.'220, 78). The liquid is introduced into a flask of about 7 or 8 c.o. capacity, provided with a long narrow neck on which is a graduated scale. The capacity of the flask up to the zero point is accurately determined by weighing with mercury, and the value of the scale divisions in fractions of a c.c. is also carefully estimated. The flask is then suspended in the boiling tube; a few c.c. of the liquid under investigation are placed in this tube and heated to boiling. After a few minutes the position of the liquid in the graduated neck is noted, and the flask is withdrawn, wiped, and weighed. The specific gravity

at the boiling-point compared with water at 4° is given by the equation

• $D_4 = \frac{1}{V_t[1 + K(t-4)]}$

in which P = corrected weight of the liquid in the flask,

and V_i = the apparent volume of the liquid at t° ,

K = the co-efficient of expansion of the glass.

It will be noticed that Schiff assumes that the liquid in the flask actually acquires the temperature of the vapour by which the flask is surrounded. Lothar Meyer (v. Neubeck, Z. P. C. 1, 652) has slightly modified Ramsay's apparatus. The bulb is best made of Jena glass, and has the capacity of about 2.5 c.c., and its weight, capacity, and thermal expansion are accurately known. It is filled with the liquid, and is suspended by means of a bent platinised-nickel wire within the flask, the neck of which can be closed by a cork. The flask contains a few c.c. of the liquid under investigation, which, when heated, may if necessary be caused to boil at any desired temperature below the ordinary boiling-point by connecting a side tube with a condenser, pressureregulator, and fall-pump. As soon as the liquid within the bulb has acquired the temperature of the boiling liquid, and no further expansion occurs, the source of heat is removed and the bulb is weighed when cold.

The specific gravity of a liquid at its boilingpoint is, however, most accurately ascertained indirectly, although this method demands far more time and apparatus, and a greater number of experimental operations, than the direct method. The method consists in accurately determining (1) the boiling-point of the liquid; (2) the specific gravity of the liquid at some convenient temperature—best at 0°; and (3) the rate of thermal expansion of the liquid from 0° up to the neighbourhood of its boiling-point. From these data the specific gravity of the liquid at the boiling-point can be readily calculated.

1. Determination of the boiling-point. This is best made in an apparatus so arranged that the inner tube, containing the thermometer, is surrounded by a jacket of vapour from the boiling liquid. The boiling liquid should contain a few scraps of platinum foil or a spiral of platinum wire; or, what is even better, a few short lengths of fine capillary tubing. If the amount of the liquid is very small the bulb of the thermometer should be surrounded with a little fibrous asbestos, as suggested by Ramsay a. Young (C. J. 47, 42). The thermometer reading must, if necessary, be corrected for the emergent column, either by the tables of Rimbach (B. 22, 3072) or by that of Thorpe (C. J. 37, 159), and should be reduced to normal pressure by the method of Crafts (B. 20, 709). The correction to standard atmosphere may, however, be ascertained with approximate accuracy by the formula

$$\theta = (p - 760) \frac{278 + t}{8200}, \text{ or } \theta = (p - 760) \frac{278 + t}{10000}$$

in which θ is the correction, t the observed boiling-point, and p the barometric pressure reduced and corrected.

The first correction is applicable to the

greater number of liquids, the second to water and the lower alcohols (Ramsay a. Young, P. M.

1885, 515).

- 2. Determination of specific gravity. This is most accurately effected, at least for substances which are liquid at ordinary temperatures, by Perkin's modification of the Sprengel apparatus. For liquids which are alterable on exposure to air a bottle with a graduated stem is most convenient. The bottle should be previously filled with dry nitrogen, and a special apparatus, analogous to that used by Thorpe (l.c.) must be employed to transfer the liquid to the bottle. A form of bottle for very viscid liquids has been described by Brühl.
- 3. Determination of thermal expansion. Of the various modes of ascertaining the thermal expansion of a liquid the so-called dilatometrical method is, on the whole, the most convenient. It consists in inclosing the liquid in a vessel of known capacity, shaped like a thermometer, and provided with a graduated and accurately calibrated stem. The instrument is placed in a bath of suitable liquid, the temperature of which can be raised to the desired point, as ascertained by a thermometer; and the height of the liquid in the stem of the dilatometer, and hence its apparent volume at the temperature of observation is noted. A series of such observations at various temperatures up to the neighbourhood of the boiling-point is thus made, from which an expression, say of the form $V_t = a + bt + ct^2 + dt^3$... may be calculated. This expression must now be corrected for the expansion of the glass of the dilatometer (obtained by observations with mercury in the usual manner), and from the corrected expression the volume, and hence the specific gravity, at the boiling-point of the liquid may be deduced.

For details of the mode of carrying out these observations v. Kopp (A. 96, 1 et seq.); Thorpe (C. J. 37, 141).

Thorpe (C. J. 63, 262 [1893]) has devised a modification of the ordinary dilatometrical method, which permits the thermal expansion of a liquid to be determined with much greater ease and rapidity than has hitherto been possible. It obviates the use of large baths, and, by reducing the size of the dilatometers to the smallest limit consistent with the proper degree of accuracy, as determined by the error of a thermometer reading, it avoids the necessity for long stems and the consequent correction for the cooled 'emergent columns.'

Results.—The first accurate determinations of the various physical constants needed to ascertain the specific volumes of liquid substances were published by Kopp in 1855 (A. 96 [1855] 1-36, 153-185, 303-335; A. 100 [1856] 19-38; v. also P. 72 [1847] 1-62, 176, 223-293). Kopp concluded, from the results of a long series of ob-

servations, that :-

(1) The selection of the temperature of equal vapour-pressures as a basis of comparison seemed to be warranted by the fact that regularities are thereby made evident which otherwise are not apparent.

(2) Differences of specific volume are proportional to differences in chemical composition.

(8) Isomeric liquids of the same chemical type have equal specific volumes.

(4) The substitution of hydrogen for an equivalent amount of oxygen only slightly affects the specific volume.

(5) One atom of carbon can replace two atoms of hydrogen without altering the specific

yolume of the compounds.

Kopp further found that the specific volume of a liquid compound was conditioned, not only by the composition, but also by the constitution of the compound. Thus the relative position of an oxygen atom in a molecule affects its specific volume; carbonylic oxygen and hydroxylic oxygen have two very different values. Sulphur, in like manner, would appear to have two specific volumes, depending on its position or mode of combination in a molecule.

Definite values for the specific volumes of carbon, hydrogen, and oxygen were obtained from the following considerations. An increment of CH₂ corresponds to an increase of specific volume of 22. Since C and H₂ occupy the same volume, we have C = 11 and H = 5·5. The replacement of H₂ by carbonylic O is attended by a slight increase in the specific volume. Kopp found that the most probable value for O in this form of combination was 12·2. For hydroxylic oxygen it is 7·8; obtained by subtracting the value for H₂ (11) from the specific volume of water, 18·8. Hence the specific volume of a compound $C_aH_bO_cO'_{d_1}$ where O is carbonylic oxygen and O' is hydroxylic oxygen, may be expressed by the formula

V = 11.0a + 5.5b + 12.2c + 7.8d.

Determinate values for the specific volumes of the halogens-and, with less precision, for phosphorus, arsenic, and antimony, for silicon, titanium, and tin-were also obtained by Kopp. As regards nitrogen it was found that in the amines $N=2\cdot3$. The group CN=28; the group NO, = 33. If, then, carbon and oxygen preserved their ordinary values in these radicles N must possess at least three different values depending on the mode of combination. There is, however, no evidence to disprove the supposition that the values for the carbon and oxygen atoms are not equally affected in these groups. This, indeed, suggests the possibility that compound radicles like CO, HO, NO2, CN, &c. may possess definite specific volumes which are not necessarily the sum of the specific volumes of the component atoms as ordinarily ascertained.

H. L. Buff (d. Suppl. 4, 129) sought to show that the specific volume of carbon, like that of oxygen and sulphur, is affected by its mode of combination-or, in other words, that carbon in unsaturated compounds has a greater specific volume than in saturated bodies-from which he surmised that the specific volume of an element is in general determined by its particular atomic value. Thorpe (C. J. 37, 392) found that isomeric liquids have not invariably the same specific volumes. There is a well-marked difference, for example, between ethylene and ethidene chlorides; indeed, ethylene compounds in general appear to have smaller volumes than those calculated by Kopp's values. Städel has shown that in the series of chlorinated and brominated ethanes and ethylenes, the isomeride of higher boiling-point, i.e. the etaylene derivative, has invariably the lower specific volume.

Since these compounds are all saturated, and the only variable constituent is a monovalent element (Cl or Br), it would appear probable that the specific volume of the halogen is also variable. Isomeric hydrocarbons manifest similar differences, whence it is obvious that either one or both of the elements must have a slightly variable volume, depending on grouping or mode of combination; it may be that the iso-group, like the groups carbonyl, hydroxyl, nitryl, &c., has a special volume, which is not necessarily the sum of the volumes of the component atoms as deduced from Kopp's values. Kopp himself found that the volumes of isomerides were in a number of cases only approximately equal, and in others quite unequal. The term 'chemical type,' used in the sense in which Gerhardt employed it, is not sufficiently distinctive to denote the differences, say, between the normal and iso-compounds, or between aniline and the picolines, and it is questionable whether Kopp would have considered such cases as coming within his rule.

The observed specific volumes of the aromatic compounds are frequently lower than the calculated values. Indeed, our views as to the constitution of the aromatic compounds would lead us to expect that the specific volume of benzene, and the volumes of the derivatives which contain the benzene grouping, would probably be different from the values deduced from observations made for the most part on compounds of totally different constitution. Kopp (A. Suppl. 5, 303 [1867]) showed from Louguinine's observations that while benzene has an abnormally low specific volume, its homologues show the constant increase of 22 for an increment of CH., which is what might be anticipated, since these homologues are produced by the addition (substitution) of methyl, ethyl, &c., to the benzene group. Jungfleisch's observations on the specific volumes of the chlorine substitution products of benzene also seem to show that the positions of the chlorine atoms affect, in a very marked manner, the specific volume of the product (C. R. 64,

911). Further observation has shown that Kopp's conclusion that liquid elements and radicles have the same volume in combination as in the free state is well founded. Thus the observed volume of NO₂=32·0, calculated = 31·5; observed volume of Br = 53·6, calculated = 53·4; observed volume of CN = 28·9, calculated = 28·9. The observed specific volume of Cl from Knietsch's determinations of the specific gravity of liquid chlorine is 22·8; the mean calculated value is 22·7. Kopp surmised that members of the same chemical family would be found to have the same specific volume; observation shows, however, that the specific volumes gradually increase with the increase of atomic mass (Thorne, Lc.).

crease of atomic mass (Thorpe, l.c.).

Schiff (A. 220, 71 [1883]) has concluded that while it is generally true that isomeric compounds have slightly different specific volumes, it is almost invariably the case that the substance possessing the higher boiling-point has also the higher specific volume (compare Städel). In the case of the metameric esters of the fatty acids, it is found that, as a rule, the specific volumes increase with the diminution of the number of carbon atoms in the acidic radicle and with the increase of the carbon atoms in the

alcoholic radicle. At the same time, it would atpear that the differences between the observed and calculated values are mainly due to the alcoholic radicle, the acidic radicle apparently having but slight influence. This is in conformity with Lossen's observations, that while the ethers and acids give experimental values which are almost in exact accordance with Kopp's values, the aldehydes and alcohols show wider variations, methyl alcohol giving too great an observed value, while the others give smaller and smaller values as the amount of carbon increases. It is, however, noteworthy that the differences between the aldehydes and derived alcohols remain almost constant, which is not the case with the aldehydes and acids, where the difference appears to increase with the molecular weight. Hence the differences between the homologous aldehydes are very nearly equal to those between the corresponding homologous alcohols (Lossen). The mode in which carbon is combined in an organic compound has, according to Schiff, a distinct influence on its specific volume; like Buff, he finds that a doubly linked carbon atom occupies a smaller volume than when singly linked. It is, however, very doubtful whether the facts at present known are sufficient to establish this conclusion.

There is, however, good reason to believe that what we call 'specific volume' is not a purely additive property. The specific volumes of sub-stances are, in all probability, affected by many more conditions than those we have hitherto taken cognisance of. The value CH2 = 22 has no other significance than as expressing the average increment in volume in successive members of a homologous series. Indeed, as the physical data increase it becomes doubtful whether even this mean value is correct. It would seem that the value augments as the series is ascended. The relation C = 2H no longer applies to carbon compounds in general. What is true of carbon and hydrogen is equally true of oxygen, whether as carbonylic or as hydroxylic oxygen. No definite or uniform values can be assigned to oxygen such that the specific volume of a liquid compound containing this element can be accurately calculated. The values given by Kopp and others are simply mean values, but the actual volumes are affected by conditions of which, as yet, we have no very precise knowledge and which we have no certain means of measuring. The values for the other elements are, of course, affected by these considerations. Thus the specific volume of chlorine is obtained on the assumption that the values for carbon and hydrogen are constant.

Lossen (A. 254, 42) has devised formulæ which take note, or express the measure, of the influences which affect the uniformity in the values of specific volumes of organic compounds. Those formulæ can only be considered as first approximations, but their value will be evident from the fact that they serve to reproduce the observed values with a greater approach to accuracy than has hitherto been possible. Out of the 407 compounds which furnished the experimental material on which these formulæ are based, the observed molecular volumes of 352 differ by less than 2 p.c. from the calculated volumes. Comparatively few of these differences are to be ascribed to experimental errors. In

the main they are caused by influences of structure and composition which as yet we have no certain means of measuring, such as the effect of substituted chlorine, or the special effect of iso- grouping, or of the ortho-, meta-, or paraposition, &c.

According to Lossen, the specific volumes of the greater number of compounds containing carbon, hydrogen, and oxygen which have hitherto been determined, may be calculated by the formula

Sp. vol.
$$G_n H_m O_p(\mu) = \{10 \cdot 24 \pm x0 \cdot 5\} (n+p) + (5 \cdot 12 \pm x0 \cdot 25m) \pm \frac{1}{4} (n-2)^2 \pm 1 \cdot 4\mu$$

In this equation x denotes a number between 0 and 1, which varies with different homologous series but which is constant for the members of the same series. The sign μ represents the number of hydrogen atoms required to convert the formula into that of a saturated compound. The term $\frac{1}{4}(n-2)^2$ is introduced to compensate for the increase in the value corresponding to CH₂ as the molecular weight increases. Gartenmeister (4. 233, 304) having shown that in the case of the fatty esters the mean increase corresponding to CH₂ is 0.5, Lossen adds the term $\left(\frac{1}{2} + \frac{2}{2} + \frac{3}{2} + \dots \frac{n-3}{2}\right)$,

which he erroneously states is equal to $\frac{1}{4}(n-2)^2$, a number always subsequently employed, but which, as comparison shows, serves to give good agreement with observed values.

For the majority of fatty compounds the formula

 $O_nH_mO_p = 10.45(n+p) + 5.225m + \frac{1}{2}(n-2)^n + 1.5\mu$

gives results agreeing with the observed values. For the alcohols, however, the expression becomes

$$C_nH_mO_p=10\cdot 1(n+p)+5\cdot 05m+\frac{1}{2}(n-2)^2+1\cdot 35\mu$$
.

If it be supposed, as seems highly probable, that for all the members of a series of similarly constituted compounds the same influences are existent, whereby the specific volumes exhibit variations from the additive quantities assumed by Kopp, then we may regard the variable x as a term which takes account, and may be regarded as the measure, of these disturbing influences, and which, though constant for the members of the same series, should, as before stated, vary for other homologous series of compounds (Thorpe a. Jones, C. J. 63, 289).

Schröder regards the specific volume of an element in combination as variable within limits determined by the nature of the chemical compound. In any one compound, however, all the elementary atoms are regarded as occupying either equal or multiple volumes. Hence every specific volume is a multiple of a certain space-unit or stere, the value of which may vary between 6.7 and 7.4, depending on the number, nature, and mode of union of the atoms. Schröder thus obtains his determinate values. The specific volumes of formic, acetic, and propionic acids increase about 22 units for each increment of CH2; in the case of alcohols the increase is about 20 units. volume of formic acid is 41.8, i.e. 2×20.9 ; that of methyl alcohol is 42.8 or 2×21.4 . Hence in formic acid, CH2O2, the O2 occupies the same volume as CH,; and in methyl alcohol, CH,O, the HO has the same volume as CH. In like

manner ethyl alcohol, C_2H_*O , has the volume 62·1, i.s. 3×20 ·7. Since $2 \times CH_2 = 2 \times 20$ ·7, then $H_2O = 20$ ·7. Acetic acid has the volume 63·6, i.s. 3×21 ·2; $2CH_2$ is 2×21 ·2 and $O_2 = 21$ ·2. The volume of acetaldehyde is 56·9, i.s. about 6·6 smaller than that of acetic acid; this would indicate that the substitution of OH by H lowers the volume by 6·6. Since $H_2O = 21$ ·4, it follows that the hydrogen and oxygen in hydroxyl each occupy one space-unit or stere. As $CH_2 = 21$, we find that carbon also occupies one stere or space-unit. Now, from the volume of formic acid which contains 6 steres, it is found on subtracting 3 steres for CH_2 and 1 stere for hydroxylic oxygen, that the carbonylic oxygen must occupy 2 steres.

We obtain, then, the following rule: The number of space-units or steres of the saturated compounds of carbon, hydrogen, and oxygen corresponds to the number of the atoms increased by as many units as there are atoms of carbonylic oxygen present.

If we calculate by means of this rule the steres of the saturated compounds, we find that they vary within narrow limits, and for the most partincrease with increasing molecular weight. In the greater number of cases the values range between 6.9 and 7.2. Ostwald has determined the value of the stere for a large number of saturated fatty compounds, with the following results:—

Hydrocarbons 6:89, 6:99, 6:82, 7:11, 7:23.
Alcohols 7:12, 6:91, 6:77, 6:88, 6:78, 6:78.

681, 6.74, 7.09

Acids . 6.97, 7.06, 7.11, 7.19, 7.24, 7.24;

Esters . 7.04, 7.08, 7.05, 7.14, 7.26, 7.43, 7.45, 7.47.

Aldehydes . 7.11, 7.05, 7.18, 7.01, 7.18, 6.93,

7.27.

In the series of the hydrocarbons, the acids, and the esters, the steres in the cases of the normal compounds increase regularly with increasing molecular weight; in the series of the alcohols the steres decrease up to the third member and then increase. The secondary and tertiary compounds have, as a rule, smaller steres than the normal compounds. Kopp concluded from the approximately equal volumes of the alcohols and corresponding acids that H, and O are volumetrically equivalent; and from the equivalence of the volumes of benzyl and amyl compounds he inferred that Co and H, are mutually replaceable without alteration of volume. Hence he assumed that the hydrogen atom occupies only half the volume of the oxygen or carbon atom. Schröder established the volume equivalence of CH2 HOH, and O'O, and he inferred from the difference in volume between alcohol and aldehyde that hydroxylic oxygen has the same volume as hydrogen and carbon, while carbonylic oxygen has twice the volume. While, then, Kopp assumes approximately $H_{z}=C=O$, Schröder makes H=C=O (Ostwald, Lehrbuch, [2nd ed.] vol. i.

In the case of unsaturated and aromatic compounds, Schröder assumes that each double linkage is attended with an increase of volume amounting to one stere; hence the above rule has to be modified in this sense when applied to compounds of this class. The value of the stere

in a number of unsaturated compounds is found

. 6.87, 7.09, 6.93, 6.99. Hydrocarbons Alcohols 6.72.

Esters and ethers . 7:14, 7:13.

These values vary, practically, within the same limits as in the saturated compounds.

As regards aromatic compounds, it would seem to follow from the identity in the volumes of benzoyl and amyl compounds, as indicated by Kopp, as well as from the corresponding relation between the isobutyl and phenyl compounds, that C.H. comprises the same number of steres as C.H. - that is, 13. Of these, 5 are occupied by hydrogen; so that the carbon group C, occupies

The values of the stere in a number of aromatic compounds are as follows:

6.85, 6.94, 6.98, 7.00, 6.95, 7.04, Hydrocarbons 7.04, 7.04, 7.06, 6.84

Other compounds 6.91, 6.87, 7.05, 6.97, 7.16, 7.26, 7.50, 7.28, 7.14, 6.96, 7.07.

The value of the stere here also varies within the usual limits; cit is comparatively small for the hydrocarbons (6.8-7.0), larger in the case of the alcohols, and still larger in that of the esters

(7.2-7.5) (Ostwald, l.c.).

There is one consideration which is vital to the whole question, and to which, therefore, a brief reference must be made. It relates to the choice of conditions under which the values we term specific volumes are really comparable. Although Horstmann and Lossen have advanced reasons against the practice, contending that at any other temperature, say 0°, relations similar to those now established are made manifest, it has been the custom, in accordance with Kopp's direction, to compare the specific volumes of liquids at the temperatures of their respective boiling-points under a standard atmosphere. Whether, however, the temperature of the boiling-point, under these circumstances, is a truly comparable condition is open to question. It has been urged by Horstmann that, since what we call atomic volume is the space not merely filled by an atom but also that in which it moves, it is not a priori probable that at temperatures which differ, say by 3000-as, for example, in the case of C_1H_{10} (boiling-point 1°) and $C_{18}H_{38}$ (boiling-point 317°)—these volumes will be the same. Moreover, as pointed out by Bartoli, the boilingpoint cannot in the nature of things be a strictly comparable condition, since it is affected by pressure to a different extent in the case of different liquids. Objections of even greater weight may be urged against the suggestions of Tschermak and Krafft to take the melting-point as a comparable state.

No doubt, theoretically speaking, a valid condition should be when pressure, volume, and temperature are expressed in terms of their critical values. But that certain regularities in the molecular volumes at the boiling-points have, in spite of this, been discovered may be explained, as Guldberg has shown, when we compare the values of T, the absolute boilingpoint, with those of T, the absolute critical temperature; in those cases in which these two constants are known, the ratio $\frac{\mathbf{T}}{\mathbf{T}}$ approximates

to $\frac{2}{8}$. Hence it follows that qualities like molecular volumes, which alter only slowly with temperature, are comparable at the ordinary boiling-points (Z. P 0.5, 374).

It ought, perhaps, to be stated that subsequent observations show that the so-called 'corresponding temperatures' deduced from Van der Waal's generalisations have not that dogree of validity as temperatures of comparison which they were originally assumed to possess. Indeed, the present condition of knowledge warrants the statement that Kopp's original method of comparison is as valuable as any yet indicated (Thorpe, C. J. 63, 775 [1893]). T. E. T. SPECTROSCOPIC ANALYSIS v. PHYSICAL

METHODS, section Optical methods, subsection Spectroscopic methods, this vol. p. 239.

SPELTER. A commercial name for zinc. SPERGULIN (C,H,O2)n. Occurs in the seedcoverings of Spergula vulgaris and S. maxima (Harz, C. C. 1879, 24). Amorphous. Its alcoholic solution exhibits dark-blue fluorescence, which is destroyed by sunshine. A small quantity of potash or Na₂CO₃ added to the al-coholic solution causes it to fluoresce green. Conc. H₂SO₄ forms a dark-blue liquid.

SPERMINE $C_{10}H_{20}N_4$ (Poehl, B. 24, 359); $C_4H_{10}N_2$ (S.). Occurs as phosphate in the spermatic fluid, in calves' liver and heart, and in some pathologic preparations that have been kept under alcohol (Schreiner, A. 194, 68). It is not identical with pyrazine hexahydride (Majert a. Schmidt, B. 24, 241; cf. Ladenburg, B. 20, 442; 21, 758; Poehl, C. R. 115, 515; Duclaux, C. R. 115, 155, 549). Crystals (from alcohol), v. sol. water, v. sl. sol. alcohol. Alkaacconory, v. soi. water, v. si. soi. acconor. Alkaline in reaction. Absorbs CO₂ from the air. Its aqueous solution is ppd. by phosphomolybdie acid and by potassium bismuth iodide. — C₁₀H₂₀N₄H₄HCl: prisms, v. e. sol. water. — C₁₀H₂₀N₄2H₂PtCl₈.— C₁₀H₂₀N₄4HAuCl₄.— C₁₀H₂₀N₄(H₂PO₂)₂6aq: [170°]; rosettes of pyrawided as bot water. mids, sl. sol. hot water.

SPIKE 01L. S.G. above 900. Slightly dextrorotatory (Schimmel, Ph. [3] 22, 329). [a]_D = 1° 24' (Voiry a. Bouchardat, C. R. 106, 551) or laworotatory (Bruylants, J. Ph. [4] 30, 139). An essential oil obtained from the blossoms of Lavandula aspica latifolia (Lallemand, A. 114, 197; Sauer a. Grünling, A. 208, 75). Smells like lavender. Contains a terpene (175°) or (158°), which yields crystalline C₁₀H_{1s}HCl, camphor, borneol, and a resin. According to Voiry and Bouchardat, oil of spike contains inactive spikol $C_{10}H_{10}O$ [0°] and $C_{10}H_{10}$ (155°-160°) [a]_D = 24°, which yields a hydrochloride [129°] [a]_D = -2°.

SPIROGRAPHIN v. PROTEÏDS, Appendix C. SPONGIN v. PROTEÏDS, Appendix C.

STACHYDRIN C,H15NO2. [210°]. Occurs with glutamine, tyrosine, and stachyose in the tubers of Stachys tuberifera (Von Planta a. Schulze, B. 26, 939). Colourless, deliquescent crystals (from water). Behaves like betaine with regard to alkaloidal reagents.—B'HCl. Prisms, v. sol. water, sol. cold water (difference from betaine).—B'2H.PtCl22aq. Trimetricorystals; a:b:c=:608:1::828.—B'HAuCl2. Small yellow prisms (from water).

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STACHYOSZ C_{1.}H_{2.2}O_{1.5} Saq. [a]₀ = 148°. Ocours in the roots of Stachys tuberifera (Planta a. Schulze, B. 28, 1692; 24, 2705). Tablets, with sweetish taste, v. sol. water. Destrorotatory. Has no action on Fehling's solution until after boiling with mineral acids, by which it is converted into galactose and an isomeride (? glucose). HNO₂ forms mucic acid, galactose, glucose, and cane-sugar. Gives a red colour on heating with resorcin and HClAq. Gives no pp. with lead acetate until NHAq is added.

STANNATES, and salts related thereto; v. under Tin.

STAPHISAGRINE v. DELPHININE.

STARCH. Amylum. $nC_{12}H_{20}O_{10}$. The value of n has not been definitely settled; it is undoubtedly high. Brown and Morris (C. J. 55, 462), employing Raoult's method for determining molecular weights, show n for soluble starch (see below) = 100, i.e. molecular weight = 32,400. The molecular weight of starch cannot be less than this. From O'Sullivan's work (C. J. 35, 783) it would seem that n is not less than 36. Pfeifer a. Tollens (B. C. 1882, 775; A. 210, 295), from the composition of some sodium and potassium compounds prepared from starch, arrive at the value n=2; the substances are probably compounds, not of starch, but of some decomposition products thereof. Sachsse (C. C. [3] 8, 732) and Nägeli (A. 173, 218) proposed 6C₈H₁₀O₈ + H₂O₈ sthe formula. Other observers (Mylius, B. 20, 694; Salomon, J. pr. [2] 28, 82) have suggested different formulæ, but the evidence is not satisfactory; we may take it, however, that the molecule of starch is not less than n = 100.

Occurrence.—Statch is present at some time or the other in all green plants. It is said to be found in almost all parts of the plant, but it is specially stored up in seeds, the pith of stems, in bulbs, tubers, rhizomes, and roots—generally those parts of the plant which serve as a store for reserve material. It is, however, a question whether the granules recognised as starch in leaves, sap, &c., outside the reserve organs, are chemically identical with the starch of these organs. The evidence, one way or the other, is unsatisfactory. Starch is not known to be an animal product. It is present in some fungi (Bourquelot, J. Ph. [5] 24, 197).

Formation.—Starch has not been prepared artificially. It is produced in the chlorophyll cells of plants, light, carbon dioxide, and water being necessary; oxygen is eliminated at the same time. No doubt, intermediate products—amylan-like bodies, sugars, &c.—are at first produced, but the granules are the first visible products of the assimilation found in the leaves. The starch thus formed is transferred to the reserve organs as such, or, more probably, as some sugar or other transformation product or products, as leaves are known to contain transforming agents (Baranetzky, Die stärkeumbildenden Fermente in den Pfanzen, Leipzig, 1878; Brasse, C. R. 99, 878).

Preparation.—Starch of commerce is prepared from various sources—viz., amongst others, wheat, rice, maize, potatoes, Maranta indica (American starch), Maranta arundinacea (arrowroot), the roots of Jatropha Manihot or Manihat utilissima (tapioca), the stems of several species of Sagus or Oycas (sago). For manufacturing methods see Thorre's Diotionary, art. 'Starch.' In the laboratory, starch can be prepared from any starch-containing material as follows:—

From materials that can be ground, such as the cereals, &c., wheat, barley, maize, rice, &c. The material is ground in a coffee-mill, and the meal steeped in a 0.6 to 1 p.c. sel. KHO or NaHO. After standing 24-36 hours the coarser portions are separated by straining, with rubbing, and a slight flow of water through a wire sieve of about 20 wires to the inch. The strained milky liquid is allowed to stand for a short time, when a layer of crude starch settles at the bottom of the vessel. The liquid, with the matter in suspension, is transferred to another vessel, and again allowed to stand, when a second deposit of crude starch takes place. The process may be repeated a third and a fourth time. The whole of the suspended matter is thus allowed to settle, when the fairly clear supernatant liquid is decanted off and rejected. The deposit is then rubbed through a fine hair sieve, with a slight flow of water, and allowed to deposit a layer of starch as before. This is repeated as long as a starch layer separates. The whole of the starch layers are then collected, again suspended in water, and allowed to settle. At times a layer contaminated with much brown matter falls out first; from this the supernatant liquid with the starch in suspension is decanted off and allowed to stand, when a fairly pure deposit of starch is obtained. Further crops can be got from the residue, but it is difficult to free them from fibre, &c.

From nuterials that cannot be ground, such as potatoes, bulbs, rhizomes, other roots, and pith. The well-washed material is rubbed down with a grater into water, to which atterwards the alkali is added. The first deposit in these cases contains, as a rule, earthy matter, but it is easily separated by allowing it to settle, which it does in a short time, and then decanting off the starchy liquid. Two or three depositions and strainings through a fine hair sieve give a clean starch.

In dealing with the cereals the starch can be separated by what is known as the acid process. The meal is steeped in water and kept at a temperature of from 25° to 27° until acid is developed. On then stirring up with water the light flocculent cell walls and undissolved albuminoids separate and allow the starch to deposit on standing. By repeated suspensions, stirrings, and depositions, clean crops of starch are obtained.

These products, like the starches of commerce, are not pure, but, as a rule, contain ash, oil or fat, albuminoids, &c. Some of them are slightly alkaline, some acid, from the condition of the water used in the last washing. Purification is effected by treatment with dilute KHO solution (0.5 p.c.), then diduct HCl (up to 1 p.c.), then with strong alcohol, and finally with water. They then can be dried by exposure to the air on layers of filter-paper.

Structure.—The starch thus obtained varies much in appearance, from the glistening silky white of potato starch to the dead chalky white of rice or maize starch. It consists of microscopic granules, varying in size from about 0.2

KAA STARCH

mm. to 0.002 mm. The same plant always yields granules of specifically the same size and shape, with as little variation as the size and shape of the leaf, hence, from the microscopic appearance of the granules, it is always possible to tell the source of a sample of starch. If it is wished to determine the source of any sample of starch, the following classification of the starches will be of some use. If, under the microscope, the granules are

(a) large, rounded, and more or less marked with rings: the starch may be potato, tapioca,

sago, &c.

(b) rounded, very slightly ring - marked: barley, rye, wheat, &c.
(c) reniform: beans, peas, &c.

(d) intermediate in size, rounded, and irregular : crocus, tulip, and other bulbs.

(e) irregular in figure, bounded by surfaces more or less plain : maize, oats, rice, &c.

(f) small granules, rounded or irregular:

fern, chestnut, parsnip, &c.
It will be observed that some of these are round, oval, or reniform, while others are irregular figures-bounded by surfaces more or less plain. The microscopic appearance does not always give the true form of the granule. but a form which is the result of the pressure of the cover glass; for example, the well-marked star with central spot in rye starch and the split and striated appearance of maize starch are produced by the pressure of the cover glass on the granules. The granules of some starches are marked with well-defined more or less concentric rings, well shown in potato starch; in others there are no markings, the granules appearing as a clear, transparent cell. It is not absolutely agreed upon whether the starch granule consist of a single body or is made up of two or more. Some hold that the properly purified granule is a single substance, the coating or layers of which differ from the contents simply in containing less water and being thus more dense. According to Nägeli (Die Stärkekörner) and others, the dense portions consist of starch cellulose, while the less dense, transparent plasma is granulose. The stratified structure is the result of the mode of growth of the starch granule, the additions being made by intussusception, i.e. from within outwards. It is said that when the granule is ruptured the granulose dissolves in cold water, leaving the starch cellulose; the former gives the well-known blue reaction of starch with iodine, while the latter is only coloured yellowish (Jessen, P. 106, 497; J. pr. 105, 65; Brown a. Heron, C. J. 35, 610; Brukner, M. 4, 889). On heating the insoluble portion with water it also gives the characteristic blue reaction with iodine. Granulose may be separated from starch cellulose (a) by digesting the granules for several days with a saturated solution of NaCl containing 1 p.c. HCl—the cellulose remains undissolved (F. Schulze, Henneberg's Jour. Landwirth., new ser., 7, 214); (b) by digesting starch with saliva at 45°-55°, this dissolves the granulose (Nägeli, Die Stärkekorner, 110; (c) by the action of certain schizomycetes, which decompose the granulose of starch-paste and leave the cellulose untouched (Fitz, B. 10, 282); and (d) by the action of malt-extract on starch paste in the cold, the cellulose is left undissolved.

A. Mayer (C. C. 1887, 6; Bot. Zeit. 1886, 698) considers that the starch granule is a homogeneous substance, and that the terms 'granulose' and 'starch cellulose' must be abandoned, for he points out that the delicate transparent skeletons left when the gelatinised granules are acted on by saliva, dilute acids, &c., are produced by the action of the reagent on the starch, and are identical with amylodextrin. I am inclined to the view that starch granulose differs from starch cellulose in being less dense in consequence of containing less water of hydration. Starch granules act on polarised light, and when examined with the microscope between two Nicols. produce very pretty effects; v. Bailey (P. M. [5] 2, 123).

Properties .- Air-dried starch sometimes contains over 20 p.c. H.O; this it loses, slowly towards the end, in a vacuum over sulphuric acid; by gradually raising the temperature to 100°, under these conditions, it soon becomes absolutely free from H₂O. The specific gravity of air-dried starch varies very considerably, the variation being due in the main to the quantity of moisture. Dry starches, however, would appear not to be absolutely alike in specific gravity; that of anhydrous potato starch is 1.650, whilst anhydrous arrowroot starch is 1.5648 (Flückiger, Fr. 5, 305; Saare, J. 1884, 1654). Dry starch takes up water, with the evolution of much heat. It does not dissolve in H.O, and has neither taste nor smell.

(a) Action of heat. Dry starch is not coloured at 100°, and, indeed, the temperature can be increased considerably beyond that point without being changed. Starch containing water is, however, coloured by a moderately low temperature, and if the heat be increased to 160° a soluble product is obtained which is known as dextrin or British gum. It is a mixture of undescribed composition. The action of heat on dry starch has not yet been accurately recorded. When the heat is increased beyond 160°, and destructive distillation begins, carbon dioxide, gaseous hydrocarbons, water, acetic acid, and an empyreumatic oil are evolved, and finally a carbonaceous porous cinder is left.

(b) Action of water. As long as the granules are uninjured, starch is insoluble in cold water; when, however, the water is heated, the granules swell up, and a gelatinous, more or less transparent mass, known as starch-paste, is produced. This varies in transparency with the starch employed, as does the temperature at which the gelatinisation takes place. E. Lippmann (C. C. 1861, 859; J. pr. 83, 51) gives the following table on this point:

Source	Swelling-up temp.	Commencement of gelatinisation	Perfect gelatinisa- tion
Rye	45°	50°	55°
Maize	- 50°	55°	62·5°
Barley	87·5°	57·5°	62·5°
Potato	46°	59°	62·5°
Rice	54°	59°	68°
Wheat	60°	65°	67·5°

If the paste is sufficiently dilute it can be filtered, but it is doubtful if the filtrate is a true solution (Picton a. Linder, C. J. 61, 156). The consistency or stiffness of starch-pastes, containing the same amount of dry starch, seems to

vary with the variety of starch employed, and, indeed, with the method of preparation, even with the same starch; but I feel inclined to think that if closer attention were given to the amount of dry starch and its purity much of this apparent difference would disappear. On the relative stiffness of flour or starch pastes, and the mode of estimating it, see Thomson (S. C. I. 1886, 143). If the paste be heated under pressure to temperatures above the boiling-point, maltose and dextrin are said to be produced, but the change has not been accurately studied.

(c) Action of glycerol. Starch heated with glycerol to 190° is dissolved; alcohol ppts. soluble starch from the solution. If the heating be continued at 200°, dextrins are formed (Zulkowski, B. 13, 1895; 23, 3295; C. C. 1888, 1000).

(d) Action of acids. Moderately strong HCl in the cold converts starch, in a few days, without changing materially its microscopic appearance, into a modification perfectly soluble in water. This body is identical with soluble starch prepared by the limited action of malt extract on starch paste (C. Lintner, J. pr. 34, 378; Brown a. Morris, C. J. 55, 450). Prolonged action of 12 p.c. HCl in the cold produces amylo-dextrin (Nägeli, Beiträge z. Kenntniss d. Stärkegruppe; Brown a. Morris, C. J. 55, 450). Boiling dilute acids convert starch, first into soluble starch, then into dextrin and maltose, intermediate products, amyloins, are said to be formed (Brown, Morris a. Moritz, E. P. No. 1809 of 1889), and finally dextrose. The complete conversion takes place the more quickly and perfectly the higher the temperature and the longer the period of the reaction (Allihn, J. pr. 22, 46; D. P. J. 250, 534). This is only accomplished by employing diluted acid. Carbonic acid, oxalic acid, &c., act like HCl and H₂SO₄, but less energetically. For the manufacture of dextrose (glucose) from starch, vide THORPE'S DICTIONARY. The action of acids has been studied chiefly by Kirchhoff, Guérin-Varry, Payen (see Gm. K.), Musculus (A. Ch. [3] 60, 203; J. pr. [2] 28, 496; Bl. 30, 4;; O'Sullivan (C. J. 25, 581); Musculus a. Gruber (C. R. 86, 1459; Bl. [2] 30, 51); Bondonneau (C. R. 81, 972); Salomon (J. pr. [2] 25, 348; 26, 342; 28, 32 a. 122); Sachsse (C. C. [3] 8, 732); Schulze (J. pr. [2] 28, 311); Sostegne (G. 15, 376); Seyberlich a. Trampedach (C. C. 1887, 376); Nigeli (Stärkegruppe, Leipzig, 1874, 83, 99). As a summary of this work it may be stated that dextrose is the final product, but that acids act on this, to some extent yielding products still imperfectly investigated; that intermediate substances, dextrin and maltose and compounds thereof, are first produced; that the rapidity of the change varies with the strength of the acid, with the temperature, and with the pressure at which the change is effected, the most complete and perfect production of dextrose resulting when the conversion is hastened under pressure in presence of a small percentage of acid, 11 to 2 p.c. or less, and the proportion of dry starch to dilute acid does not exceed 1 to 3. Gallasin (C. Schmitt a. Cobenzl, B. 17, 1000; Rosenbek, B. 17, 2456), a gummy body, is found in commercial glucose. This is identical with isomaltose obtained by Fischer (B. 28, 3687) by the setion of strong HCl on dextrose (Scheibler a. Mittelmeier, B. 24, 301).

Action of diastase (malt extract). Diastase does not act on ungelatinised starch in the cold (O'Sullivan, C. J. 80, 133; Brown a. Heron, C. J. 35, 596), but Kjeldahl has shown that this is not true of all starches. This is probably due to some condition of the starch connected with the state of ripeness of the material whence it was obtained. The action, and the products thereof, of diastase on starch paste has been the subject of much study, but as yet only the broad facts are agreed upon. When starch paste is heated to 60° or thereabouts, and a little prepared diastase solution or cold water extract of malt added, the pastiness begins immediately to disappear, the solution rapidly loses the power of giving a blue colour with iodine. and acquires, for a short time, the property of giving with that reagent a deep reddish-brown colour. This, too, it rapidly loses if the diastase is in sufficient quantity. The solution is then perfectly clear when some starches are employed, with others there is more or less flocculent suspended matter in a clear solution. In the cold this dissolution takes place slowly. So far the reaction can be followed with little trouble, but when it comes to a question of the products of the action, the subject becomes more difficult. Musculus (A. Ch. [3] 55, 203) states that when diastase dissolves starch paste at 70°-75°, the products consist of 1 mol. sugar and 2 mols. dextrin, and that no further action takes place. Payen (A. Ch. [4] 4, 286) asserts that more than 50 p.c. of the solid matter dissolved by the reaction is sugar, and says (A. Ch. [4] 7, 382) that four samples taken from an operation in the space of $1\frac{1}{2}$ hours contained 17.9, 20.9, 25.8, and 26.03 p.c. sugar on the total solids dissolved. Schwarzer (J. pr. [2] 1, 212) agrees with Musculus in finding equivalent quantities of dextrin and sugar in solution, but differs from him in supposing that dextrin is formed first, then sugar, and that the action ceases when definite equivalent proportions are produced. He says less sugar is produced at 65° than at lower temperatures; above 65°-70° the proportion of sugar to dextrin is as 1 eq.: 3 eqs.; below 60°, when the principal phase of the reaction is finished. the dextrin and sugar are in the proportion of 1 to 1. The change was considered complete when the solution no longer gave a colour with iodine. These investigators took the sugar as dextrose and estimated the dextrin by difference. O'Sullivan (C. J. 25, 581; 30, 137) showed that the sugar produced was not dextrose but maltose, and that the method of estimating the dextrin was wrong. He also demonstrated that dextrin and maltose were the invariable products of the transformation, and that by continuing the action the whole of the dextrin could be converted into maltose. It was, however, indicated in this work that another body-from which it was impossible to eliminate the cupric reducing power, and which seemed to be a mixture of maltose and dextrin-was amongst the products. Although this work laid the foundation of all that has since been done in the transformation products of starch, it received for a time no attention from the Continental chemists. Musculus (Bl. 22, 32) states that the saccharification of starch paste with diastase ceases when half the matter in solution is sugar. He attri-

butes his original impression that only one-third was converted into sugar to the varying structure of the starch granules, the coating of one variety offering a greater resistance to the action of the diastase than that of another. He still holds that the action is a molecular splitting-up of the starch molecule, attended with hydration, into dextrin and sugar. Bondonneau (C. R. 81, 1212) concludes that the action is not a splitting-up, but that the starch molecule must pass through four isomeric modifications, viz., amylogen [α]_D = +216°, α-dextrin = +186°, β-dextrin = +176°, and γ -dextrin = +164°, before it arrives at the end-product, glucose. These bodies increase in cupric-reducing power as they descend to the final product. Petit (Bl. 24, 519) mentions, as a constituent of the transformation products, a sugar soluble in alcohol, fermentable, and without action on alkaline copper solution. This is, undoubtedly, to be traced to the fact that maltose does not reduce as much copper oxide as dextrose. O'Sullivan (C. J. 30, 125; 35, 770) showed conclusively when working under clearly-defined conditions that maltose and dextrin were the only products of the action, although, as stated, he pointed out the presence of a body which gave a reduction with copper oxide equal to 9-10 p.c. dextrose. The opticity of this body ([a]_j = $+204^{\circ}-206^{\circ}$) was such as to indicate a mixture of 12.3-15.3 p.c. maltose from the reduction, and the remainder dextrin. He concluded that if the amount of reduction of the products be calculated as maltose, and the opticity due to this be subtracted from the total opticity observed for them, the remainder will agree with the activity of an amount of dextrin obtained by subtracting the determined maltose from the total products. He further showed that: (a) malt extract begins to dissolve starch at the temperature of gelatinisation, or a few degrees lower; (b) perfectly gelatinised starch is almost completely dissolved in the cold (10°-20°); (c) at 63° the action takes place according to the equation

A.
$$C_{18}H_{30}O_{18} + OH_2 = C_{12}H_{22}O_{11} + C_6H_{16}O_8$$
; Starch $Maltose$ Dextrin (d) at 64° - 70° to B. $C_{18}H_{30}O_{15}$ $+ OH_2 = C_{12}H_{22}O_{11} + 4C_8H_{10}O_5$; Starch $Maltose$ Dextrin (e) at 70° - 71° $(C.~J.~1879)$ to B^* . $C_{72}H_{120}O_{26} + 3OH_2 = 3C_{12}H_{22}O_{11} + 6C_6H_{16}O_5$; (f) and 71° - 75° to $C.~C_{72}H_{120}O_{26} + OH_2 = C_{12}H_{22}O_{11} + 10C_6H_{16}O_5$; (g) and he stated that although the proportions

(g) and he stated that although the proportions of maltose and dextrin indicated by these equations are easily obtainable when the strict conditions are adhered to, it was only necessary to vary the proportions of malt extract and starch, and time and temperature, to obtain with ease products containing from 16 to 92 p.c. maltose. It is further pointed out that the final product, maltose, was very slowly converted into dextrose by some samples, at least, of malt extract. O'Sullivan (C. J. 85, 770) showed that soluble starch was the first product of the action, and that the changes afterwards brought about may be styressed:

B.
$$C_{72}H_{120}O_{60} + 2OH_2 = 2C_{12}H_{22}O_{11} + C_{48}H_{50}O_{46}$$

B'. $C_{72}H_{120}O_{60} + 3OH_2 = 3C_{12}H_{22}O_{11} + C_{38}H_{50}O_{66}$
 $C_{72}H_{120}O_{60} + 3OH_2 = 3C_{12}H_{22}O_{11} + C_{38}H_{50}O_{56}$
 $C_{72}H_{120}O_{60} + 4OH_2 = 4C_{12}H_{22}O_{11} + C_{24}H_{40}O_{26}$
and finally:
 $C_{21}H_{10}O_{20} + 2OH_2 = 2C_{12}H_{22}O_{11}$.

From the action of malt extract on these products he concluded that it is possible that only one β-dextrin exists. The theory of splitting up and breaking down of the starch molecules, as represented by the equations, does not account for all the facts eliminated. A theory which arranges all the molecules in solution in groups, dependent one on the other-and capable, therefore, of undergoing a simultaneous change, on of being moved at the same time-and the re-arrangement of these groups attendant upon the hydration of a definite proportion of the molecules in each of them, is more in accord with the eliminated facts. Märker (L. V. 22, 69) states that at 60° four molecules starch yield three of maltose and one of dextrin, at 65° there is less maltose, and at a higher temperature two molecules starch yield one of maltose and one of dextrin. Musculus and Gruber (Bl. 30, 54) look upon starch as a polysaccharide containing at least five times the group C12H20O10. When this is acted upon by diastase, or dilute acids, it is broken down with hydration into maltose and a dextrin containing a C12H20O10 group less than starch; that this dextrin is broken down in the same way, maltose and a dextrin containing a C12H20O10 group less than the first one, and so on through the series by successive stages, until finally the solution contains only maltose. They point to the existence of three dextrins giving no reaction with iodine, and call them a, β , and γ achroo-dextrins. From the optical activity and K they attribute to these bodies, they do not agree with O'Sullivan; these factors do not agree with those of a mixture of maltose and dextrin. Brown and Heron (C. J. 35, 596) have eliminated out of the possible varying proportions of maltose and dextrin indicated by O'Sullivan eleven distinct transformations: viz. soluble starch, erythro-dextrin a and β , achroo-dextrins a to η , and maltose. They agree with O'Sullivan that the dextrins are without action on alkaline copper solution. and that the dextrins and maltose are the only products of the reaction. They do not mention the body from which O'Sullivan could not eliminate the reducing power, and they did not observe dextrose amongst the final products with malt extract. They agree with him that the higher the temperature at which the transformation takes place the less maltose is found amongst the products. They represent the normal reaction taking place between 10° and 60° by the equation

 $10O_{12}H_{20}O_{10} + 8H_{2}O = 8C_{12}H_{22}O_{11} + 4C_{6}H_{10}O_{3}$ Starch Maltose Dextrin

They consider the starch molecule to be at least $10C_{12}H_{20}O_{10}$, and that the hydrolysis of it begins by the formation of maltose and erythro-dextrin a, containing $9C_{12}H_{20}O_{10}$; that this, in its turn, yields maltose and erythro-dextrin β , $8C_{12}H_{20}O_{10}$, and so on to the end—product, maltose, They thus agree with Musculus and Gruber as to the

character of the action, but disagree with them is to its quantitative nature.

Herzfeld (B. 12, 2120; 13, 3469) agrees with O'Sullivan and others that erythro- and achroo- dextrins are without reducing power on copper solution, but he points to the presence of a substance amongst the transformation products which seems to hold a position between dextrin and maltose; he names it malto-dextrin. K=about ½ maltose, [a]₁ = +171.6°; thus K corresponds to 33.3 p.c. maltose. A mixture consisting of one-third maltose and two-thirds dextrin would have an opticity [a]₂ = +199°; hence this contradicts the statement of O'Sullivan, confirmed by Brown and Heron, that, taking the reducing power as maltose, the opticity of the remainder of the transformation products corresponds to dextrin. Herzfeld considers that Bondonneau's \(\gamma\)-dextrin is maltodextrin.

Brown a. Morris (C. J. 47, 527) confirm the presence of malto-dextrin, but they show that Herzfeld was dealing with an impure body, and that when its true K and $[a]_1$, viz. K = 211 and $[a]_1 = +193\cdot1^\circ$, are examined it is found that they correspond with a mixture of maltose and dextrin. It is completely converted into maltose by malt extract at 50° to 60°. They do not agree with Herzfeld that it is a hydration product of dextrin, but hold that it is produced from starch and the polymeric dextrins by the fixation of a molecule of water upon the ternary group $(C_{12}H_{20}O_{10})_3$, thus $\left\{ \begin{matrix} C_{12}H_{20}O_{10} \\ (C_{12}H_{20}O_{10})_3 \end{matrix} \right\}$. They have discarded the series of equations, and consider that equilibrium is attained when a condition of things represented by the equation

 $10C_{12}H_{20}O_{10} + 8H_{2}O = 8C_{12}H_{22}O_{11} + 2C_{12}H_{20}O_{10}$ Starch Maltose Dextrin is arrived at. This is always the result when the change takes place at 50° to 60°, or when a higher transformation-product is degraded at that temperature. This degradation is due to the hydrolysis of the more complex polymeric dextrins and malto-dextrin. Bourquelot (C. R. 104, 576) looks upon the action of diastase on starch as a successive fixation of a water molecule with the production of maltose and a lower dextrin until the reduction of the degraded products is K=51.52 (about 82.5 p.c. maltose), but he does not describe his dextrin or dextrins, and he concludes, as has already been clearly proved, that heat alters, not alone the quantity of diastase, but the quality.

Brown and Morris (C. J. 55, 462), from determination of the molecular weights of some of the transformation products, conclude, as suggested by O'Sullivan in 1879, that the dextrins are metameric, and not polymeric, as they hitherto considered them. They therefore abandon their former theory of the hydrolysis of starch by disatase, and, as far as I can see, come to a broad agreement with the theory enunciated by O'Sullivan. They mention another product, amylo-dextrin, $[a]_1 = +206^\circ$, $K = 9^\circ$ 0. Like malto-dextrin, it appears to be a compound of maltose and dextrin, $\{C_{12}^{14}H_{22}^{-0}O_{13}\}_{s}^{1}$. Its opticity and K agree with the body described by O'Sullivan in 1872, and mentioned above.

A new phase has been given to the trans-

formation by C. J. Lintner (Zeit. ang. Ch. 1892, 263). He says he has isolated a body, which he calls isomaltose, from amongst the products. It is less fermentable and less soluble in alcohol than maltose, with $[a]_D = +139$ and K = 52, the opticity being nearly that of maltose and the reducing power about 84 p.c. thereof. Diastase converts it into maltose completely.

Since the publication of the above Morris a. Wells (Transactions of the Institute of Brewing, 5, 133), and Moritz (ibid. 4, 141) point to the presence of a whole series of amyloins or malto-dextrins amongst what they call restricted starch-conversions, and they assert that isomaltose is a low amyloin—i.e. one in which the maltose constituent largely predominates. These amyloins begin with a high proportion of the dextrin residue, and end with a high proportion of maltose. Their optical activity and reducing power are such as would be yielded by mixtures of maltose and dextrin.

Schifferer (In. Dissertation, Basel) denies in toto the existence of the amyloins, and asserts that nothing is to be found amongst the products of the action of diastase on starch but achroo-dextrin, isomaltose, and maltose. His dextrin, however, is a reducing dextrin; even otherwise, the work will not bear criticism.

Action of other enzymes. Ptyslin (ptyslase). This enzyme of saliva liquefies starch paste (Nügeli, Die Stärkektörner, p. 113; Lefberg a. Georgieski, Bl. [2] 25, 393; Dobroslavine, Bl. [2] 26, 452; Maercker, L. V. 22, 69; Watson, C. J. 1879, 539; Musculus a. De Mering, Bl. [2] 31, 105; Lea, J. Physiol. 11, 226). The products are maltose, a reducing, unfermentable dextrin, and a little dextrose. Ungelatinised starch is not acted upon by ptyslase; at a temperature slightly below the gelatinising point the starch is dissolved, and the action is most rapid when the ferment acts at 60° on previously-boiled starch paste (Bourquelot, C. R. 104, 71 a. 177).

Enzymes capable of dissolving starch have been observed in the pancreatic juice (Brown a. Heron, Pr. 1880, 394), in the small intestine (Hoppe-Seyler, Phys. Ch. 275; Brown a. Heron, l.c.), in the liver (Wittich, Pf. 7, 28; Bernard, C. R. 85, 519; Abele, Th. J. 6, 271), and in many other animal tissues (Ellenberger a. Hofmeister, Th. J. 12, 501; Paschutin, Th. J. 1,304). The stomach, pancreas, and peritoneal lymph of fishes contain an enzyme capable of dissolving starch (Richet, Th. J. 14, 359; Kruckenberg, Unter. Phys. Inst. Heidelberg, 1, 2). Blood contains a diastatic enzyme, for starch injected into the blood yielded maltose and dextrin (Binmerman, Pf. 20, 201; Ploz a. Tiegel, Pf. 6, 249).

Starch-dissolving enzymes exist in the leaves and other parts of most plants (Baranetzy, Die stärkeumbildenden Fermente in den Pflansen, Leipzig, 1878; Vines, Ann. Bot. 1891, 409).

Certain organisms, bacteria, moulds, &c., are capable of secreting an enzyme or enzymes having the power of dissolving starch. The nature of the dissolution products has, as yet, been very imperfectly studied; we have simply the general statement that they are sugar or sugars and dextrin (Wortman, Z. P. C. 6, 287; Fitz, B: 10, 282; Marcons, C. R. 95, 345 a. 856; Gayon a. Dubourg, C. R. 103, 885;

STARCH:

Atkinson, Pr. 82, 299; Takamine, E. P. 5700 a. 17874, 1891). Bacillus amylobacter yields dextrin and a small quantity of a crystalline body (Villiers, C. R. 112, 485 a. 113, 144 a. 536). Under the influence of Bacillus suaveolens, dextrin, glucose, alcohol, aldehyde, formic, acetic, and butyric acids are produced. Amylic alcohol is the result of the action of Bacillus amylosymicus, no doubt intermediate bodies; dextrin and sugar are at first produced. Atkinson states that the moulds grown on steamed rice in the manufacture of saké, in Japan, secrete an enzyme, which first converts starch into dextrin and maltose, and further acts on the maltose and dextrin, with the production of dextrose.

Some gums of the arabin group contain a starch-dissolving enzyme (O'Sullivan, C. J. 1891,

1061).

Maize, malted and raw, and other grains contain an enzyme capable of dissolving starch and yielding as a final product dextrose (Cuisinier, C. C. 1886, 614). Its action on starch is not very vigorous, but it acts more rapidly on dextrin and converts maltose very rapidly into dextrose (Geduld, Wochenschrift f. Brauerei, 8, 620; Lintner, Zeit. f. ges. Brau. 1892, 123). It would be interesting to determine in what respect this enzyme differs from that of the moulds, and to establish their separate existence.

Action of the halogens. Chlorine does not stain starch. Bromine colours it yellow. Iodine gives with it an intense blue. This reaction is a distinctive test for starch. The colour is destroyed by heating, but returns on cooling; but if the solution be boiled for some time, the colour does not reappear. The blue colour is also discharged by arsenious and sulphurous acids, by alkalis and carbonates thereof, and, indeed, alcohol can remove the iodine. A solution of iodine in strong alcohol does not colour dry starch. Some observers consider that the production of this blue colour is not due to a definite chemical combination of iodine with starch (Vogel, N. Rep. Pharm. 22, 349; 25, 565; Pellet, M. [3] 7, 988; Tomlinson, P. M. [5] 20, 168; Duclaux, A. Ch. [4] 25, 264), while others attribute a definite formula to the combination. According to Bondonneau (C. R. 85, 671), it is $(C_6H_{10}O_5)_5I$; Mylius (B. 20, 688) considers it to contain HI, and gives the formula $(C_{24}H_{40}O_{20}I)_4IH$ as probable. He finds that the HI can be displaced by metallic iodides. Stocks (C. N. 56, 212; 57, 183) and Seyfert (Zeit. ang. Ch. 1, 15) contradict this. Rouvier (C. R. 114, 128 a. 1866) attributes the formula (C₆H₁₀O₅)₈I to the compound. Starch is oxidised by chlorine and by bromine to gluconic acid (Habermann, A. 172, 11; Herzfeld, A. 220, 364).

Action of alkalis. Weak solutions of the alkalis do not act on starch in the cold, but solutions containing over 3 p.c. real alkali cause the granules to swell up with the formation of a thick transparent paste, and, finally, a clear solution, a compound of starch with the alkali being formed (Schmidt, A. 51, 81; Ventzke, J. pr. 25, 65) which, according to the latter, is optically inactive, but this, no doubt, is incorrect, for Béchamp (C. R. 39, 653) gives the opticity [a] = +211° for the starch dissolved, and Thomsen (B. 18, 2169) shows that the ac-

tivity of dilute soda solutions is $[a]_D = +168$. On neutralisation this becomes much higher, corresponding, in fact, with Béchamp's number. The product does not reduce alkaline copper solution (Brown a. Heron, C.J. 35, 617). The potassium compound is obtained by ppg. the solution in dilute KHO with alcohol, pressing the pp., dissolving in H_2O , and re-ppg. with alcohol. This process repeated three or four times is said to yield a pure compound of the composition $C_{24}H_{39}O_{30}K$ (Pfeiffer a. Tollens, A. 210, 288). A sodium compound $C_{24}H_{39}O_{30}Na$ has been obtained in the same way (Reichardt, Z. 1870, 404). These formulæ are, however, very improbable. Alcoholic soda does not act on starch (Dragendort, J. f. Landwirthschaft, 7, 2066).

A Proposition of the Proposition of the States

Starch heated with ammonia yields brown, amorphous, nitrogenous bodies (Thénard, C. R.

52, 444).

Fused with KHO, starch, like other carbohydrates, yields oxalic acid, acetic acid, and

other products.

Action of alkaline earths. Barium, strontium, and calcium compounds similar to the sodium and potassium bodies have also been prepared. When solutions of soluble starch are ppd. with solutions of lime in sugar syrup, pps. are produced which are not very definite in composition, the percentage of lime showing a variation between C₈H₁₀O₃CaO and (C₈H₁₀O₃)₄CaO. Similar baryta compounds have been examined. When a solution of soluble starch is saturated with strontia and alcohol added, a strontium compound is ppd. (Lintner, Zeit. f. ang. Ch. 1888, 232). On distilling starch with lime acetone, mesityl oxide, isophorone, and ketones are produced (Harvat, C. C. 1887, 38).

On digesting starch with acetic anhydride, a triacetate is said to be formed $C_vH_1O_2(C_zH_2O_z)$, (Schützenberger a. Naudin, Bl. [2] 12, 110; A. Ch. [4] 21, 235; Michael, Am. 5, 359). This substance is amorphous; it is stained blue by iodine, and is decomposed by alkalis, with the

reproduction of starch.

Qualitative determination. The presence of starch is indicated by the granular appearance under the microscope, and starch granules are distinguished from all others by being stained blue by iodine solution and yellow by bromine. If the plasma in which the granules are contained is alkaline, it must be rendered slightly acid, or sufficient iodine solution must be employed to destroy the alkalinity. A solution of iodine in potassium iodide is usually employed, but an alcoholic solution answers the purpose. When the test is applied for starch in solution, the solutions must be cold and slightly acid and the reagent must be added in small quantities at a time. It is sometimes necessary to test a solution for soluble starch in presence of a-dextrini.e. the dextrin giving a reddish-brown colour with iodine. If this is in excess the reddishbrown colour covers the blue; ammonia added cautiously, drop by drop, discharges the reddishbrown, and if soluble starch be present the blue becomes definite and distinct. Care must be taken to avoid excess of ammonia (O'Sullivan). Small quantities of starch, which would otherwise not be observable, may be detected in the 'last runnings' of malt wort by adding a little

STAROH

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tannin and then alcohol to the solution. The starch is ppd. in this way, and on washing the pp. with water will yield the characteristic reaction with iodine (Burckhardt, Chem. Zeit. 1877, 1158). Starch, when moistened with an alcoholic solution of a-naphthol and a few drops of warm concentrated sulphuric acid added, acquires a deep violet-red colour (Ihl, Chem. Zeit. 11, 19).

Quantitative determination. There are very few materials containing starch of which a sufficiently accurate average sample can be obtained to render a definite estimation of the starch therein of much value.

In some cases separation of the starch, by one of the methods given for its preparation, gives results of sufficient accuracy to satisfy the requirements.

In the case of potatoes, the percentage of starch is deduced from the specific gravity, a set of specially-constructed tables being used; but this method, on the face of it, cannot yield more than an approximation. The specific gravity of the washed potatoes is taken in the usual way, a balance constructed to meet the requirements of the case being employed. About 5 kilos. of the potatocs are weighed in a strong wire basket in air, and then in water; thence, weight in air

specific gravity = weight in air - weight in water. According to the tables of Behrend, Märker, and Morgan, we have from

	Per cent. of	ŀ	Per cent. of
Sp. gr.	starch	Sp. gr.	starch
1.080	13.9	1.120	22.5
1.090	16.0	1.130	24.6
1.100	18.2	1.140	26.7
1.110	20.3		20 ,

In cases in which fair average samples of the material can be obtained, several methods have been proposed, all depending on the conversion of the starch, or the starch transformation products, into dextrose by digestion with dilute HCl or H2SO4, the dextrose being estimated with Fehling's solution, volumetrically or gravimetrically, and the starch calculated therefrom according to the equation $C_aH_{10}O_a + H_2O = C_0H_{12}O_a$ (v. Sachsse, C. C. [3] 8, 732; Märker, Handb. der Spiritusfabrication, 4 Auf., Berlin, 1886, 93; Soxhlet, Zeit. f. ges. Brau. 1881, 177; Faulenbach, Zeit. f. phys. Chem. 7, 510; Zipperer, Rep. An. Chem. 6, 699). Dubrunfaut dissolved the starch by rubbing the material with concentrated HCl, diluting the solution with water to a certain volume, and determining the opticity. The starch was calculated from $[a]_j = 192.4^\circ$.

Effront (Bl. [2] 47, 5) dissolves the starch with malt extract, determines the optical activity of the solution, then heats it with ammonia, after which he treats it with sodium hypochlorite and with HCl, and again determines the opticity; but this method is open to many objections.

These methods are unsatisfactory, inasmuch as it is difficult, if not impossible, to completely convert starch or starch products into dextrose, there being a probable error at one time from overconversion, at another from under-conversion: and, indeed, both may occur at the same time, the amount of reduction of Fehling's solution taken as dextrose never being a correct measure of the starch transformed. Another objection to the method is due to the fact that dilute acids convert other substances besides starch into bodies capable of reducing copper oxide.

Girard (C. R. 104, 1629) titrates starch with iodine solution, 1 grm. of starch taking up 0.157

grms. iodine.

Asboth (Chem. Zeit. 11, 785) proposes to add an excess of baryta water to the gelatinised starch and then alcohol. The dried pp. contains 19.8 p.c. BaO, the remainder is starch. This method, too, cannot be of any use.

O'Sullivan (C. J. 45, 2) described a method by which starch in most materials can be estimated with accuracy. If a fair average sample of the material cannot be obtained by grinding and powdering alone, it is first dried in warm. dry air and then powdered. The following is the method as applied to the cereals, but it is also applicable to all materials when treated as just described.

Fivegrams, or thereabouts, accurately weighed more if the material contains less than 40 p.c. starch-of the finely-ground material are introduced into a wide-necked flask of 100 to 120 c.c. capacity. To this sufficient alcohol of sp. gr. 0.82 is added to saturate it, and after a time 20 to 25 c.c. ether are introduced. The clear, ethereal solution is decanted off after standing for a few hours, and the residue again treated two or three times with ether. It is then extracted with alcohol, sp. gr. 90, at 35° to 38°, and treated with a large bulk of water, with which it is left in contact for at least 24 hours. If any sign of fermentation shows itself, a little salicylic acid solution may be used with the water. The residue, after being completely extracted with water, together with the filter, through which all the extracts should have been passed, is transferred to a beaker of about 100 c.c. capacity, and made up with water to about 40 to 45 c.c. This is heated to boiling for a few minutes in a water bath, care being taken, by continual stirring, to insure a homogeneous paste; then cooled to 62° to 63°, and 0.025 to 0.035 gram prepared diastase or its equivalent of malt extract added. the digestion being then continued at the temperature stated for a few hours. At the end of that time the contents of the beaker are boiled for a few minutes, thrown on to a filter, and the filtrate received in a 100 c.c. measuring flask. The residue is carefully washed with small quantities of boiling water at a time, and the filtrate made up at 15.5° to 100 c.c. A determination of the reducing power calculated as maltose, and of the remainder of the optical activity as dextrin, gives the data for calculating the quantity of starch. This holds good even though the amyloin theory of the breaking down of starch be proved to be accurate.

Example.- 5 grms. barley-flour treated as described, 0.03 grm. prepared diastase being employed, gave 100 c.c. solution of sp. gr. 1.01008 = 2.539 grms. solid matter. 9.178 grms. this sol. reduced 0.241 grm. CuO. Opt. act. in

If cold-water mait extract be used, a portion of its must be heated for the same time and at the same tem-perature as the assay; then bolled, and the opticity and leducing power determined; these factors calculated on the quantity employed must be allowed for.

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200 mm. tube = +21-1 divs. (Soleil-Ventzke-Scheibler saccharimeter). Hence

0.241 + 0.7256 (K of maltose = 62.5) = 0.1748 grm. maltose;

9.178 grms.: 101.003 (the wt. of 100 c.c. sol.) ::0.1748 : x;

x = maltose in the 100 c.c. sol. = 1.923; Opt. act. maltose $[a]_j = +154^\circ$ and of dextrin $[a]_j = +222^\circ$.

Hence 1 grm. maltose in 100 c.c. sol. in 200 mm. tube = 8.52 divs. of instrument mentioned, and 1 grm. dextrin under like circumstances = 11.56 divs. Then 1.923 × 8.02 = 15.422 divs. opt. activity of the maltose, 21.1 - 15.422 = 5.678 divs. opt. activity of the dextrin, and 5.678 + 11.56 = 0.491 grm. dextrin in the 100 c.c. sol. Dextrin is derived from starch without any increase of weight: 100 grms. starch yield 105.5 maltose; honce

1.055 : 1.923 :: 1 : x starch - maltose; x = 1.822 grms. starch.

1.822 + 0.491 (as dextrin) = 2.313 starch; in the 5 grms. taken = 46.26 p.c.

It is clearly shown in the paper quoted that if starch is not estimated in the way indicated no reliance can be placed on the results. It happens when dealing with some varieties of material that the aqueous extract contains soluble starch (blue colour with iodine). This cannot be looked upon as starch; it must be estimated in the solution as the soluble modifi-

Soluble starch may be prepared (a) by triturating starch with sharp sand or powdered glass so as to disintegrate the granules and extracting with cold water; (b) by the limited action of malt-extract or of acid.

Delffs (P. 109, 648) prepared soluble starch by triturating starch with sand and water; the solution gave a dark blue colouration with iodine. Flückiger (Z. 1861, 104) prepared a similar solution by acting on starch with a concentrated solution of calcium chloride and treating the resulting gummy mass with water, when, on filtration, a solution is obtained which exhibits all the characteristics of soluble starch. Musculus (Bl. [2] 22, 26; A. Ch. [5] 2, 385) does not consider this a true solution; he prepares the body by boiling starch with very dilute sulphuric acid, saturating the solution with chalk, and evaporating to a syrup. This deposits small granules which gradually increase in size, are soluble in hot water, and may be purified by precipitation with alcohol. It possesses no reducing power; its rotatory power is four times that of glucose. Bondonneau (C. R. 80, 671) has prepared soluble starch by this method, but does not find it altogether soluble under all conditions. Soluble starch is undialysable. Fuming nitric acid converts it into a mononitro-derivative, CaH, (NO2)O3; dilute nitric acid oxidises it to carbonic and oxalic acids; bromine and silver oxide to gluconic acid (Reichardt, B. 8, 1020; 7, 424).

Nägeli (Beiträge s. näheren Kenntniss der Stärkegruppe, Leipzig, 1874, p. 33, 99; A. Ch. 178, 218) gives the following method: 1 kilo. potato starch is allowed to stand 6-8 weeks with 6 litres hydrochloric acid, S.G. 106; this is then purified by solution in hot water; it crystallises in sphero-crystals (Jaquelain, A. Ch. [2] 48, 178). According to Brown a. Morris, this is

not soluble starch (v. above). Zulkowski (B. 18, 1895) prepares soluble starch by heating dry potato starch with glycerol at 180°-190° for half an hour. The solution is cooled, precipitated by alcohol, and the precipitate purified by solution in water and reprecipitation by alcohol.

Salomon (J. pr. [2] 28, 82) finds that soluble starch is the first product of the action of dilute acids on starch; it does not reduce Fehling's solution, and has an optical activity $[a]_0 - 211.5^{\circ}$. O'Sullivan (C. J. 1879, 772) prepares soluble starch by dissolving starch paste at 73°-74° with the least possible quantity of cold water extract of malt, boiling the solution as soon as it becomes clear, filtering, and concentrating. The soluble starch falls out on cooling as a white precipitate, which is purified by dissolving in hot water and allowing to cool when it separates out again. It has a reducing power, 3.5-0.78, and an optical activity $[\alpha]_j = 219.5$ -222.0, the reducing power being probably due to a small quantity of maltose; v. also Action of

acids on starch, above.

STEARIC ACID C₁₈H₃₆O₂. Mol. w. 284. (232° cor. at 15 mm.) (Krafft, B. 17, 1629); (359°-383°) (Carnelley a. Williams, B. 12, 1360). H.F. 126,000 (Von Rechenberg). S.G. (liquid) ⁶⁹ ·845; (solid) ² ·1·01; ¹⁰ ·1·00. S.V.S. 332·6 (R. Schiff, A. 223, 264). S. (alcohol) 2.5 in the cold. S. (benzene) 22 at 23°. S. (CS2) 30 (Vogel, J. 1866, 892). Occurs as glyceryl stearate in very many fixed animal and vegetable fats and oils (Chevreul, A. Ch. 88, 225; [2] 2, 354; 23, 19; Braconnot, A. Ch. 93, 250; Redtenbacher, A. 35, 46; Bromeis, A. 35, 86; 37, 303; Stenhouse, A. 36, 57; Erdmann, J. pr. 25, 497; Francis, A. 42, 256; Gottlieb, A. 57, 35; Laurent a. Gerhardt, A. 72, 272; Hardwick, C. J. 2, 232; Crowder, P. M. [4] 4, 21; Berthelot, A. Ch. [3] 41, 216, 432; 47, 297; Pebal, A. 91, 138; Heintz, A. 92, 295; Johnston, C. J. 29, 8).

Formation.—1. By saponification of cetylocetoacetic ether, obtained from cetyl iodide and sodium acetoacetic ether (Guthzeit, 4.206, 351), 2. By heating cetyl-malonic acid at 150°.—3. From ricinoletic acid by treatment with water, P, and I, followed by zinc and HClAq (Claus, B.9, 1916).—4. By heating oleic acid with iodine (1 p.c.) for several hours at 275° and distilling the product in a current of superheated steam (De Wilde a. Reychler, Bl. [3] 1, 295).

Preparation. - Suet or cacao fat is saponified by NaOHAq, the acids ppd. by H₂SO₂ and crystallised from alcohol. An alcoholic solution of the impure stearie acid (4 pts.) saturated at 0° is heated to 60° and mixed with a boiling alcoholic solution of Mg(OAc)₂ (1 pt.). The ppd. magnesium stearate is boiled with HClAq and the stearie acid recrystallised from alcohol (Heintz). Stearie acid can also be readily obtained from shea-butter which contains no other solid fatty acid (Buff a. Oudemans, J. pr. 89, 215).

Properties.—Pearly plates, insol. water, sol. alcohol and ether. Tasteless and inodorous. May be distilled in vacuo and, in small quantity, under atmospheric pressure, but in this case it is partly decomposed with formation of hydrocarbons, stearone, water, CO₂, acetic acid, and butyric acid. Fusion with P₂O₂ forms Cl₂H₂O₃ [54°-60°]. Nitrie acid forms sebacie, glutarie,

succinio, and other acids. Or and water at 140° form bromo- and dibromo-stearic acids (Oudemans, J. pr. 89, 193). Distillation in vacuo with NaOMe yields C₁₇H₁₆ (Mai, B. 22, 2133). Salts.—KA'. Hygroscopic crystals. S. 4

in hot water. Partially decomposed by a large quantity of water into an insoluble acid salt and free potash.—KHA'₂. Silvery scales (from alcohol). S. (alcohol) 36 in the cold; 27 at 78°. Boiling water converts it into a more acid salt. NaA'.—NaHA'2: insol. water.—BaA'2: minute laminæ, insol. water.—CaA'2.—SrA'2.—MgA'2: minute laminæ (from alcohol).—CuA'2: lightblue amorphous powder.—PbA'2: amorphous powder, insol. ether. —Pb₂OA'2.—AgA': white pp.

Methyl ether MeA'. [38°]. Crystalline, insol. water (Hanhart, C. R. 47, 230).

Ethyl ether EtA'. [33°]. (224°). Formed by heating the acid with alcohol at 200° (Lassaigne, A. 13, 168; Berthelot, A. 88, 312) by passing HCl into an alcoholic solution of stearic acid (Redtenbacher, A. 35, 51) and by heating stearin with a little NaOEt (Duffy, C. J. 5, 197; Bouis, C. R. 45, 35). Crystalline mass, partially decomposed by distillation. V. sol. alcohol.

decomposed by distillation. V. sol. alcohol.

Ethylene ether O.H.A'₂. [76°]. Fro
AgA' and C.2H.Br. (Wurtz, A. Ch. [3] 55, 436).

Isoamyl ether C.H.,A'. [25°].

Octyl ether C.₈H.,A'. [45°].

Getyl ether C.₆H.₃A'. [55°-60°]. Lamin
(from ether) (Berthelot, A. Ch. [3] 56, 70).

Laminæ

Glyceryl ethers v. vol. ii. p. 622. mixture of stearic acid and glycerin saturated with HCl at 100° forms C₃H₃Cl(OH)(OC₁₈H₃₂O) $[28^{\circ}]$

Phenyl ether PhA'. [52°]. (mm.) (Krafft a. Bürger, B. 17, 1380). (267° at 15

p-Tolyl ether C, H,A'. [54°]. (276° at 15 mm.).

Chloride C18H28OCl. [23°]. (215° at 15

mm.). Crystalline mass.

Amide C18H35O.NH2. [109°]. Formed by distilling ammonium stearate at 230' under pressure; the yield being 50 p.c. (Hofmann, B. 15, 984; cf. Carlet, Bl. 1859, i. 76). Formed also by the action of NH, on the ether or on the chloride. Converted by the action of Br and NaOHAq into stearyl-heptadecyl-urea (Turpin, B. 21, 2486).

Anilide C18H35ONHPh. [94°]. by distilling aniline over stearic acid at 230°

(Pebal, A. 91, 152). White needles.

Phenyl hydrazide C_{1,}H₃₅,CO.N.H₂Ph. [107°]. Formed by heating stearic acid with phenyl-hydrazine. White unctuous plates (from alcohol), sl. sol. cold alcohol, benzene, and ether (Strache a. Iritzer, M. 14, 37)

Nitrite C_1H_2ON . [42°]. (275° at 100 mm.). S.G. $\frac{1}{2}$ 815; $\frac{100}{2}$ 779. Formed by distilling stearamide with P_2O_5 (Krafft a. Stauffer, B. 15, 516, 1730) or by heating cyanostearic acid at 250° (Hell a. Sadomsky, B. 24, 2779).

References. - Bromo-, DI - BROMO - IODO-, CHLORO-, IODO-, NITRO-, and OXY-STEARIC ACID.

Isosteario acid (C.H.,),CH.CO,H. [38.5°]. (278° at 101 mm.). Formed from di-octylacetoacetic ether or di-octyl-malonic acid (Conrad a. Guthzeit, A. 204, 11, 165). Colourless leaflets (from alcohol).—NaA': needles (from alcohol). AgA': thick white pp.

Ethyl ether Ei $\mathring{\mathbf{A}}$. (275°-280° at 100 mm.). 70t. IV.

STEARIC ALDEHYDE C.,H.O. (213° uncor. at 22 mm.). Formed by distilling calcium stearate with calcium formate (Krafit, B. 13, 1417). Plates with bluish glitter, sl. sol. ether.

STEARIN v. Stearyl derivative of GLYCERIN. STEAROLIC ACID C18H32O2. Mol. w. 280. [48°]. (260°). Formed by heating bromo-oleis acid or the dibromide of oleic acid with alcoholic potash at 100° (Overbeck, J. pr. 97, 159; A. 140, 49). Needles (from alcohol), insol. water. Br Forms $C_{18}H_{22}Br_2O_2$ and $C_{18}H_{32}Br_1O_2$ [70°]. I and FeI₂ in CS₂ form $C_{18}H_{32}Br_1O_2$ [51°] (Liebermann a. Sachsse, B. 24, 4116). Potash-fusion yields myristic acid $C_{18}H_{28}O_2$ and an acid $C_{18}H_{39}O_3$ [21°] (Marasse, Z. [2] 5, 571; B. 2, 359). Alkaline KMnO, oxidises it to subcric and stearoxylic acids (Hazura a. Grüssner, M. 9, 952). HNO, yields . azelaic, stearoxylic, pelargonic, and nitrosopelargonic acids (Limpach, A. 190, 294). Phenylhydrazine at 140° gives C₁,H₃,CO,N₂H₂Ph [82°] (Holt, B. 25, 2670).—BaA₂,—CaA₂ aq.—AgA'.

STEARONE (C₁,H₃),CO. Di.heptadecyl

ketone. [88°]. S.G. (liquid) 43 7979 (Krafft, B. 15, 1715). Formed by heating stear; a acid (9.5 g.) with P.O. (5g.) at 210° (Kipping, C. J. 57, 537; cf Bussy, A. 9, 269; Redtenbacher, A. 35, 57; Varrentrapp, A. 35, 80; Rowney, C. J. 6, 97; Heintz, P. 94, 272; 96, 65). Got also by dis-tilling the stearyl derivative of heptadecyl-urea with lime (Turpin, B. 21, 2486). Plates, sl. sol. hot alcohol. Br forms C₃, H_{ak}Br₂O [72°].

Oxim (C1,H33)2C:NOH. [63°]. White powder, m. sol. hot benzene and alcohol, insol. water and alkalis (Spiegler, B. 17, 1575; Kipping, C. J. 57, 540).

STEAROXYLIC ACID C18H32O4. 312. [86°]. Formed by the oxidation of stearolic acid (Överbeck, A. 140, 63; Hazura a. Grüssner, M. 9, 952). Plates or needles, sl. sol. cold al-cohol. BaA'₂.—AgA': crystalline powder. STEARYL-GLYCERIN v. GLYCERIN.

STEEL v. Iron, vol. iii. p. 53, and Dictionary OF APPLIED CHEMISTRY, vol. ii. p. 360.

STIBINE. Synonym of antimony hydride, v. vol. i. p. 288.

STÎLBENE v. DI-PHENYL-ETHYLENE.

STILBENE ALCOHOL v. HYDROBENZOÏN. STILBENE DIBROMIDE v. DI-BROMO-PHENYI-ETHANE

STILBENE DICARBOXYLIC ACID v. Di-Phenyl-Maleïg Acid.

STILBENE DICHLORIDE v. DI-CHLORO. PHENYL-ETHANE.

STOICHIOMETRY. The laws of chemical combination, and their application to chemical calculations; v. Combination, CHEMICAL, LAWS OF. vol. ii. p. 235.

STORAX. A balsam produced by Styrag officinalis, a shrub growing in the Levant. It occurs in two varieties, liquid storax and reed storax, the latter containing a large quantity of bark. Liquid storax is a brownish-yellow sticky mass containing styrene, styracin, cinnamic acid, phenylpropyl cinnamate, a little ethyl cinnam. ate, a substance [65°] smelling like vanilla (possibly ethyl-vanillin), and (a) and (β)-storesinol (W. von Miller, N. R. P. 24, 1; B. 9, 274; A. 188, 184; 189, 838).

(a)-Storesinol C₃₈H₅₈O₅ i.e. C₃₆H₅₈(OH)₅. [160°-168°]. Amorphous, v. sol. dilute KOHAq.4

but conc. KOHAq ppts. CasH soO.K. Yields a mono and tri-acetyl derivative.

(8)-Storesinol. [140°-145°]. Amorphous. Forms amorphous $C_{36}H_{36}O_4K$, which is more sol.

water than its (a)- isomeride.

STRONTIA. Oxide of strontium (q.v. p. 516).

STRONTIUM. Sr. At. w. 87.3. Mol. w. not known. Very little known about properties. Doubtful if approximately pure Sr has yet been isolated. S.G. c. 2.4 to 2.58 (Franz, J. pr. 107, 253; Matthiessen, J. 8, 324). For emissionspectrum v. B. A. 1884. 444. H.C. [Sr,O] =

128, 440 (Th. 3, 258).

Occurrence. - Compounds of Sr are widely distributed, but not in very large quantities. SrCO, occurs in small quantities in all specimens of arragonite; very small quantities are found in many calc-spars, marbles, and dolomites. SrSO, is an ingredient of many heavy spars. SrCO, is found as strontianite, and SrSO, as celestine in a few localities; brewsterite contains Sr silicate, with silicates of Ba or Ca. Traces of SrSO, and SrCl, are found in many mineral springs, in some hard river-waters, in sea-water, and in the sshes of certain plants, especially Fucus vesiculosus.

Historical.—A mineral found at Strontian, a village in Argyleshire, in 1787, and supposed to be barium carbonate, was observed to colour flame reddish by Crawford and Cruikshank in 1790 (Mem. Manchester Soc.). The supposition made by C. a. C. that the mineral contained a new element was confirmed by Hope (T. E. 4, 3), Klaproth (Crell's Ann. 1793 [ii.] 189; 1794 (i.) 99), and Kirwan-Higgins (Crell's Ann. 1795 (ii.) 119, 205). The metal was isolated by Davy in

1808 (T. 1808. 345).

Formation.-1. By electrolysing moist SrO₂H₂ or SrCl, in contact with Hg and a little naphtha, and heating the amalgam so formed (Davy, T. 1808. 345).-2. By heating saturated SrCl2Aq with Na amalgam to 90°, quickly washing the Sr amalgam so formed, drying it by filter paper, and distilling off the Hg in a stream of H (Franz, J.pr. 107, 253).—3. By heating SrO or SrO,H, intimately mixed with Mg powder, a mixture of Sr with MgO is obtained (Winkler, B. 23, 125,

Preparation .- A porous clay cylinder is placed in a crucible, and SrCl₂, mixed with a little NH₄Cl, is placed in the crucible and in the cell, so that when the mixture is fused the surface of it is at a higher level in the cell than in the crucible. A cylinder of sheet iron surrounding the cell serves as the positive electrode, and an iron wire passing through a tobacco pipe, the bowl of which dips under the molten mixture in the cell, serves as the negative electrode. The crucible is heated till the mixture of SrCl2 and NH4Cl melts, temperature being kept so that there is always a solid crust on the surface of the mixture in the porous cell. A current from 5 or 6 Bunsen cells is passed through the molten mass; Sr is separated and runs into small pieces, which are pro-tected from the air by the solid crust of SrCl. and NH,Cl; the pieces of Sr are removed by an iron spoon and kept under petroleum.

For the preparation of pure Sr salts from strontianite v. Barthe a. Falières (Bl. [3] 7, 104). Properties.—A yellowish white metal, somewhat harder than Ca or Pb; can be beaten into

thin leaves; melts at full red heat. According to Mallet (A. 190, 62), Sr is slightly volatilised at a very high temperature. Easily oxidised by exposure to air; decomposes cold water rapidly; dissolves in dilute acids, not in HNO, Aq, giving salts and H. Combines directly with S and the halogens. Sr is a strongly positive metal, less positive than the alkali metals and Ca, but more positive than Mg; it is closely related to Ca and Ba, less closely to Mg; it also shows resemblances to Zn, Cd, and Hg (v. Alkaline earths, metals OF THE, vol. i. p. 112; and MAGNESIUM GROUP OF OF THE, vol. 1. p. 112; and MAGNESIUM GROUP OF ELEMENTS, vol. iii. p. 163). The atomic weight of Sr has been determined (1) by determining CO₂ in SrCO₂ (Stromeyer, S. 19, 228 [1816]; Salvétat, C. R. 17, 318 [1843]); (2) by ppg. Cl from SrCl₂ by Ag (Rose, S. 19, 228 [1816]; Pelouze, C. R. 20, 1047 [1845]; Marignac, A. 104, 169 [1856]. 106, 168 [1858]; Dumas, A. Ch. [3] 55, 191 [1859]); (3) by determining water in SrCl.,6H₂O (Marignao, A. 106, 168 [1858]); (4) by transforming SrCl.,6H₂O into SrSO, (Marignao, l.c.). The S.H. of Sr has not been determined directly. The V.D. of no compound of Sr has been determined.

Reactions and Combinations (v. Bunsen, A. 94, 111).—1. Exposed to air or oxygen rapidly forms SrO, or SrO2H2 if moisture is present.-2. Burns brilliantly when heated in oxygen, sulphur vapour, chlorine, bromine, or iodine vapour; also in dry carbon dioxide. - 3. Decomposes cold water rapidly, giving off H and forming SrO₂H₂. - 4. Dissolves rapidly in dilute hydrochloric or sulphuric acid; reacts slowly with conc. sulphuric acid; scarcely acted on by nitric acid, even when hot and conc .- 5. Reduces silica and silicates when heated therewith to full redness.

Strontium, antimonate of; v. vol. i. p. 286. Strontium, arsenates of; v. vol. i. p. 309. Strontium, arsenite of; v. vol. i. p. 307. Strontium, borates of; v. vol. i. p. 530.

Strontium, bromide of, SrBr. Mol. w. not determined. By heating St in Br. By dissolving SrCO, in HBrAq and evaporating, long white needles of the hydrate SrBr2. 6aq are obtained (Löwig, Mag. Pharm. 33, 7); S.G. 2·358 (Favre a. Valson, C. R. 77, 579); these crystals do not effloresce over H.SO, (Rammelsberg, P. 55, 238), but on heating give off their water, leaving SrBr2 as a white solid, S.G. 3.985 (F. a. V., l.c.), that melts at red heat without decomposition (R., l.c.). $[Sr,Br^2] = 157,700 \ (Th. 3, 258)$. Carnelley (C. J. 33, 279) gives melting-point as c. 630°. Combines with ammonia to form 2SrBr., NH, (Rammelsberg, P. 55, 238).

Strontium, chloride of, SrCl2. Mol. w. not determined.

Formation.—1. By burning Sr in Cl.—2. By passing Cl over hot SrO (Weber, P. 112, 619). 3. By heating SrO in a stream of HCl (Chevreul, 3. Ch. 84, 285).—4. By decomposing SrCO₂ by conc. CaCl₂Aq or MgCl₂ by heating together, then dissolving out SrCl₂ and crystallising (SrCO₂ + MgCl₂Aq = SrCl₂Aq + MgO + CO₂; Wackenroder's Patent; v. B. 19, Ref. 638).—5. By heating a mixture of SrSO₂, CaCl₂, and characteristics of the state of the s

coal with a little chalk, lixiviating, and crystallising (SrSO, + CaCl, + 4C = SrCl, + CaS + 4CO; Mactear, D. P. J. 262, 288). Preparation.—Strontante (SrOO₂) is dissolved in HOlAq, the solution is digested in absence of air with more SrOO₂ (to remove iron, &c.), poured off and evaporated to the crystallising point; the crystals of SrOI₂ flaq that separate are purified by re-crystallisation, then dried and heated to 100° until they cease to lose weight.

Properties.—A white crystalline powder, with a sharp, bitter taste. Melts at 825° (Carnelley, C. J. 83, 280) to a glass-like mass with an alkaline reaction. S.G. 2.96 at 0°; 2.77 at mp. (Quincke, P. 138, 141). S. 44.2 at 0°, 48.3 at 10°, 53.9 at 20°, 60 at 30°, 66.7 at 40°, 74.4 at 50°, 83.1 at 60°, 87.5 at 65°, 88.8 at 66.5°, 89.6 at 70°, 92.4 at 80°, 96.2 at 90°, 101.9 at 100°, 109.1 at 110°, 116.4 at 118.8°; saturated SrCl_Aq boils at 118.8° (Mulder). Gerlach (Fr. 8, 245) gives the following data:—

B.G. SrCl.Aq	P.o. SrCl. 1	S.G. SrCl.Aq	P.c. SrCl.
1.0453	5	1.2580	25
1.0929	10	1.3220	30
1.1439	15	1.3633	33
1.1989	20		

SrCl₂ is insol. absolute alcohol; it dissolves in aqueous alcohol in proportion to the amount of water present (Gerardin, A. Ch. [4] 5, 156). [Sr,Cl²] = 184,550; [Sr,Cl²,Aq] = 195,690 (Th. 3, 258). For connection between solubility in water of SrCl₂ and temperature v. Etard (C. R. 113, 854).

Reactions and Combinations.—1. Heated to redness in water vapour, HCl is given off and SrO remains (Kraus, P. 43, 138; Kahnheim, J. 1861. 149).—2. Heated with bromine to 200° is partially decomposed to SrBr. (Potilitzin, B. 7, 733; 8, 760); the amount of decomposition varies with temperature and the relative masses of SrCl. and Br.—3. Combines with water. Solution of SrCO, in HClAq evaporated yields long, six-sided, hexagonal needles of the hexahydrate SrCl. 6H.O; S.G. 1-933 at 17°. By keeping these crystals over H.SO, in vacuo for some months the dihydrate SrCl. 2H.O is formed.—4. Combines with ammonia to form SrCl. 2NH (H. Rose, P. 20, 155).

Strontium, cyanide of; v. vol. ii. p. 347.

Strontium, ferrocyanide of; v. vol. ii. p. 337. Strontium, fluoride of, SrF₂. A white, orystalline powder; scarcely sol. water or HFAq. Prepared by the action of HFAq on SrO or SrCO₂ (Berzelius, P. 1, 20); also by fusing 2 parts SrCl₂ with 1 part NaF and 1 part NaCl, and lixiviating the product (Röder, Dissertation [Göttingen, 1863] 14; Feldmann, B. 21, Ref. 866 [Patent]). Poulenc (C. R. 116, 987) obtained SrF₂, as an amorphous powder, by the reaction of HFAq and SrCl₂Aq; S.G. 2·44; partly decomposed to SrO by heating in air to c. 1000°. By fusing with alkali chlorides, or with KHF₂, P. obtained SrF₂ in regular octahedral crystals.

Strontium, hydride of. By heating to redness a mixture of 103 parts SrO (made from SrCO₂) with 24 parts Mg powder, in an iron tube, in an atmosphere of H, Winkler (B. 24, 1975) obtained a greyish-brown powder that quickly oxidised in air to SrO₂H, with evolution of H, and was decomposed very rapidly by water or HClAq with violent evolution of H. Analyses

indicated that the substance might be a mixture of c. 66 p.c. SrH with c. 29 p.c. MgO, c. 4 p.c. SrO, and a very little Mg.

Strontium, hydrosulphide of, SrS₂H₂xH₃O. By saturating SrOAq with H₂S and evaporating in vacuo over H₂SO₄; or by dissolving SrS in water, evaporating, filtering from SrO₂H₂, and evaporating over H₂SO₄ in vacuo. Large, white crystals; melts when heated in water of crystallisation, and then gives SrS. Aqueous solution boiled gives off all H₂S and forms SrO₂H₂ (v. Rose, P. 55, 430; Berzelius, P. 6, 442).

Strontium, hydroxide of, SrO₂H₂. Mol. w. not determined. Prepared by the action of water on SrO. Also by heating celestine (SrSO₄) with charcoal, dissolving SrS so formed in water, heating with CuO or ZnO, filtering from CuS or ZnS, evaporating to dryness, and heating to redness (cf. Banum Hyddoxide, vol. i, p. 442).

A white solid; S.G. 3·625 (Filhol, A. Ch. [3] 21, 415). Sol. water, forming a markedly alkaline solution reacting similarly to BaO.H_Aq and CaO.H_Aq. Scheibler (C. C. [3] 13, 33) gives the following data, showing solubility in water, expressed in terms of SrO, Had the hydrate SrO.H., SH_O, dissolved:—

m	S.		m		8.	
Temp.	SrO	SrO.H.8H.6	Temp.	SrO	SrO.H.8H.O	
0°	•35	·90 ·	55°	2.54	6.52	
5	•41	1.05	60	3.03	7.77	
10	•48	1.23	65	3.62	9.29	
15	•57	1.46	70	4.35	11.16	
20	•68	1.74	75	5.30	13.60	
25	.82	2.10	80	6.56	16.83	
30	1.00	2.57	85	9.00	23.09	
35	1.22	3.13	90	12.00	80·78	
40	1.48	3.80	95	15.15	38·8 6	
45	1.78	4.57	100	18.60	47.71	
50	2.13	5.46	101.2	19.40	49.75	

Dry SrO₂H₂ takes up only traces of CO₂ from the air (Heyer, B. 19, 2684); but the hydrate SrO₄H₂·H₂O absorbs CO₂ till it is changed to SrCO₃ (H., l.c.); according to Finkener (B. 19, 2958) a basic carbonate is formed.

The octohydrate, SrO₂H₂·8H₂O, crystallises in tetragonal crystals (a:c=1:6407) from SrOAq; S.G. 1·396 at 16°; in air falls to powder, giving the monohydrate SrO₂H₂·H₂O, which loses H₂O at 100° (v. Finkener, l.c.; Müller-Erzbach, B. 19, 2874; 20, 1628). Weisberg (B. 11, 511) says that Cl reacts with the hydrates of SrO₂H₂ to give SrCl₂ and Sr(ClO₂).

says that Cr reacts with the hydrates of SrO₂B₂ to give SrCl, and Sr(ClO₂)₂.

Strontium, iodide of, SrI₂. A white solid; by dissolving SrCO₂ in HIAq, evaporating, and heating the hexahydrate, SrI₂.6H₂O₂ which crystallises out. S.G. 4415; melts at red heat; strongly heated in air gives SrO and I (Croft, J. pr. 68, 420). Thomsen gives [Sr,I²,Aq] = 143,460 (Th. 3, 258).

Strontium, manganocyanide of; v. vol. ii. p. 342.

Strontium, nitride of. By heating Sr amalgam containing from 20 to 25 p.c. Sr (prepared by electrolysis and heating the product in accuo) in a stream of N, Maquenne (Bl. [8] 7, 366) obtained a dark-coloured compound of Sr and N to which he gave the formula Sr₂N₂.

Strontium, oxides of. Two oxides have been isolated, SrO and SrO₃.

STEONTIUM OXIDE STO. (Strontium monocide. Strontia.) Mol. w. not known. Prepared by strongly heating SrO₂H₂, Sr(NO₃)₂, SrOO₂ (Brügelmann, Fr. 29, 127; Heyer, B. 19, 2684); also by strongly heating SrI₂in air (Croft, J. pr. 68, 420). Best prepared similarly to BaO (v. BARIUM MONOXIDE, vol. i. p. 443). A grey-white, porous, infusible solid; prepared by heating SrCO, or SrO, H, forms a mass of regular cubes with S.G. 4.75 referred to water at 4° (Brügelmann, l.c.). According to Moissan (C. R. 115, 1034), SrO melts to a transparent liquid at c. 30006 and this solidifies to a crystalline mass. Thomsen gives [Sr, O] = 128,440 (Th. 3, 258). Dissolves in water (for data v. Strontium hydroxide); from this solution the octohydrated hydroxide SrO,H,,8H,O separates on evaporation. By passing moist air over SrO the monohydrated hydroxide, SrO2H2.H2O, is formed (Heyer, B. 19, 2684). SrO is a strongly basic oxide, reacting with acids to form salts SrX, where X = SO. 2NO₃, ²PO₄, &c.

STRONTIUM DIOXIDE SrO₂. (Strontium per-oxide.) Mol. w. not known. Addition of H.O.Aq to SrOAq ppts. the octohydrate SrO. SH.O (Thénard, A. Ch. [2] 8, 312; Schöne, B. 6, 1172; cf. Conroy, C. J. [2] 11, 812). By drying this pp. at 100° SrO. is obtained as a white powder, having similar properties to those of barium dioxide (q.v. vol. i. p. 443). SrO, is not obtained by methods similar to those generally used

for making BaO2.

Strontium, oxychloride of. According to André (A. Ch. [6] 3, 66) crystals of the compound SrCl. SrO.9H.O(=Sr.OCl. 9H.O) are deposited from a mixture of saturated SrCl2Aq and saturated SrOAq; the crystals are very unstable in air.

Strontium, oxysulphide of. Schöne (P. 117, 59) obtained SrS. SrO. 12aq(Sr.OS. 12aq) by slow oxidation of SrS,Aq.

Strontium, platinocyanide of; v. vol. ii. p.

Strontium, salts of. Compounds obtained by replacing H of acids by strontium. These compounds belong to the type SrX, where X is SO,, CO,, 2NO,, 3PO, &c. The Sr salts are very definite compounds; not many basic salts are known. The chief salts of oxyacids are the following: bromate and hypobromite, carbonate, chlorate, chlorite and perchlorate, chromate and dichromate, iodate and periodates, molybdate, nitrate, nitrite, and hyponitrite, selenate and selenites, sulphate, sulphite, thibsulphate, and thionates (v. Carbonates, nitrates, &c.).

Strontium, selenide of. Obtained as a white solid, rapidly decomposing in air with separation of Se, by heating a small quantity of SrSeO, in H to dull redness; [Sr,Se] = 87,160 (Fabre, C. R.

102, 1469)

Strontium, silicofluoride of, SrSiF.2H.O. Four-sided prisms; S.G. 2.999; loses 2H₂O when gently warmed; prepared by dissolving SrCO, in H₂SiF₆Aq and evaporating (Berzelius, Lehrbuch [5th edit.], 3, 385]. Fresenius (Fr. 29, 143) gives S. 3·2 at 15°; S. in alcohol (50 p.c. by vol.) ·06 at 15°.

Strontium, sulphides of. Three sulphides have been isolated : SrS, SrS,, and SrS,.

STRONTIUM MONOSULPHIDE SrS. Formed by cheating together Sr and S in the ratio 87:32;

also by reducing SrSO, by charcoal; also by passing CS, vapour mixed with H. H.S. or CO. over red-hot SrCO₃ (cf. Barium monosulphide, vol. i. p. 444). A white powder, which slowly becomes yellowish when exposed to air. Does not phosphoresce (Schöne, P. 117, 59). For phosphorescence of SrS mixed with small quantities of other salts v. Becquerel (C. R. 107, 892). Sabatier (A. Ch. [5] 22, 5) gives [Sr,S] = 49,600. SrS does not combine with S when heated therewith, but polysulphides are formed by boiling an aqueous solution of SrS with S (Schöne, P. 117, 59). SrS dissolves in water; on crystallising SrO₂H₂ separates and SrS₂H₂ remains in solution (H. Rose, P. 55, 430).

STRONTIUM TETRASULPHIDE STS .. xH,O. The hexahydrate, SrS, 6H2O, is obtained, as a reddish crystalline solid, by boiling 100 parts SrS in water, and evaporating the solution in vacuo at a temperature not higher than 16°. From a solution at 20°-25° the dihydrate SrS, 2H,O separates. An aqueous solution of SrS, oxidises in air to the oxysulphide SrO.SrS, 12aq, and then to SrS₂O₃, while S separates and some SrCO₃

is formed (Schöne, P. 117, 59).

STRONTIUM PENTASULPHIDE SrS, xH20. amorphous, yellowish, hygroscopic solid; formed by evaporating a solution of SrS, saturated with S in the cold. After drying at 100°, CS, dissolves out the S, leaving SrS, (Schöne,

l.c.). Strontium, sulphydrate of; v. Strontium HYDROSULPHIDE, p. 515.

Strontium, sulphocyanide of; v. vol. ii. p. M. M. P. M.

STROPHANTHIN C₃₁H₄₈O₁₂ (A.); C₂₀H₃₄O₁ (F.). $[\alpha]_D = 30^\circ$. Extracted by alcohol at 70° from the seeds of Strophanthus hispidus (Gallois, C. R. 84, 261; Fraser, Ar. Ph. [3] 3, 229; Pr. E. 124, 370; Ph. [3] 18, 69; Elborne, Ph. [3] 17, 743; 18, 219; Gerrard, Ph. [3] 17, 923; Arnaud, C. R. 107, 179; Gley, C. R. 107, 348). White micaceous crystals, sol. water, v. sol. alcohol, insol. ether. Dextrorotatory. Bitter. Resembles ouabain in toxic effects. Decomposed by boiling dilute acids (even H2S) into glucose and crystalline strophanthidin, which yields a resin on further boiling with dilute H, SO, (F.). H2SO, and a trace of FeCl, gives a reddishbrown pp., changing to emerald-green (Helbing, Ph. [3] 17, 924).

STRUTHIIN v. SAPONIN. STRYCHNIC ACID C20H22NO(NH).CO2H. Formed from strychnine, alcohol, and Na at 50°-55° (Tafel, A. 264, 50). When heated in a current of H at 190° it changes to strychnine. K2Cr2O, and H2SO, give a brown-red colour or pp.

Nitrosamine C20H22NO(N.NO).CO2H. Gelatinous pp. Exhibits Liebermann's reaction.

Methylo-iodide C₂₀H₂₂N(MeI)O(NH).CO₂H. Formed methyl-strychnine and HI (Tafel, A. 264, 55). Colourless needles (containing aq), v. sl. sol. cold alcohol and cold water.—NaA' aq: v.e. sol. water, m. sol. alcohol. Converted by MeI into crystalline C20H22N(MeI)(NMe).CO2Me.

Methyl-strychnic acid. Methylo-iodide. C₂₀H₂₂N(MeI)O(NMe).CO₂H. Formed from dimethyl-strychnine and HI (Tafel, A. 264, 58). Needles, m. sol. boiling water and hot alcohol.

Decxystrychnic acid C,H2eN(NH).CO2H aq. formed by heating deoxystrychnine with alcoholic NaOEt at 180° (Tafel, A. 268, 253). Needles (containing aq) (from dilute H,SO,) or anhydrous prisms (from alcohol), sl. sol. hot water. Quickly converted by acids into deoxystrychnine. Yields a nitrosamine.

Isostrychnic acid C20H2NO(NH).CO2H. Formed from strychnine, Na, and alcohol at 70°. Got also by heating strychnine with baryta-water at 140° in absence of air. Minute needles. K₂Cr₂O₇ and dilute H₂SO₄ form a brown liquid on heating, and a brown pp. with excess of K₂Cr₂O₇.—HA'HI aq: prisms, m. sol.

cold water and alcohol, insol. ether.

Nitroso-derivative NO.C₂₀H₂₁NO(NH).CO₂H aq. Sol. alkalis, but ppd. by CO₂. Yields a nitrosamine, which gives Liebermann's reaction with phenol and H2SO4. --HA'HCl: needles, insol. water.

Methylo-iodide

C20H22N(MeI)O(NH).CO2H. Crystalline, m. sol. hot water .- NaA': minute needles. Converted by methyl iodide at 100° into crystalline C₂₀H₂₂N(MeI)O(NMc).CO₂Me 2aq.

Methyl-isostrychnic acid

C20H22NO(NMe).CO2H. From isostrychnic acid hydroiodide and McI at 100° (Tafel, A. 268, 240). Small colourless prisms (containing 2 aq). Its alkaline solution is not coloured by air (difference from isostrychnic acid).

Methylo-iodide

C.H., N(MeI)O(NMe).CO.H aq [271°-275°]. Formed from methyl-strychnine methylo-iodide and HI (Tafel, A. 264, 77). Needles, m. sol. hot water and hot alcohol, insol. ether.

Nitroso-methyl-isostrychnic acid

NO.C₂₀H₂₁ON(NMe).CO₂H. Formed from the preceding acid, alcohol, HCl, and amyl nitrite. Green needles (from benzene). When heated with benzoic aldehyde and ZnCl₂ it gives a green mass, which dyes like malachite green. Diazo-benzene chloride forms a brownish-orange dye.

STRYCHNINE C_{.1}H_{.2}N_{.2}O_{..} Mol. w. 33a. [221°] (Blyth); [284°] (Claus a. Glassner, B. 14, 773); [268°] (Logbisch a. Schoop, M. 6, 858); [269°] (Stochr). (270° at 5 mm.). S.G. ½ 1.359 (Clarke, 4m. 2, 174). S. 015 in the cold; 04 at 100°. S. 014 in the cold (Dragendorff, J. 1865, 739); 025 at 14.5° (Crespi, G. 13, 175). S. (alcohol) 3 at 8°; 1.8 at 78°. S. (95 p.c. alcohol) 936. S. (ether) 08. S. (benzene) 607. S. (isoamyl alcohol) 53 at 12°; 4.3 at 99°. Occurs in nux vomica, in St. Ignatius beans, in the wood of Strychnos Colubrina, in Strychnos Tieuté, and in other species of Strychnos (Pelletier a. Caventou, A. Ch. [2] 10, 142; 26, 44; Pelletier a. Dumas, A. Ch. [2] 24, 176; Liebig, A. 47, 171; 49, 244; Regnault, A. Ch. [2] 68, 113; Gerhardt, Rev. Scient. 10, 192; Nicholson a. Abel, C. J. 2, 241; Henry, Ph. 8, 401; Corriol,
Ph. 11, 492; Robiquet, Ph. 11, 580; Henry,
jun., J. Ph. 16, 752; Berlekom, Z. [2] 2, 443; Shenstone, Ph. [3] 8, 445). Occurs also in the bark of Erythrophlaum guineense, from which the pigmies of Central Africa prepare their arrow-poison (Holmes, Ph. [3] 21, 921).

Preparation .- 1. The nuts (1 kilo) are softened by steam, dried, powdered, and digested with alcohol (5 kilos of S.G. 856) acidulated with

H.SO, (45 g.). Lime is added to the filtrate; and, after standing, the decanted liquid evaporated; the residue dissolved in dilute soid; and the filtrate ppd. by ammonia. The strychnine is separated from brucine by crystallisation from alcohol (Henry) .- 2. The dilute alcoholic extract of nux vomica is evaporated to a small bulk and ppd. by lead acetate. The filtrate is mixed with magnesia and left for a few days. The pp. is dissolved in alcohol of 83 p.c. and evaporated to crystallisation. Strychnine is first deposited, and afterwards brucine. The bases are further purified by crystallisation of their nitrates, the nitrate of strychning separating first.

Properties.-Trimetric prisms, permanent in the air and not altered by light. Lævorotatory, the rotation varying greatly with the nature of the solvent (Hoorweg, A. 166, 76; Tykociner, R. T. C. 1, 146). The dispersive power is constant (Grimbert, J. Ph. [5] 16, 295). At 169° it forms a sublimate of minute needles (Blyth). Very bitter. Alkaline in reaction. Strychnine is a violent poison, acting on the spinal cord and producing convulsions (Lovett, J. Physiol. 9, 99). 03 g. may be fatal. Strychnine dissolves with difficulty in acids, the solubility being greater the more dilute the acid; when a conc. solution of a strychnine salt is slightly acidified a pp. is formed which dissolves in excess of acid, forming a solution which yields a pp. on dilution. Thus H.SO, added to a conc. solution of strychnine sulphate ppts. the acid sulphate B'H₂SO₄, the mother-liquor retaining 113 p.c. of salts. HCl added to a solution of strychnine hydrochloride ppts. B'HCllag in needles, the mother-liquor retaining 413 p.c. of salt (Han-riot a. Blarez, C. R. 96, 1504). Strychnine is readily soluble in dilute hypophosphorous acid (Jones, Ph. [3] 20, 256). KCy added to a solution of a salt of strychnine ppts. the pure base (Flückiger, N. J. P. 38, 138; Weith, B. 4. 527). A solution of ICl gives a yellow pp. v. sol. HCÍAq, from which it crystallises on cooling (Dittmar, B. 18, 1612).

Reactions.—1. Dry distillation yields carbazole, H, C, H, and C, H, (Loebisch a. Schoop, M. 7, 614). - 2. Distillation with lime yields (3)-methylpyridine, methyl-indole (scatole), C2H4, NEtH2, and NH₃ (Stochr, B. 20, 810, 1108, 2729; J. pr. [2] 42, 405).—3. Distillation with soda-lims gives carbazole, scatole, and (8)-methyl-pyridine (Loebisch a. Malfatti, M. 9, 628).—4. Distillation with KOH gives indole (Goldschmidt, B. 15, 1977) and batyric acid (Loebisch a. Schoop, M. 7, 93) .- 5. Distillation with zinc-dust at 400° in vacuo yields solid C₂;H_{2;N.O}, which dissolves in alcohol with blue fluorescence, and gives no colour with K₂Cr₂O, and H₂SO₄. Zinc-dust at a red heat gives H, C₂H₁, C₂H₂, NH₃, and carbazole (Loebisch a, Schoop, M. 7, 609), and (γ)-lutidine (Scichilone a. Magnanini, G. 12, 444).— 6. Alkaline KMnO, yields oxalic acid, CO, NH,, and a crystalline acid [195°] (Hoogewerff a. Van Dorp, R. T. C. 2, 181). Half the nitrogen is given off as ammonia (Wanklyn a. Chapman, C. J. 21, 161).-7. KMnO, in dilute acid solutions yields an amorphous acid C₁H₁₁NO₂ aq (?) (Plugge, R. T. C. 2, 270), which yields amorphous C₁₁H₁₆AgNO₂ aq (Hanriot, C. R. 96, 1671).—8. By treatment with CrO₂ and H₂SO₄ it yields the same oxidation product C, H, N,O, as that ob-

tained from brucine under the same treatment (Hanssen, B. 18, 1917).—9. PCl, (1 pt.) acting on strychnine hydrochloride (8 pts.) under boiling chloroform yields a compound crystallising from benzene in needles [224°], possibly penta-chlorostrychnine (Stoehr, J. pr. [2] 42, 414).—10. Boiling HNO, forms cacostrychnine and picric acid (Shenstone, C. J. 47, 142); nitric acid forms 20 p.c. of di-nitro-di-oxy-quinoline carboxylic acid C₁₀H₄N₂O₂, which yields KA', is reduced by SnCl₂ to C₁₀H₂N₂O₄ (a body having acid and basic properties), and when heated with water is split up into CO, and di-nitro-di-oxy-quinol-ine (Tafel, B. 26, 353).—11. Baryta water in sealed tubes at 140° forms two bases, C2, H2, N2O4 and C_{s.}H₂₈N₂O₅, both crystallising from water (Gal a. Etard, C. R. 87, 362).—12. Alloxan added to a solution of strychnine in a saturated solution of SO, forms small colourless prisms of B'C,H,N,O,H,SO, aq (Pellizzari, A. 248, 150).— 18. Iodoform (5 g.) and strychnine (12 g.) dissolved in hot alcohol (500 c.c.) deposit on cooling crystals of B', CHI,, sol. ether and chloroform, but decomposed by light, hot water, and dilute acids (Lextrcit, C. R. 92, 1057).—
14. Chloro-acetic acid at 180° forms C₁₃H₂₁N₂O₄, a base which crystallises in silky needles, v. sol. hot water and alcohol, insol. ether (Roemer, Z. 1871, 435). It yields $(C_{33}H_{21}N_{2}O)_{3}PtCl_{3}$.

15. AcCl forms B'AcCl, which gives (B'AcCl)_PtCl_{4}(Konrad, J. 1874, 876).—16. Chloro-acctone at 185° yields B'O,H,ClO, S. 6·5 at 15°, which yields B'O,H (B'C,H,ClO),PtCl, 2aq and B'C,H,OSO,H 1 aq (Konrad).—17. Aqueous SO₂ and alloxan give colourless prisms of B'SO₂HC₄H₂N₂O₄ aq (Pelliz-

Eari, G. 18, 329).

Detection.—1. H,SO, forms a colourless solution which with K.Cr₂O, gives a blue colour, changing through violet and red to yellow (Otto, A. 60, 273). A drop of nitric acid and PbO, or MnO, may be used instead of K,Cr₂O, (Marchand, B. J. 24, 400; Davy, A. 88, 402). KMnO₄ and Ag₅O act in like manner (Lyman, Fr. 12, 126). The colour with H2SO4 and K2Cr2O2 is not shown in presence of brucine (Hanriot, C. R. 97, 267), and is interfered with by quinine, morphine, and sugar (Brieger, J. 1850, 617; Vogel, J. 1853, 686; Flückiger, Fr. 28, 102).—2. A minute quantity of KClO, added to a warm solution in dilute HNO, gives a scarlet colour, changed by ammonia to brown, and then, on evaporation to dryness, becoming green (C. L. Bloxam, C. N. 55, 155).-3. Ammonium vanadate in H2SO4 gives a blue colour, turned red by potash (Mandelin, Fr. 23, 240).—4. Chlorine water gives a pp.-5. Strychnine can be extracted from beer containing the poison by shaking with animal charcoal, the charcoal being subsequently extracted with alcohol (Graham a. Hofmann, A. 83, 39; cf. Wagner, Fr. 6, 387).—6. Obtained from acid liquids by adding ammonia and immediately shaking with chloroform (Cloetta, Fr. 5, 265; Gray, Fr. 12, 125). -7. A liquid containing strychnine sulphate may be shaken with benzene without loss of strychnine, but if the liquid be neutralised by magnesia the free strychnine can be extracted by benzene (Dragendorff, Z. [2] 2, 27).-8. A 1 p.c. solution of strychnine strongly acidified by HCl is ppd. by K, FeCy, while brucine remains in solution (Holst A. Beckürts). This may be used as a volumetric method. Strychnine and brucine may also be

method: Stryonnine and brucine may also se separated by crystallisation of their picrates (Gerock, Ar. Ph. [8] 27, 158).

Salts.—B'HOlligaq (Regnault, A. 26, 17).

Trimetric crystals; a:b:c:= 484:1:466 (Stoehr, J. pr. [2] 42, 399). Neutral in reaction. S. 2

at 22°. Levorotatory. [a]_r = -28°.—B'HAuCl.

Orange crystals (from alcohol) (Nicholson a. Abel, C. 7, 2, 24; 4, 71, 24). Decomposed by boiling C. J. 2, 241; A. 71, 84). Decomposed by boiling water (O. De Coninck, Bl. [2] 45, 131).—B'₂H₂PtCl₆: golden scales (from alcohol). S.G. 18.5 1.779 (Clarke, Am. 2, 175).—B'₂H₂PtCl₃ aq (Schmidt, A. 180, 295).—B'₂H₂ZnCl₄ aq: prisms (Grafinghoff, Bl. [2] 4, 391).—B'₂H₂CdCl₄ (Galletly, N. ed. P. J. 4, 94).—B'HHgCl₃. Crystals (from the content of alcohol).—B'HgCl₂: insol. alcohol, water, and ether.—B'₂H₂SQ₂HgCl₂.—B'₂H₂PdCl₄: dark-brown needles (from alcohol).—B'HCl2HgOy₂: tables (Brandis, A. 66, 268).—B'HgCy2: small prisms, sl. sol. water and alcohol, insol. ether. -B'HBraq: needles, sol. water and alcohol.-B'HI aq: plates or needles, almost insol. cold water.—B'HI,. S. 007 at 15°. Reddish-brown pp. got by adding a solution of I in HIAq to a salt of strychnine. Crystallises from alcohol in dark-brown needles with bluish metallic lustre. Dichroic (brown and yellow) in polarised light. M. sol. hot alcohol, sl. sol. chloroform, nearly M. Sol. Hot sicond, St. Sol. chloroform, nearly insol. C9, (Tilden, C. J. 18, 99; Herapath, Pr. 8, 149; Bauer, Ar. Ph. [3] 5, 289; Jörgensen, A. Ch. [4] 9, 116).—B'HHgI,: yellow tables (from alcohol) (Groves, C. J. 2, 97).—B'H, F. 2aq: prisms (Elderhorst, A. 74, 77).—B'HNO; needles.—B'HClO, aq: prisms, sl. sol. cold water (Boedeker, A. 71, 62).—B'H, SO, 2aq: needles.—B'HSO. Four, sided prigns. Level needles.—B'₁H₂SO₄. Four-sided prisms. Levorotatory [a]₁ = -26° .—B'₂H₂SO₄ 5aq: long thin prisms. Got by crystallisation between 109° and prisans. Got by erystatination between 109° and 95°.—B'₂H₂SO₄6aq. Obtained by cooling a conc. solution to 95°-50° (Lextreit, J. Ph. [5] 6, 259; Rammelsberg, B. 14, 1231; cf. Baumhauer, C. J. 44, 485).—B'₂H₂CrO₄; lemon-yellow needles, sl. sol. water and alcohol. -B'2H2S2O348q. S. I in the cold. Formed by atmospheric oxidation of a mixture of strychnine, alcohol, and ammonium sulphide (How, G. N. 18, 232).—
B'₂H₂S₀. Formed from strychnine and alcoholic ammonium polysulphide (Hofmann, B. 1, 81; 10, 1087) and by atmospheric oxidation of a solution of strychnine in clooholic H2S (Schmidt. B. 5, 1267; 10, 1288; A. 180, 288). Orange needles, insol. water, alcohol, and ether.—
B'H,PO, 2aq. S. 19. Needles (Anderson, A. 66, 56).—B',H,PO, 9aq: rectangular tables.—
B'H,AsO, 9aq. S. 7 in the cold; 20 in hot water.
—B'HAsO, efflorescent cubes. S. 3 in the cold; 10 at 100°.—B' H. FaCt. Asa. Caratellian powels. 10 at 100°.—B',H,FeCy, 4aq. Crystalline powder (Holst a. Beckurts, Ar. Ph. [3] 25, 318; cf. Brandis, A. 66, 257). By atmospheric oxidation in presence of water it is converted into strychnine and the ferricyanide (Beckürts, B. strychnine and the ferricyanide (Beckürts, B. 18, 1235).—B'H₄FeCy₄: white powder, sol. hot water. Acid in reaction.—B'₂H₃FeCy₆ (aq. golden prisms.—B'₄(H₄CoCy₆) 4aq.—B'₄(H₂NiCy₄) 8aq (Lee, B. 4, 789).—B'₂H₂PtCy₄ 2aq: needles (from alcohol).—O xalate B'₂H₄C₄O₄: flat needles.—B'₂H₄C₄O₄.—B'H₅Cy₆O₄.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇.—B'H₅Cy₇O₇. Red pp., v. sl. sol. hot water (Christensen, J. pr. [3] 45, 367).—B'₂2H₂Pt(SCy)₈. Red crystals (Clarke

and Owens, Am. 3, 851).— Gyanurates: B'₂H₂O₂C₄N, aq. [287°]. Prisms, al. sol. water, m. sol. alcohol.—B'H₂O₄C₅N, aq. [295°]. Needles (Claus, J. pr. [2] 88, 228).—Nitroprusside. S. 12 (Davy, Ph. [3] 11, 756). Succinate B'₂C₄H₄O₄6\(\frac{1}{2}\)aq. (Crespi, G. 13, 176).—Tartates: B'₂C₄H₄O₄.—B'₂O₄H₄O₄. 4aq; white afflorescent needles (Arnna. J. pr. 52, 221). efflorescent needles (Arppe, J. pr. 53, 331).—
B',O,H₂O₆ aq (Pasteur, A. Ch. [3] 38, 437).—
B'O,H₆O₆ 3aq.—B'C,H₅(SbO)O₆. Needles (Stenhouse, A. 129, 25).—Malate B'₂C,H₆O₅ 3\frac{1}{2}aq.—
Pyrotartrate B'₂C,H₆O₅ 3\frac{1}{2}aq.—
Mucate $B'_{2}C_{n}H_{10}O_{n}$. Long needles (Ruhemann a. Dufton, $C.\ J.\ 59,\ 754$).

Di-hydrate B'2aq. Strychnol. Formed by warming strychnine with alcoholic NaOEt, adding water, and evaporating. The brown oily layer that forms is allowed to solidify, dissolved in water, and ppd. by CO₂. The pp. is dissolved in NH₃Aq and re-ppd. by expelling NH₃ by air (Loebisch a. Schoop, M. 7, 83). The same body is got by heating strychnine (15 g.) with BaO2H2 (30 g.) for 12 hours at 140° (Tafel, B. 23, 2737). Minute wedge-shaped needles, sl. sol. cold water, insol. alcohol and ether. Darkens at 150°. Sol. dilute alcohol and solutions of ammonium salts; sol. acids. Converted into strychnine on warming with dilute acids. Dilute HNO, and a little NaNO, give a crimson colour. Bromine water gives a pale-purple colour. Does not give the strychnine reaction with H2SO4 and K2Cr2O7. On heating at 100° with NaOMe and MeI it is converted into C21H22N2O2Me5I 2aq, crystallising in needles.

Tri-hydrate v. Reaction 10. Pentahydrate B'5aq. [215 [215°]. Got by heating strychnine with alcoholic NaOEt (Tafel). Needles, more soluble than the dihydrate. Becomes very hygroscopic when dried in vacuo.

Benzoyl derivative C21H21BzN2O2. V. sl. sol. water (Schützenberger, A. 108, 353; C. R.

47, 233).

Methylo-iodide B'MeI. S. 5 in the cold (Stahlschmidt, P. 108, 513). Poisonous (Crum Brown a. Fraser, Tr. E. 25). Formed by heating with MeI in sealed tubes. Pearly plates. Yields B'MeI₃ (Jörgensen, J. pr. [2] 3, 157) and the salts B'MeBr, B'MeCl 2aq, B',Me,PtCl₃, B'MeAuCl,, B',Me,SO,5aq, B'McHSO. B'MeH, PO, 2aq, B'MeCl2 HgCl2, B'MeNO, and B'2Me2FeCy4.

Methylo-hydroxide B'MeOH or $C_{20}H_{22}O(NH) \gtrless_{CO}^{NMe}>0$. Formed from B'MeI by successive treatment with Ag.SO, and baryta (Tafel, B. 23, 2733; A. 264, 62). Colourless crystals (containing 4aq), v. sol. alcohol, but a product containing less water soon separates. Poisonous. Gives the same colour-reactions as strychnic acid. Alcohol and Na yield a compound [158°]. MeI forms B'MeIMeOH crystal-

lising in plates, decomposed at 280°. Isomeride of the methylo-hydroxide H₂₈N₂O₃7aq. Formed from the methylo-C₂₂H₂₈N₂O₂ 7aq. iodide of isostrychnic acid, Ag, and Ag,O at 40° (Tafel, M. 264, 81). Colourless needles; v. s. sol. hot water and alcohol, insol. ether.

Methyl-strychnine methylo-hydrox. ide $C_{11}H_{22}N_2O_3$ i.e. $C_{20}H_{22}O(NMe) \ll \frac{NMe}{CO} > 0$. Formed from B'MeIMeOH by successive treat-

ment with Ag.SO, and baryta. Got also by the action of Ag.O on the methylo-iodide of methyl. strychnic acid (Tafel, B. 23, 2785; A. 264, 66). Prisms (containing 6aq), v. sol. hot water and alcohol, nearly insol. ether. Gives a blood-red colour with HNO₃, CrO₃, or FeCl₃. Forms with acids salts which differ from those prepared by the action of silver salts on B'MeIMeOH. Forms a crystalline nitroso-derivative, v. sol. water and warm alcohol, forming a yellow solution changed by NaOH to brownish-red and olive-green. HI yields the methylo-iodide of methyl-strychnic acid. Diazobenzene sulphonic acid gives a brownish-red dye .- Hydroiodide. S. 7. Plates. — Methyloiodide C₂₄H₂₁N₂IO₃.
 S. 1. Needles.

Isomeride of methyl-strychnine methylo-hydroxide C2142,N2O, 3aq. Formed from the methylo-hydroxide of methyl-isomethyl-iso-Isomeride of strychnic ether (Tatel, A. 264, 82). Crystals, v. sol. hot water and alcohol, insol. ether. Yields a dye with diazo-benzene sulphonic acid.

Ethylo-iodide B'Etl. S. 6 at 15°; 2 at 100°. Formed by heating strychnine with alcohol and EtI at 100° (How, A. 92, 338). Foursided prisms. Not attacked by KOHAq. Gives the strychnine reaction with K2Cr2O, and H2SO. Converted by moist silver oxide into the base B'EtOH 2aq, which yields the salts B'EtNO,, B'Et_PtCl_s, B'EtHCO,, B'EtHCrO, aq, B'EtCy [105°] (Claus a. Merck, B. 16, 2748), and B'EtI. (Jörgensen, A. Ch. [4] 11, 115).

Isoamylo-chloride B'CsH11Cl jaq. Formed by heating strychnine with isoamyl reinloride (How, Tr. E. 21, 1, 27). Prisms. Yields B'O₂H₁₁OH, B'C₃H₁₁I₃, B'O₃H₁₁I₃, crystallising in black prisms (Jörgensen, J. pr. [2] 8, 145), and B'EtHCrO..

Bromo-ethylo-bromide B'C,H,Br. Formed by heating strychnine with ethylene bromide and alcohol (Ménétriès, J. pr. 85, 230). White crystals, sl. sol. cold water and alcohol. Converted by AgNO, into B'C.H.Br.NO, and by Ag.SO, into B'C,H,Br.SO,H, whence baryta produces alkaline B'C,H,Br.OH. - (B'C,H,Br),PtCl, -B'C_H,BrI3: shining brown laming. -Moist Ag₂O converts B'C₂H₄Br₂ into B'C₂H₄OH, which is alkaline and is converted in aqueous solution by chlorine into C23H21Cl3N2O2.-B'C2H2CrO4H. -(B'C,H,Cl),PtCl,

Chloro-ethylo-hydroxide B'ClC,H,OH. Got by heating strychnine with glycolic chlorhydrin at 150° (Messel, A. 157, 7). Silky needles (containing aq). Yields (B'C₂H₄OH)₂SO₄2aq, which is converted by baryta into crystalline

which is converted by baryta into drystaline (B'C,H,OH)OH2 aq.—(B'C,H,OH)_PtCl₀.

Bensylo-chlorideB'C,H,Cl. [263°]. Prisms (containing aq). Yields (B'C,H,Cl)_PtCl₄ [216°], B'C,H,NO₃ [c. 264°], (B'C,H,),Cr₂O, and B'C,H,SCy [237°] (Garzarolli, M. 10, 1).

Bensylo-hydroxide B'C,H,OH. Plates. Chlorostrychnine $C_{:1}H_{:1}C!N_{:2}O_{::}[a]_{D} = -105^{\circ}$. Formed, together with diand tri-chlorostrychnine, by passing Cl into a solution of strychnine hydrochloride (Laurent, A. Ch. [3] 24, 312; A. 69, 14; Richet a. Bouchardat. C. R. 91, 990). Crystalline, v. sol. alcohol, ether, and chloroform. Chlorostrychnine forms a hydrate C₂₁H₂₁ClN₂O₂ Saq on heating with alcoholis potash. - B', H, SO, 7aq.

Dichloro-strychnine $C_{21}H_{20}Cl_2N_2O_2$. Needles (from alcohol).

(a) Tri-chloro-strychnine C₁₁H₁₂Ol₁N₂O₂. Formed by saturating a solution of strychnine hydrochloride with Ol. Minute crystals (from alcohol). Yields a trihydrate which is not very poisonous.

(β)-Tri-chloro-strychnine C₂₁H₁₉Cl₁N₂O₂.

Formed by heating strychnine hydrochloride with PCl₂ and chloroform (Stochr, J. pr. [2] 42, 412; B. 20, 813). Microcrystalline powder (from alcohol). Gives the strychnine reaction with K₂Cr₂O, and H₂SO, —B'HCl: plates (from dilute alcohol).—B'H₂SO, —B'HCl: plates (from dilute alcohol).—B'H₂SO, Plates, m. sol. water.

Brome-strychnine C₂₁H₂₁BrN₂O₂. [222°].

Formed by adding Br (2 at.) to a solution of

Brome-strychnine \$\overline{O}_{21}\Hat{H}_{21}\Br\N_2\O_2\$. [222°].

Formed by adding Br (2 st.) to a solution of strychnine hydrochloride (1 mol.), ppg. by alkali, and recrystallising from alcohol (Shenstone, C. J. 47, 139; Beckürts, B. 18, 1236; Loebisch a. Schoop, M. 6, 855). Trimetric crystals; abc=1.459:1:1:195 (Miers, C. J. 47, 144).—B'HCl.—B'HBr.—B'HNO,.—B'2\H2\SO,7aq.

Methylo-iodide B'MeI. Pearly plates,

Methylo-iodide B'MeI. Pearly plates, sol. alcohol. Converted by moist Ag₂O into B'MeOH4ag.

B'MeOH4aq.
Dibromide C₂₁H₂₁Br₃N₂O₂. Got by adding Br to a solution of strychnine at 40°. Bright yellow crystalline powder.

Di-brome-strychnine C₂₁H₂₁Br₂N₂O₂. Got by adding Br to strychnine in chloroform. Trimetric crystals, v. sol. chloroform and dilute alcohol.—B'HCl: needles.

Nitro-strychnine C₂₁H₂₁(NO₂)N₂O₂. [225°]. Formed by adding strychnine nitrate to H₂SO₄ (Loebisch a. Schoop, M. 6, 845; 7, 59). Golden plates (from alcohol). Gives no colour with H₂SO₄ and K₂Cr₂O₇. Dissolves in acids and alkalis. On heating with alcoholic potash it is converted into xanthostrychnol C₂₁H₂₁N₃O₄, which forms ruby-red crystals (containing 2aq) and gives salts with acids and bases.—B'HCl.—B'2H₂PtCl₈.—B'2KOH: red deliquescent needles.—B'2H₂O₂H₂2aq.—Ag₂O₂₁H₁₀N₃O₄: unstable pp.

[a] Di-nitro-strychnine C₂₁H₂₀(NO₂)₂N₂O₂.

(a)-Di-nitro-stryohnine C₂₁H₂₆(NO₂)₂N₂O₂.

[226°]. Formed by passing nitrous acid gas into an alcoholic solution of strychnine nitrate (Claus a. Glassner, B. 14, 774). Orange-yellow plates. Converted by dilute HNO₃ into cacostrychnine.—B'HNO₄: yellow nodules (from

acetone), v. sl. sol. hot water.
(8)-Di-nitro-strychnine. Formed by dis solving strychnine (60 g.) in fuming HNO₃ (300 g.) at -10° (Hanriot, C. R. 96, 585). Transparent amber-yellow prisms (from chloroform-alcohol), sol. hot water and alcohol, v. sol. chloroform. Decomposes at about 202°.—B'HCl.—Nitrate: plates (from hot water).

Amido-strychnine v. vol. i. p. 184. Di-amido-strychnine, ibid. Cacostrychnine v. vol. i. p. 654.

 Its salts are more soluble than those of strychnine.—B'HI aq. Groups of prisms.—B'₂H₂Or₂O₃.

Thin yellow needles.—B'₂H₂PtCl₄.

Methylo-iodide B'Mel. Crystals. S. c. 10

at 100°.

Strychnine sulphonic acid C₂₁H₂₁(SO₃H)N₂O₄. Formed by dissolving dry strychnine sulphate in fuming H₂SO₄ (containing 30 p.c. anhydride extra) in the cold and allowing to stand a fortinight (Loebisch a. Schoop, M. 6, 857). Deliquescent mass. Does not give the strychnine reaction with K₂Cr₂O₄ and H₂SO₄. Strychnine sulphonic acid. Formed by

Strychnine sulphonic acid. Formed by heating strychnine with H₂SO₄ (2 pts.) at 100° (Stoehr, B. 18, 3429; Guareschi, G. 17, 109). Amorphous powder, v. sl. sol. water and alcohol, sol. dilute acids and alkalis. Does not give a colour with K₄Cr₂O₂ and H₂SO₄. Not poisonous.—NH₄A': v. sol. water, insol. alcohol.—KA': m. sol. water.—BaA'₂: amorphous pp.

Strychnine disulphonic acid

 $C_{21}H_{20}(SO_3H)_2N_2O_3$. Got by heating strychnine with H_2SO_4 and SO_5 at 150°. Amorphous, v. sol. water, v. sl. sol. benzene, insol. alcohol and ether.—Na₂A" 6aq.—BaA": plates, sol. water.—BaA" 7aq.—Ba(HA"):: vellow powder.

v. Sol. water, v. Sh. sol. belizens, insol. account and ether.—Na, A" 6aq.—BaA": plates, sol. water.—BaA"7aq.—Ba(HA"),: yellow powder.

STRYPHNIC ACID C, H₃N₃O₂. Got by adding HOAc to a mixture of uric acid and KNO₂ and evaporating (Gibbs, B. 2, 341). Small pale-yellow crystals, sol. hot water. Sodium-amalgam forms crimson crystals. — KA' 1½aq: yellow needles.—MgA', 6aq.—CaA', 2aq.—SrA', 6aq.—BaA', 2aq.—PhA', -Ph₂A', O3aq.

STYCERIC ACID v. PHENYL-GLYCERIO ACID.

STYCERIC ACID v. PHENYL-GLYCERIC ACID.

STYCERIN CHPh(OH).CH(OH).CH_OH.

Formed by heating CHPhBr.CH_Br.CH_OH (v.
DI-BROMO-PHENYL-PROPYL ALCOHOL) with 30 pts.

water and some AgOAc at 150°-165° (Grimaux,
J. 1873, 404). Yellow gummy mass with bitter
taste. V. sol. Aq and alcohol, nearly insol. ether.

STYPHNIC ACID v. TRI-NITRO-RESORCIN.
STYRACIN v. Cinnamyl ether of Cinnamic
ACID.

STYRENE C₃H₈ i.e. C₄H₄.CH:CH₂. Styrol. Styrolene. Cinnamene. Phenyl-ethylene. Mol. w. 104. (144°) (Schiff, A. 220, 93). S.G. 2° 9074. µ_p = 1·541 (Madan, C. J. Proc. 1, 107). S.V. 131 (Schiff). R_∞ 58·1 (Nasini a. Bernheimer, G. 1, 93). Occurs in liquid storax (Bonastre, J. Ph. 17, 338; Simon, A. 31, 265; Blyth a. Hofmann, A. 52, 293, 325) and in coal tar (Berthelot, A. Suppl. 3, 368; Krämer a. Spilker, B. 23, 3282).

Formation.—1. By distilling cinnamic acid alone or with lime or baryta (Gerhardt a. Cahours, A. Ch. [3] 1, 96; Kopp, C. R. 53, 634; Howard, C. J. 13, 135; Kraemer, Spilker, a. Eberhardt, B. 23, 3269).—2. By distilling cupric cinnamate (Hempel, A. 59, 316).—3. By distilling balsam of Peru with pumice (Scharling, A. 117, 184).—4. By distilling dragon's blood alone or with zinc-dust (Glénard a. Bondault, A. 53, 325; Bötsch, M. 1, 610).—5. By heating acetylene at a dull-red heat (Berthelot, C. R. 62, 905, 947; A. 141, 181).—6. By passing ethylene alone or mixed with benzene or diphenyl through a redhot tube (Berthelot, Z. [2] 4, 884; A. 142, 257; Barbier, O. R. 79, 660; Ferko, B. 20, 660).—7. By passing ethyl-benzene through a red-hot tube (Berthelot, Z. [2] 4, 589).—8. By heating C.H., CH., CH., Br alone or with alcoholic potash

at 180° (B.; Thorpe, Z. 1871, 130).—9. By heating C₄H₄.CHBr.CH₂ with alcoholic KCy (Radziszewski, B. 7, 140).—16. By distilling C₄H₄.CH(OAc).CH₄ (R.).—11. By heating C₅H₄.CH(OH).CH₄ (derived from acetophenone) with ZnCl₂ (Emmerling a. Engler, B. 4, 147).—12. By the action of acetylene on benzene inpresence of AlCl₃ (Varet a. Vienne, Bl. [2] 47, 918; C. R. 104, 1375).—18. From phenyl-acetylene, zinc, and HOAc (Aronstein a. Hollemann, B. 22, 1184).

Properties.—Oil, with aromatic odour. Inactive to light (Van't Hoff, Bl. [2] 25, 175). Miscible with alcohol and ether. Changes on keeping, or on heating in a sealed tube at 300°, to solid metastyrone. Combines with Cl₂ and Br₂. HBr forms C₂H₂.CHBr.CH₃. HCl forms PhOHCl.CH₂ only (Schramm, B. 26, 1709). Potash has no action. Fuming HNO₃ forms nitro-styrene. Chromic acid mixture forms benzoic acid. Cono. H₂SO₄ changes it to metastyrene. On heating with aqueous NaHSO₃ at 120° styrene forms the compound C₃H₂.NaHSO₃ (306°) (W. von Miller, N. R. P. 24, 31). Condenses, in presence of H₂SO₄, with toluene and xylene, forming diphenyl-propane and phenyl-tolyl-propane respectively (Kraemer a. Spilker, B. 23, 3169).

Metastyrene (C₃H₃)z. S.G. ½ 1054. μ₀
1.593 (Madan, C. J. Proc. 1, 107). Occurs in

Metastyrene (C_8H_8)_x. S.G. ¹² 1'054. μ_D 1'593 (Madan, C. J. Proc. 1, 107). Occurs in liquid storax (Kovalevsky, A. 120, 66). Formed from styrene on keeping or on heating in a sealed tube at 200°. Formed also by heating styrene with aqueous NaHSO_x at 110° (Miller, A. 189, 341). Transparent solid without tasto or smell, becomes sticky when warmed. Highly refractive. Insol. water and alcohol, sl. sol. ether. Inactive to light (Van't Hoff, B. 9, 1339; cf. Berthelot, C. R. 85, 1191). Changes to styrene on distillation. Cl and Br act slowly, forming the same compounds as with styrene.

Di-styrene C₁₆H₁₆i.e. Ph.CH:CH.CHMe.Ph(?). (c. 315° i.V.). S.G. 2 1-027; ¹⁵ 1-016. V.D. 7-07 (calc. 7-2). Got by boiling cinnamic acid with H₂SO, (1 vol.) and water (1½ vols.) (Erlenmeyer, A. 135, 122; Fittig a. Erdmann, A. 216, 187). Liquid, with blue fluorescence, which slowly disappears. Inactive to light. If kept boiling for a long time it decomposes, forming toluene, styrene, high boiling products, and

probably iso-propyl-benzene.

Reactions.—1. Chromic mixture gives benzoic scid.—2. Bromine gives the di-bromide $C_{15}H_{15}Br_2$ [102°], crystallising from ether in needles. V. e. sol. CS_2 , ether or benzene, v. sol. hot alcohol.

Solid distyrene $C_{1a}H_{1e}$. [119°]. A product of the distillation of cinnamic scid or of its Ca salt (Engler a. Leist, B. 6, 256; Miller, A. 189, 840). Formed also by passing C_0H_1 , C_1H_2 , over red-hot lime (Radziszewski, B. 6, 494). Tables. Yields a dibromide $C_{1e}H_{1e}Br_2$ [238°], crystallising from benzene in needles (Liebermann, B. 22, 2256).

References.—Amido-, Bromo-, Bromo-amido-, Bromo-nitro-, Chloro-, Chloro-, Nitro-,

and NITRO-AMIDO-STYRENE.

STYRENE DIBROMIDE v. DI-BROMO-ETHYL-BENZENE.

STYRENE DICARBOXYLIC ACID C_{1e}H₄O₄
i.s. [1:2] CO₂H.O₂H₄.CH:CH:CO₂H. o-Carboxycimamicacid. [175°]. Formed by heating the salts
of oxy-carboxy-phenyl-propionic acid (Gabriel

a. Michael, B. 10, 1558, 2200). Slender needles (from water). Changed on fusion into the lactone of oxy-carboxy-phenyl-propionic acid.—PbA".—Ag,A": sticky pp.

Isomeride v. p-Carboxy-cinnamic acid, vol. ii, p. 190.

STYRENE DICHLORIDE v. wa-Di-Chloro-DI-ETHYL-BENZENE.

STYRENE DI-IODIDE V. DI-IODO-ETHYL-

STYRENE DISULPHOCYANIDE C_sH_s(SCN)₂. [102°]. Formed by heating C_sH₃CHBr.OH₂Br with potassium sulphocyanide in alcohol (Nagel, A. 216, 323). Pale-yellow needles, v. sol. ether, hot benzene, and toluene. Crystallises from benzene as C₁₆H₈S₂N₂C₆H₈ [62°]. Alcoholic ammonium sulphide at 100° forms (C₈H₈)₂S [151°]. Cold fuming HNO₂ gives rise to the compound [1:4] C₈H₄(NO₂).CH(SCy)CH₂(SCy) [112°] crystallising from alcohol in needles.

DI-STYRENIC ACID C17H16O2 6.6.

Ph.CH:CH.CPhH.CH₂CO₂H or Ph.CH:CH.CH.(CO₂H).CH₂Ph. Formed by boiling cinnamic acid with H₂SO₄ (1 vol.) diluted with water (1 vol.) (Fittig a. Er³mann, 4. 216, 182). White amorphous powder. V. sl. sol. water, v. e. sol. ether, alcohol, or glacial acetic acid. It melts below 50°. May be distilled almost undecomposed.

Reactions.—I. Sodium amalgam has no action.—2. Br in CS₂ forms no bromide.—3. Boiling H₂SO₄ (I vol.) mixed with water (1½ vols.) does not affect it.—4. Chromic mixture gives only benzoic acid.

Salts.— $Ca(C_i, H_i, O_s)_s$.— BaA'_s — AgA'_s . Ether.—EtA'. Liquid.

STYROGALLOL $C_{ie}H_sO_s$ i.e.

C₆H₁<C_C>C₆H(OH)₂
CH.CO — >0 (?). Formed from e cinnamic acid, gallic acid, and conc. H₂SO₄ at

cinnamic acid, gallic acid, and conc. H₂SO₂ at 50° (Jacobsen a. Julius, B. 20, 2588; von Kostanecki, B. 20, 3137). Yellow needles, which may be sublimed; al. sol. hot alcohol. Not melted at 350°. With mordants it dyes like nitro-alizarin.

STYROLENE ALCOHOL v. DI-OXY-ETHYL-BENZENE.

STYRONE v. CINNAMYL ALCOHOL.

STYRONE DIBROMIDE v. (di)-Bromo-PHENYL-PROPYL ALCOHOL.

STYRYL-ACRYLIC ACID v. PHENYL-PEN-TINOIC ACID.

STYRYIP AMYL KETONE CARBOXYLIC ETHER CI, H₂O₃ i.e. C₆H₃.CH:CH.CO.OEt₄.CO.₂Et. [102°]. Formed from di-ethyl-acetoacetic ether, benzoic aldehyde, and HCl in the cold (Claisen a. Matthews, A. 218, 184). Triclinic prisms (from ligroin). Yields C₁,H₂₂Br₂O₃ [55°] orystallising in small prisms.

STYRYL-ANGELIC ACID C, H, O, i.e. C, H, OH:CH.CH:CEt.CO, H. [127]. Formed by heating cinnamic aldehyde with butyric anhydride and sodium butyrate at 165° (Perkin, C.J.

dride and sodium butyrate at 165° (Perkin, C. J. 81, 413). Crystals, v. sol. alcohol.—AgA'.

STYRYL BUTENYL KETONE C_{1:}H₁, O i.e.
C₄H₂, CH:OH:OO.OH:OMe₂ (179° at 14 mm.).

Formed by passing HCl into a mixture of bensoic aldehyde and mesityl oxide (Claisen a. Claparède, B. 14, 351). Yellowish liquid, smelling like strawberries. Yields C_{1:}H₁, Br₄O [180°].

FORMAL OROTONIC ACID C₁₂H₁₂O₂. [158°]. Formed by heating cinnamic aldehyde with propionic anhydride and sodium propionate (Perkin, C. J. 31, 413). Prisms (from ligroin).—AgA': white pp. sl. sol. sold water.

STYRYL ETHYL KETONE CARBOXYLIC ACID C₄H₁.CH₂CO₂H. Cinnamatoric Charles (Contraction of the Contraction of the Cont

moyl-propionic acid. Benzylidene-levulic acid. [120°]. Formed from β-acetyl-propionic acid, benzoic aldehyde, and dilute KOHAq (Erdmann, A. 258, 130). Leaflets (from water). May be reduced to C.H., CH., CH., CO.CH., CH., CO., Ethy. Co.,

C.H. CH:CH.O.C.H. (217°). S.G. 981. Formed from w-chloro-styrene and NaOEt at 180° (Erlenmeyer, B. 14, 1868). Aromatic liquid. Converted by heating with water into alcohol and phenyl-acetic aldehyde.

STYRYL-ETHYL-PYRIDINE C, H, N

i.e. C.H.CH:CH.CCOH:CH basole. [58°]. (356° cor.). Formed by heating methyl-ethyl-pyridine with benzoic aldehyde and ZnCl, at 220° (Plath, B. 21, 3087). Needles or plates, insol. water, v. sol. alcohol and ether, sl. sol. ligroin. Bromine yields the dibromide C.H., CHBr.CHBr.C.H., EtN. [128°]. — B'HCl. C₄H₁, OHDF OHDF C₅H₁, EtN. [128°]. — B HCI. [193°]. — B'₂H, PtCl₄ 2aq. [188°]. Needles.— B'HAuOl., [168°].—B'HSnCl₃ 3aq. [246°].— B'HHgCl₃, [196°].—B'C₄H₃N₃O₇. [203°]. STYRYL-GLYOXAL. Oxim C₁₆H₅NO₂ i.e. C₄H₅CH:CH.CO.CH:N.OH. [144°]. Formed from

nitroso-acetone, benzoic aldchyde, and alcoholic NaOEt (Claisen a. Manasse, B. 22, 529). Crystals (from water or benzene). Gradually decomposes, with evolution of HCy.

STYRYL-GLYOXYLIC ACID C, H,O, i.e. C.H..CH:CH.CO.CO.H. Formed by saponification of its amide by conc. HClAq, and also by saturating a mixture of benzoic aldehyde and pyruvic acid with HCl (Claisen, B. 13, 2124; 14, 2472). Gummy mass, sol. water. Split up by alkalis, even in the cold, into benzoic aldehyde and pyruvic acid.—AgA': pp.

Amide CHPh:CH.CO.CO.NH. [130°]. pared by the action of conc. HClAq and HOAc on the nitrile of cinnamic acid. Flat prisms or

plates. Sol. ether and hot water.

Reference. - NITRO-STYRYL-GLYOXYLIC ACID. STYRYL-HYDANTOIC ACID C,,H,,N,O. [185°]. Formed by boiling styryl-hydantoin with baryta water (Pinner a. Spilker, B. 22, 692). White plates, sol. alcohol and hot water. Boiling HClAq converts it into styryl-hydantoin.—AgA'.

STYRYL-HYDANTOÏN v. DI-OXY-STYRYL-m-PYRAZOLI STYRYLIDENE-THIO-GLYCOLLIC ACID v.

CINNAMYLIDENE-THIO-GLYCOLLIC ACID.

DI-STYRYL-KETONE v. DI-BENZYLIDENE-ACETONE and NITRO- and OXY- DI-STYRYL-KETONE. STYRYL-DI-METHYL-GLYOXALINE

 $C_{19}H_{14}N_{2}$ i.e. $C_{0}H_{1}CH:CH.C \leqslant_{N-CMe}^{NH.CMe}$ Formed from di-methyl di-ketone, cinnamic aldehyde, and alcoholic ammonia at 100° (Wadsworth, C. J. 57, 11). Crystals, v. sol. alcohol.—B',H.PtCl_a: minute yellow needles.
STYRYL METHYL KETONE t. BENZYLIDENE-

ACRIONE and Nitro- and Oxy- STYRYL METHYL

STYRYL METHYL KETONE CARBOXYLIG ETHER C. BENZYLIDENE-ACETOACETIC ETHER. vol. i. p. 24.

STYRYL.METHYL.OXAZOLE DIHYDRIDE

 $C_eH_eCH:CH.C \leq_{N.CH_2}^{O.CHMe}$. [817]. Formed from '8-bromo-propylamine hydrobromide, cinnamoyl

chloride, and alcoholic potash (Elfeldt, B. 21, 3226). Transparent crystals.— B'₂H₁PtCl₂, [198°].—B'C₆H₁N₁O₇. [183°]. Needles.

STYRYL-METHYL-PYRIDINE C₁₄H₁₃N

i.e. C.H., OH: OH. O.H., Melhyl-stilbazole. (c. 323°). S.G. 2 1-0717. Formed by heating benzoic aldehyde with (αγ)-di-methyl-pyridine and ZnCl, at 215° (Bacher, B. 21, 3072). Oil, v. sol. alcohol and ether. Gives $C_{1i}H_{13}Br_{.2}N$. [140°]. May be reduced to $C_{1i}H_{13}N$ (c. 293°) and C, H2N (c. 288°).-Hydroiodide. [211°]. B'.H.PtCl6aq. [183°].—B'HAuCl,. [142'].— B'HĤgCl₃.—B'C₆H₃N₃O₇. [193°]. Yellow needles.

STYRYL-DI-METHYL-PYRIDINE DICARB-

 $\begin{array}{ll} \textbf{OXYLIC ACID } \textbf{C}_{11}\textbf{H}_{12}\textbf{NO}_{4} \\ \textbf{\textit{i.e.}} \textbf{ C}_{6}\textbf{H}_{3}.\textbf{CH}:\textbf{CH}.\textbf{C} \\ \textbf{C}_{(CO_{2}}\textbf{H}):\textbf{CMe} \\ \textbf{N.} \end{array} \hspace{-0.5cm} \textbf{N.} \hspace{0.5cm} \textbf{[241°]}.$

Formed from its ether, which is got by the action of nitrous acid gas on an alcoholic solution of the dihydride C₂₁H₂₃NO₄ [149°], obtained from cinnamic aldehyde, acetoacetic ether, and alcoholic NH, (Epstein, A. 231, 1). Minute colourless tablets (containing 2aq), sl. sol. water, sol. alcohol. Melts at 219° when hydrated. Converted by hypochlorous acid into C₁, H₁₈NO, 2aq (Messinger, B. 19, 196).—K₂A" 3aq. —(H₂A")₂H₂PtCl₈.—H₂A"HCl. Decomposed by water.

Ethylether Et, A". [39°]. Yields the salt (Et,A"),H2PtCl, [195°].

STYRYL-METHYL-THIO-GLYCOLLIC ACID v. CINNAMYL-THIO-GLYCOLLIC ACID.

STYRYL-(a)-NAPHTHOQUINOLINE

C₂₁H₁₅N i.e. C₆H. CH:CH:CH

-C. N ;C.CH;CHPh. [104°]. Formed by distilling the carboxylic acid

 $C_{10}H_6$ < $C(CO_2H):CH$ C.CH:CHPh [256°], which is

got by the action of (a)-naphthylamine on cinnamic aldehyde and pyruvic acid (Döbner a. Peters, B. 23, 1233). Concentric groups of yellowish needles, sl. sol. alcohol.—B'2H,PtCl, 2aq: orange-yellow pp. - B'2H2Cr2O7. - B'C4H2N3O7. [230°]. Golden needles.

Carboxylic acid C₂H₁₈NO. [256°]. Yields BaA'₂2aq, CuA'₂ aq, and AgA'. Styryl-(β)-naphthoquinoline

[175°].

Formed in like manner from (β) -naphthylamine. White silky needles or pearly plates.—Salts: B'2H2PtCl8 2aq. - B'2H2Cr2O7. - B'CH3N3O7.

[254°]. Golden needles, sl. sol. ether. Carboxylic acid C₂₂H₁₅NO₂. Lemon-yellow needles, sl. sol. hot alcohol.

STYRYL-OXAZOLE DIHYDRIDE C,H,NO i.e. C₆H₅CH:CH.C (O.CH₂. [58°]. Formed from CH.Br.CH., NH.CO.CH:CHPh and alcoholic potash (Elifeldt, B. 24, 3225).—B',H.PtCl. r194°]. Orange-yellow powder. B'C, H, N, O, [189°]. Yellow needles.

· STYRYL-PENTOXAZOLE DIHYDRIDE

C,H,CH:CH.O (0.CH, OH, [56°]. Formed' by the action of alcoholic potash on the y-bromopropyl-amide of cinnamic acid (Elfeldt, B. 24, 8227). Needles.—B',H.,PtCl., Decomposes at 198°.—B'C,H,N,O,. [196°].
STYRYL-PHENOL v. OXY-DI-PHENYL-ETHYL-

(a)-STYRYL-PYRIDINE C,H,, N i.e.

C.H.CH:CH.O CH:CH CH. Stilbazole. [91°]. (325° cor.). Formed by heating benzoic aldehyde with methyl-pyridine and ZnCl, at 220° (Baurath, B. 20, 2719; 21, 818). Crystals, m. sol. alcohol.

Reactions.—1. Br forms $C_{13}H_{11}Br_2N$ [167°]. 2. HIAq reduces it to $C_{13}H_{13}N$ [-3°].—3. Na and HOEt reduce it to C12H13N (288° cor.).

Salts.—B'HCl 4aq: needles. Melts at 177° when anhydrous.—B'₂H₂PtCl₆ 2aq. [188°]. Red needles.—B'HAuCl₄. [185°]. — B'HHgCl₅ aq. [183°].—B'HI₄. [159°]. Prisms, with blue reflex. Reference.—OXY-STYRYL-PYRIDINE.

(Py. 3)-STYRYL-QUINOLINE C17H13N i.e.

C_eH, CH:CH N:C.CH:CHPh. [100°]. Formed by distilling its carboxylic acid (Doebner a. Peters, B. 22, 3008). Got also by heating (Py. 3)methyl-quinoline with benzoic aldehyde and ZnCl₂ (Wallach, B. 16, 2008; Jacobsen Reimer, B. 16, 2606). Crystals. Yie Yields C17H18Br2N [1740] .- Salts: B'2H2PtCl, 2aq.-B'H,Cr2O, 21aq.

References .- NITRO- and OXY- STYRYL-QUIN-

OLINE.

STYRYL-QUINOLINE CARBOXYLIC ACID

C₆H₄< C.CH:CHPh [295°]. Formed from cinnamic aldehyde, pyruvic acid, and aniline in alcohol (Doebner a. Peters, B. 22, 3006). Yellow needles, insol. water, sl. sol. ether.—

MgA'₂: concentric groups of needles.

STYRYL-QUINOLINE SULPHONIC ACID
C₂H₄(SO₂H)N.CH:CHPh. Formed by heating (Py. 1)-methyl-quinoline (B. 2)-sulphonic acid with benzoic aldehyde and ZnCl, for six hours at 170° (Busch a. Koenigs, B. 23, 2682). Crystals (containing 2aq). V. sol. 50 p.c. acetic acid. STYRYL THIENYL KETONE C₁₈H₁₀SO i.e.

C₆H₂CH:CH.CO.C₄H₃S. [80°]. Formed by passing HCl into a mixture of thienyl methyl ketone and benzoic aldehyde (Brunswig, B. 19, 2895). Needles. Yields a dibromide C₁₈H₁₀Br₂SO [157°] crystallising from alcohol in plates

DI-STYRYL-DI-VINYL KETONE v. DI-PHENYL-DI-BUTINYL KETONE

STYRYL-VINYL METHYL KETONE v.

PHENYL-BUTINYL METHYL RETONE.

SUBERCOLIC ACID C.H. (CO.H). in small quantity by the action of alcoholic potash on di-bromo-suberic acid (Hell a. Rempell, B. 18, 820). White powder, yielding at 2250-230° a sublimate of slender white needles.— BaA".—CaA".—MgA" 2aq.—Ag₂A": white pp. SUBERCONIC ACID. [165°-170°]. A crys-

talline product of the action of alcoholic potash on bromo-suberic acid (Ganttner a. Hell, B. 15,

149). SUBERENE CARBOXYLIC ACID C.H. O [54°]. Formed by boiling chloro-suberonie said by heating suberic said (1 pt.) with aniline

C.H., ClO, with NaOHAq (Spiegel, A. 211, 119). Pearly plates, volatile with steam. Reduced by sodium-amalgam to suberane carboxylic acid C.H.,O.

SUBERIC ACID C₂H₁₄O₄. Mol. w. 174. [140°]. (c. 800°). (279° at 100 mm.) (Krafit, *B. 22, 816). S. 142 at 15°. S. (ether) 8 at 15°. H.C.p. 992,409 (Louguinine, C. R. 107, 597); 985,600 (Stohmann, J. pr. [2] 40, 215). H.F. 249,400 (S.).

Formation .- 1. By the action of nitric acid upon cork (Brugnatelli, Crell. Ann. 1787, i. 145; Bouillon-Lagrange, A. Ch. 23, 2; J. Ph. 8, 107; Chevreul, A. Ch. 62, 323; 96, 182; Brandes, S. 32, 393; 33, 83; 36, 263; A. 9, 295; Bussy, J. Ph. 8, 107; 19, 425; Boussingault, J. pr. 7, 211; Harff, N. Br. Arch. 5, 303).—2. By the action of nitric acid upon oleic and stearic acids (Laurent, A. Ch. [2] 66, 157; Bromeis, A. 35, 89), upon castor oil (Tilley, A. 39, 166; Dale, A. 132, 244; 199, 145; Grote, A. 130, 208), upon inseed oil (Saco, A. 51, 222), upon cooca-nut oil (Wirtz, A. 104, 261), upon almond oil, upon spermaceti (Arppe, A. 120, 292; 124, 89), upon palmitolic acid (Schröder, A. 148, 33), upon paraflin (Pouchet, C. R. 79, 320), upon palm oil (Ganttner a. Hell, B. 13, 1165; 14, 1549), and upon myristic acid (Noerdlinger, B. 19, 1896) .-3. Occurs among the products of the distillation of crude fatty acids in superheated steam (Cahours, C. R. 94, 610).—4. From di-oxy-steario acid and alkaline KMnO, (Spiridonoff, J. pr. [2] 40, 250).—5. Suberic ether is formed by the electrolysis of CO₂Et.CH₂.CH₂.CH₂.CO₂K, the yield being 28 p.c. of the theoretical amount (Crum Brown a. Walker, A. 261, 120).

Properties.-Long needles (from water) or tables. May be sublimed in needles. Not volatile with steam.

Reactions .-- 1. Yields hexane when distilled with baryta .- 2. Forms suberone on distilling with lime .- 3. Bromine at 160° forms bromoand di-bromo-suberic acids, which when boiled with potash yield oxy- and di-oxy- suberic acids (Gal a. Gay-Lussac, C. R. 70, 1175).

Salts.—K.A". S. 85 at 14°.—Na.A" aq. S. (of Na.A") 50 at 14°.—NaHA".—(NH.)2A". S. 38 at 25°.—BaA": crystalline powder, less sol. hot water than cold. S. 2·2 at 7·5°; 1·8 at 100°.—SrA". S. 2·9 at 14°; 1·9 at 100°.—CaA"aq. S. 62 at 14°; 42 at 100°.—MgA" 2aq. S. 13·5 at 20°.—ZnA". S. 041 at 14°.—CuA" aq: blue pp. -CuA" 2aq. • S. (of CuA") ·024 at ·16°.-CdA" aq. S. (of CdA") ·08 at 17°.-HgA". CdA" aq. S. (of CdA") '08 at 17°.—HgA". S. '012 at 7°.5°.—Al₂OA"₂. S. '094 at 6.5°.—PbA". S. '0.08 at 18°.—Pb₃A"O_{...}—MnA" 3aq. S. 108 at 18°.—Fe₄A"O. S. '0015 at 9°.—CoA" 4aq.—CoA" 2aq. S. (of CoA") 1·16 at 14°; 85 at 10°.—NiA" 4aq. S. (of NiA") '79 at 7·5°.—Ag₄A". S. '0075 at 8°.

Methyl ether Me.A". S.G. 12 1014. Ethyl ether Et.A". (282°). S.G. 13 9853; 35 9783 (Perkin, C. J. 45, 517). M.M. 12.461 at 14°

Amide C.H., N.O. Crystalline. Amic acid C. H.; (CONH.). CO.H. [c. 170°]. Formed by distilling ammonium subcrate. Crystalline, v. sol. hot water.

Anilide C.H.; (CO.NHPh), [188°]. Formed

(1 pt.) (Gerhardt a. Laurent, A. Ch. [8] 24, 185).

Pearly plates (from alcohol), v. sol. ether.

Phenylamic acid C₆H₁₂(CO.NHPh).CO₂H. Formed at the same time as the anilide. Minute laminæ, sl. sol. hot water.—AgA': white pp

References .- Bromo . CHLORO . and Oxy-SUBERIC ACID.

Isosuberic acid is DI-ETHYL-SUCCINIC ACID (Hell, B. 22, 67)

SUBERIC ALDEHYDE C₈H₁₄O₃. (202°). A product of the action of fuming HNO₃ on palmitolic acid (Schröder, A. 143, 34). Oil, partially decomposed by distillation. Oxidised by bromine water to suberic acid.

SUBEROCARBOXYLIC ACID v. HEXANE TRICARBOXYLIC ACID.

SUBEROMALIC ACID v. OXY-SUBERIC ACID. **SUBERONE** C₂H₁₂O. Mol. w. 112. (180° i.V.). V.D. 3.73 (calc. 3.89). Formed, together with hexane, by distilling subcric acid with lime (Boussingault, A. 19, 308; Tilley, A. 39, 167; Dale a. Schorlemmer, C. J. 27, 935; A. 199, 147; Wislicenus, A. 275, 356). Colourless liquid, smelling like peppermint. Oxidised by HNO, (S.G. 1.4) to n-pimelic acid [102°]. Does not reduce AgNO, or Fehling's solution. Combines with bromine, forming a product which, when distilled over KOH, gives C₁H₁₂O (Ladenburg, B. 14, 2406). Combines with HCy yielding C₁H₁₂(OH)CN, which is converted by HCl into suberyl-glycollic acid C₂H₁₂(OH).CO₂H [80°], from which conc. HClAq at 130° produces chloro-suberane carboxylic acid C,H12Cl.CO2H, a thick oil, converted by KOH into suberene carboxylic acid C,H₁₁.CO₂H [54°], which may be reduced by sodium-amalgam to suberane carboxylic acid C.H,3.CO2H, and this may be oxidised by HNO, to a dibasic acid $C_aH_{14}O_4$ or $C_aH_{12}O_4$ (Dale a. Schorlemmer, C. J. 39, 539; Spiegel, A. 211, 117). Suberone is reduced in alcoholic solution by sodium to C,H,O, a colourless liquid, with mouldy smell (185°), S.G. $\frac{15}{15}$ 9595, which unites with phenyl cyanate forming C,H,3O.CO.NHPh [85°], and also with HI forming a compound which is converted by alcoholic potash into suberonylene C,H₁₂ [114.5°] and a little C,H₁₃OEt. The compound C,H,O is reduced by conc. HIAq at 250° to C,H, Suberonylene combines with bromine (Markownikoff, C. R. 110, 466).

Oxim C,H,2:NOH. Liquid, smelling like peppermint, sol. alcohol, ether, alkalis, and acids (Nägeli, B. 16, 497). Reduced by sodiumamalgam to C, H13.NH

SUBERO-TARTARIC ACID v. DI-OXY-SUBERIO ACID.

SUBERYL-GLYCOLIC ACID v. Oxy-suberanic ACID.

SUBLIMATION. The passage of a solid body, when heated, to the state of vapour without melting. The temperature of sublimation is definite for every solid, and is dependent on the pressure. There is a definite pressure for each definite solid below which the substance cannot exist as a stable liquid, so that if heated below this pressure it passes from the solid directly to the gaseous state; but if heated under pressures greater than this pressure the substance first liquefies and then vaporises. As the definite pressure is considerably below that of the atmosphere for most substances, but few bodies undergo sublimation, properly so called, when heated under ordinary conditions. Sublimation is treated fairly fully in Thorpe's DICTIONARY OF AP-PLIED CHEMISTRY (vol. iii. p. 609), and instances are given where the process is made use of it M. M. P. M. manufacturing operations.

SUBSTITUTION. The replacement of one element in a compound by another element is the primary meaning given to the term 'substitution.' As our ways of looking at composition, and changes of composition, are saturated with the conceptions of the molecular and atomic theory, substitution is better described as the replacement of an atom in a molecule by another atom. But the term must be widened to include cases wherein an atom is replaced by a group of atoms, which group is regarded in that reaction as if it were a single atom. The moment attention is paid to the number of atoms that can be substituted for some specified atom in a molecule the conception of chemical equivalency is found necessary to give a common foundation to the facts that are observed (v. EQUIVALENCY, vol. ii., especially pp. 449-451). The properties of a molecule are changed by the substitution of an atom or atomic group in the place of one, or more, of the atoms in the original molecule; the prosecution of the inquiry into the connections between the properties of molecules derived, by substitution, from some parent molecule leads to the hypothesis of types, which is afterwards merged in the wider subject of chemical classification (v. Classification, Chemical, vol. ii. p. 196; EQUIVALENCY, vol. ii. pp. 450-451; TYPES, in this vol.).

Experiments show that the substitution of a more positive by a less positive atom, or atomic group, is accompanied by a change of properties in the direction that the substitution-product is more acidic than the parent substance. This field of inquiry has been cultivated systematically in recent years, and measurements have been made of the effects of substitution-changes of the kind indicated on the affinities of many acids. The results obtained have led, and are leading, to new conceptions of the nature of allinity, and of the constitutions of molecules (v. Physical methods, section Electrical methods, pp. 197-207 in this vol.).

M. M. P. M. SUCCINAMIDINE C,H,N, i.e.

CH₂.C(NH₂)NH. Formed by the action of CH₂.C(NH₂) ammonia on succinic-di-imido-di-ethyl ether C₂H₁(C(OEt):NH)₂ (Pinner, B. 16, 362, 924, 1643, 1655). The salt B"2HCl forms minute needles, dissolving in water with formation of NH₁Cl and succinimidine C2H4(NH)3.

SUCCINAMIDOXIM C2H4(C(NH2):NOH)20 Succinene diamidoxim. [188°]. Formed by adding hydroxylamine hydrochloride and Na₂CO₂Aq to an alcoholic solution of the nitrile of succinic acid (Sembritzki, B. 22, 2958). Crystals, sol. hot water, sl. sol. hot alcohol, insol, ether. Coloured reddish-brown by FeCl, insol. ether. Coloured reddish-brown by FeUl₃. Fehling's solution gives a dirty green pp. Ac₂O forms C₂H₄(C(NH₂):NOAc), [168°]. NaOEt and EtI form C₂H₄(C(NH₂):NOEt), [119°]. BzOl and NaOH produce the benzoyl derivative C₂H₄(C(NH₂):NOBz), [192°], crystallising in needles, converted by heating with water at 159° into $C_2H_4(C < \stackrel{N.O}{N})$ CPh), [159°]. Aqueous potassium evanate and HCl form $C_2H_4(C(NOH).NH.CO.NH_2)$, [164°].

ous potassium oyanate and HCl form $C_1H_1(C(NOH).NH.CO.NH_2)_2$ [164°].

Succinimidoxim $C_1H_2(C(NOH))$ NH. Formed by heating the nitrile of succinic acid with hydroxylamine at 65° (Sembritzki, B. 22, 2964). Prisms (containing 2aq). Sol. hot water, insol. alcohol. Alcoholic NaOH forms a blue solution turning green. FeCl₃ gives a dark-violet colour.—

Ag₂C,H₃N₃O₂: pearly plates.

Di-acetyl derivative C₄H₃Ac₂N₃O₂.

[171°]. Crystalline powder, sol. water.

Di - benzoyl derivative C,H,Bz,N,O,.
[189°]. Crystals, insol. water, sol. hot alcohol.
SUCCINIC ACID C,H,O, i.e.
CO,H.CH,,CH,CO,H. Mol. w. 118. [182°]

CO₂H.CH₂.CH₂.CO₂H. Mol. w. 118. [182°] (Kräfft a. Noerdlinger, B. 22, 816; Reissert, B. 23, 2245); [185°] (Davidoff, B. 19, 406). (261°). S.G. 1·55. S. 2·88 at 0°; 5·14 at 14·5°; 121 at 100° (Bourgoin, Bl. [2] 21, 110; 29, 243; Miczynski; M. 7, 263). S. (alcohol) 7·5 at 15°. S. (ether) 1·25 at 15°. H.C.v. 357,100. H.C.p. 356,800. H.F. 226,200 (Stohmann, J. pr. [2] 40, 207); 229,000 (von Rechenberg). S.H. ·290 (from 0°-50°); 365 (0°-150°) (Hess, A. Ch. [2] 35,410). Heat of Neutralisation: Gal a. Werner, C. R. 103, 871.

Occurrence.-In amber (Agricola ; Berzelius. A. Ch. 94, 187; Lecanu a. Serbat, J. Ph. 8, 541; 9, 89; Liebig a. Wöhler, P. 18, 162; D'Arcet, P. 36, 80), in turpentine from several species of pine, in Chelidonium majus (Walz, N. J. P. 15, 22; Zwenger, A. 114, 350), in lettuce (Köhnke, B. J. 25, 443), in Papaver somnifcrum, in unripe grapes (Brunner a. Brandenburg, B. 9, 982), in exudations from the bark of mulberry trees (Goldschmiedt, M. 3, 136), in beet juice (von Lippmann, B. 24, 3299), and in rhubarb (Brunner, B. 19, 595). Occurs also in the thymus gland of the calf, the spleen of the ox (Gorup-Besanez, A. 98, 28), in certain pathological exudations (Heintz, A. 76, 369; Brieger, H. 5, 368), in the urine of rabbits fed on carrots (Meissner a. Jolly, J. 1865, 675; cf. Salkowski, Pf. 4, 91), and in human urine after eating asparagus (Hilger, A. 171, 208).

Formation.—1. By the action of HNO, on many organic substances, including fats, fatty acids from butyric acid upwards, wax, spermaceti, sebacic acid, and azelaic acid (Bromeis, A. 35, 90; 37, 292; Sthamer, A. 43, 346; Ronalds, A. 43, 356; Radcliff, A. 43, 351; Arppe, A. 95, 242; Dessaignes, A. 70, 102; 74, 361; Erlenmeyer, B. 7, 696; Noerdlinger, B. 19, 1895). - 2. In the alcoholic fermentation of sugar (Pasteur, Bl. 1852, 52; A. 105, 264).—3. In the fermentation of asparagine (Piria, A. 68, 343), of calcium malate (Dessaignes; Liebig, A. 104, 363), of ammonium tartrate (König, B. 14, 211), and of flesh (Sal-kowski, B. 12, 649).—4. By reducing fumaric and maleic acids with sodium-amalgam (Kekulé, A. Suppl. 1, 133).—5. By reducing malic and tartaric acids with HI (R. Schmitt, A. 114, 106; Dessaignes, A. 115, 120; 117, 134).—6. By heating its nitrile (ethylene cyanide) with alcoholic potash at 100° (Maxwell Simpson, A. 118, 373), or by treating it with dilute nitric acid (Jungfleisch, Bl. [2] 19, 197).—7. From bromo-acetic soid and reduced silver at 180' (Steiner, B. 6, 184).— 8. From \$\mathcal{B}\$-chloro-propionic ether by successive treatment with KCy and potash (Wichelhaus, \$Z. [2] 8, 247).—9. From sodium acetoacetic ether by treatment with chloro-acetic ether and saponification of the product (Wippermann, \$B. 3, 337; Noeddecke, \$A. 149, 224).—10. By heating ethane tricarboxylic acid at 160° (Bischoff, \$B. 13, 2162).—11. By potashfusion from gum arabic, milk sugar, and carminic acid (Hlasiwetz, \$A. 138, 76; 141, 340).—12. By reducing acetylene dicarboxylic acid with zinc and HOAc at 60° (Aronstein a. Hollemann, \$B. 22, 1183).—13. Its ether is formed by electrolysis of \$CO_Et.CH_cCO_K\$ in aqueous solution; the yield being 60 p.c. of the theoretical (Crum Brown a. Walker, \$A. 261, 115).

Preparation.—1. By distilling amber, heating the watery distillate, filtering, and allowing to crystallise. The product is freed from oils by treatment with nitric acid.—2. By neutralising tartaric acid (2 kilos) with NH_Aq, adding to the aqueous solution (40 litres) K.HPO₄ (20 g.), MgSO₄ (10 g.) and a little CaCO₃. Fermentation is started by diluting a little (5 c.c.) of the solution with water (25 c.c.) and exposing it to the air for a few days. When fermentation has set in, the liquid is returned to the main quantity, and the whole kept at 25°-30° for seven weeks. The liquid is evaporated somewhat, clarified by white

of egg, and boiled with lime. After cooling, the calcium succinate is collected and decomposed by H.SO.. The yield is good (500 g.) (Koenig, B. 15, 172).

Properties.—Monoclinic prisms, permanent in air, acid in taste. V. sol. water, m. sol. alcohol, sl. sol. ether. Resolved on boiling into water and anhydride; the lactone O,H,O, being also formed. BaCl₂ completely ppts. hot neutral solutions (Schmitt a. Hiepe, Fr. 21, 536). BaCl₂ followed by NH₂Aq and alcohol ppts. succinic (but not benzoic) acid. FcCl₃ gives in neutral

solutions a reddish-brown pp. PbAc₂ gives a pp. sol. excess.

Reactions .- 1. Not attacked by HNO, CrO, or chlorine water. MnO2 and H2SO, yield acetic acid. KMnO, in neutral solution oxidises it to oxalic acid and CO₂; and, in acid solution, to CO₂ (Berthelot, Bl. [2] 8, 390; Sorokin, J. R. 11, 383) .- 2. Yields ethylene and CO2 when decomposed in alkaline solution by an electric current (Kekulé, A. 131, 79; Bourgoin, A. Ch. [5] 20, 80; cf. Kolbe, A. 113, 244). In perfectly neutral solution only CO2, CO, and O are given off at the positive pole. - 3. Potash-fusion yields oxalic acid.-4. PCl, forms successively: succinic anhydride C2H,(CO)2O, succinyl chloride C_H_((COCI)₂, fumaryl chloride C_H_(COCI)₃, di-chloro-fumaryl chloride C_HCl(COCI)₃, di-chloro-maleyl chloride C_CI_(COCI)₂, two tetrachlorinated di-chloro-maleyl chlorides, viz.: C,Cl₂(CCl₂)(COCl) and C₂Cl₂(CCl₂)₂O (v.DI-CHLORO-MALEIO ACID), and finally per-chloro-ethane, 2C₂Cl₆ (Kander, J. pr. [2] 31, 1).—5. On long boiling it yields the dilactone of diethyl ketone s-di-ω-carboxylic acid CO.O.O.OH, CH, [75°] (c. 203° at 15 mm.), orystallising from alcohol in plates, converted by HClAq into hydrochelidonic acid CO(CH₂CH₂CO₂H)₂ [143°], which yields an oxim [129°] (Volhard, A. 258, 206).—6. Converted into succinic anhydride by treatment with

P.O. Acci, BzCl, Ac.O. or succinyl chloride (Anschütz, B. 10, 325, 1881).—7. A solution containing 5 p.c. succinic soid and 1 p.c. uranium succinate when exposed to sunlight turns green and gradually gives off CO2, leaving propionic acid in solution (Seekamp, A. 133, 253). Barium succinate (1 mol.) heated with NaOMe (1 mol.), for 3 hours at 300° yields propionic acid (Mai, B. 22, 2133).-8. Heated with a large excess of lime it yields ethane as chief product (Han-riot, Bl. [2] 45, 79).—9. The salts on distillation yield a liquid product (160°-250°) which yields benzene when distilled over zinc-dust (Von Richer, J. pr. [2] 20, 206; cf. Fumaro, G. 11, 273). Hydroquinone is also a product of the distillation of succinates .- 10. The sodium salt heated with P.S. yields thiophene (Volhard a. Erdmann, B. 18, 454).—11. The Na salt heated with aldehydes and NaOAc forms oxyacids of the form R.CH(OH).CH(CO₂H).CH₂.CO₂H (Fittig, B. 18, 2523).—12. By heating with phthalic anhydride and NaOAc at 250°, exhausting the product with water and alcohol, and boiling the residue with aniline, there is got 'diphthalsuccinanilide' C₁₀H₂₄N₂O₄ [267°] converted by boiling with HOAc and HCl into 'diphthalsuccindehydranilide ' C,0H20N2O2, crystallising from HOAc in small yellow prisms, not liquid at 280° (Roser, B. 18, 3122).—13. By heating with glycerin at 200° it yields 'succinin' C₃H₅(OH)A", a gummy mass, insol. cold water, alcohol, and ether (Fumaro a. Danesi, G. 10, 58). Alkalis and acids split it up into glycerin and succinic acid.—14. a-Chloropropionic ether and alcoholic potash give C.H. (CO.O.CHMe.CO.Et), (c. 302° at 730 mm.) (Wurtz a. Friedel, A. Ch. [3] 63, 101; Wislicenus, A. 133, 262).

Salts.—(NH₁)₂A". Hexagonal prisms, v. sol. water and alcohol. Yields succinamide when heated.—(NH₁)HA". Triclinic crystals, v. sol. water and alcohol (Brooke, Ann. Phil. 22, 286). Formed by evaporating a solution of the neutral salt.—K₂A" 2aq. Deliquescent crystals, sol. alcohol, insol. ether.—K₂A" 3aq. Trimetfic crystals (Salzer, B. 16, 3025).—KHA" 2aq. Efflorescent six-sided prisms.—NaHA". 2aq. Efflorescent six-sided prisms.—NaHA". Triclinic prisms.—NaHA" 8aq: monoclinic crystals.—BaA". Sl. sol. water, insol. NH₂Aq and alcohol. S. 42 at 8°; '48 at 12°; '28 at 67° (Miczynski).—CaA" 3aq: small needles, deposited gradually on mixing cold conc. solutions of sodium succinate and CaCl₂. On mixing the hot solutions CaA" aq is ppd. S. 1·1 at 0°; 1·3 at 24°; '8 at 68° (Miczynski, M. 7, 266).—CaH₂A", 22aq.—SrA": monoclinic prisms.—BeA" 2aq (Atterberg, Bl. [2] 21, 162).—Be₂(OH)A" 2aq.—MgA" 6aq. Prisms (Fehling, A. 49, 154).—MgK₂A",—Mg₂A", 20, aq.—CrA" aq: soarlet pp.—CuA" (dried at 200°). CuA"2NH₂.—CuA"4NH₃ (Schiff, A. 123, 45).—Fe(OH)A": brownish-red pp.—NiA" 4aq.—MnA" 4aq. Triclinic prisms (Handl, Sits. W. 82, 254).—PbA" (dried at 100°). White powder, al. sol. water, v. sol. KOHAq and HNO₂.—Pb₂OA";: sticky pp., got by addifig lead subcoetate to sodium succinates.—Pb₂OA"; (dried at 200°): white powder.—ZnA" (dried at 200°). Crystalline powder.—ZnA" (dried at 200°). Crystalline powder.—ZnA"3NH₄. (Lutschak, B. 5, 30).—CdA".—(UVO)A" aq.—A(UVO)A" aq.—R(UVO)A" aq.—Na(UVO)A" aq.—Ra,A". White amorphous pp.—Quinine salt (C₂, H₄, N₂O₂, H₄A" aq. Prisms

8. '11 at 10° (Hesse, A. 135, 831).— Cinchonine salt $(C_{2s}H_{2s}N_{2}O)_{2}H_{4}A''$ aq. Thick crystals (Hesse, A. 122, 226).— Cinchonidine salt $(C_{2s}H_{2s}N_{2}O)_{2}H_{4}A''$ 6aq. Silky prisms. S. '4 at 10° (Hesse, As 135, 342).— Urea salt $(CON_{2}H_{1})_{2}H_{4}A''$. Six-sided monoclinic prisms; a:b:c=1:483:1:1:365; $\beta=83^{\circ}$ 28' (Lischmidt, Sits. W. 52, ii. 238).— Ethylene-diamine salt $C_{2}H_{1}(NH_{2})_{2}H_{2}A''$. [182°]. Thick white prisms, v. sol. water, insol. ether (Mason, C. J. 55, 10).— Benzylamine salts $(C,H,NH_{2})_{2}H_{2}A''$. [145°]. Thin plates, sol. alcohol (Werner, C. J. 55, 628).— $(C,H,NH_{2})H_{2}A''$. [117°]. Rectangular prisms (containing aq), v. sol. water.

(containing ad, v. sol. water.

Methyl ether Me_A". [19°]. (195° cor.).
S.G. 2º 1·1209 (Emery, B. 22, 3185); ½ 1·1261;
½ 1·0383 (Perkin, C. J. 45, 516). M.M. 6·232
at 18·2°. S.V. 159·7 (Lossen, A. 254, 64). H.C.
(solid) 703,600. H.C. (liquid) 708,500. H.F.
(solid) 205,400 (Stohmann, J. pr. [2] 40, 353).
Formed from succinic acid, MeOH, and gaseous
HCl (Fehling, A. 49, 195). Formed also from
succinyl chloride and NaOMe in ether, and from
Ag,A" and MeI. Crystalline, sol. alcohol.

Methylethylether MeEth". (208° cor.).
C.G. 2 1.093. S.V. 184.6. Formed by the action of Ethagh" on MeI (Köhler, A. 221, 88). On saponification by baryta it yields H_Ah", HMeh", and HEth" (Lossen a. Köhler, A. 262, 200).

Mono-ethyl ether HEth". Formed by

Mono-ethyl ether HEth". Formed by boiling succinic anhydride with alcohol (Heintz, J. 1859, 280). Syrup, miscible with water, alcohol and ether.—AgEth": amorphous, sl. sol. water.—The salt NaEth": amorphous, sl. sol. water.—The salt NaEth" is converted by POCl. into CO2Et.C.H., COCl (144° at 90 mm.), which is split up by distillation into EtCl and succinic anhydride, and is converted by phenyl hydrazine into CO2Et.C.H., CO.NH.NHPh [107°], crystallising in white needles, itself converted into O(CO.C.H., CO.N.H.Ph), [137°] by successive treatment with HOH and HCl (Michaelis a. Hermans, B. 25, 2748). The salt NaEth" is converted by a-chloro-propionic ether into CO2Et.C.H., CO.CHMe.CO2Et (280°) S.G. 2 1-119, which is split up by boiling with baryta water into succinic and lactic acids (Wurtz a. Friedel, J. 1861, 378).

Ethylether Et.A". (216:5° cor.). S.G \(\frac{1}{2} \) 10465; \(\frac{2}{35} \) 10383. M.M. 8:380 at 17:8° (Perkin). S.V. 209*4. Formed by boiling succinic acid (20 pts.) with alcohol (3 pts.) and H.SO. (1 pt.) (Eghis, B. 6, 1178; cf. D'Arcet, A. Ch. [2] 58, 291). It is also produced by heating C.H.Br. in alcohol with potassium succinate in sealed tubes (Davidoff, Bl. [2] 46, 818; 19, 406). Oil. Converted by Na into the dihydride of dioxyterephthalic ether. Not attacked by hydroxylamine (Jeaurenaud, B. 22, 1273). Succinic ether (40 g.) treated with cyanamide (20 g.) and an alcoholic solution of K (18 g.) for 5 hours with inverted condenser yields C.H.(CONKCy), and C.H.(CO.KCy). These bodies may be converted by AgNO₃ into Ag salts, which may be separated by HNO₃, in which silver 'succincyanamate' dissolves, while silver 'succinyldicyan-di-amide' is insoluble. The Ag salts may then be suspended in alcohol and decomposed by H.S (Möller, J. pr. [2] 22, 214). Succinyl di-cyan-di-amide C.H.(OO.NHOy), [105*] crystallies in monoollinic pyramids (containing 2aq), decomposed by warm water into succining 2aq), decomposed by warm water into succining 2aq), decomposed by warm water into succining 2aq), decomposed

seid and eyanamide. It may also be prepared acid and cyanamids. It may also be prepared by the action of NaNH.Cy on succinyl chloride, and by warming O₂H₄(CO)₂NOy with cyanamide. The salt C₂H₄(CO.NAgOy)₂†aq crystallises in plates, sol. NH₂Aq.—Et₄A"5TiCl₄ (Demarçay, C. R. 70, 1414).—Et₄A"2TiCl₄.—Et₄A"TiCl₄.

Ethyl propyl ether EtPrA". (231°).

S.G. § 1.0387. S.V. 230.2 (Wiens, A. 253, 300).

Yields, on saponification by baryta, salts of EtHA", PrHA", and H.A" (Lossen a. Köhler.

A. 262, 201).

A. 202, 201).

Ethyl butyl ether Et(C,H₀)A" (247°).

S.G. § 1.0218. S.V. 255.9 (W.).

Ethyl heptyl ether Et(C,H₁₅)A".

(291.4°). S.G. § 9850. S.V. 332.9 (W.).

n-Propyl ether Pr,A" (247.1°). (Wiens, A. 253, 300); (250.8°) (Perkin, C. J. 53, 561). S.G. $\frac{6}{0}$ 1·0189 (W.); $\frac{1}{2}$ 1·0157; $\frac{15}{13}$ 1·0062; $\frac{25}{23}$ 9986 (P.). S.V. 257·8. Formed by passing HCl into succinic acid in propyl alcohol.

Isopropyl ether Pr.A". (228°). S.G. 2

1.009 (Silva, A. 154, 255).

Propyl butyl ether Pr(C,H,)A". (258.7°). S.G. \(\frac{1}{6}\) 10166. S.V. 277-8 (Weins, A. 253, 300). Isobutyl ether (PrCH₂)₂A". (265° cor.). S.G. \(\frac{1}{15}\) 9737; \(\frac{25}{35}\) 9667. M.M. 12·707 at 14·5° (Perkin, C. J. 45, 519).

Isoamyl ether (C₂H₁₁)₂A". (290° cor. at 728 mm.). S.G. 13 961. Formed from Ag₂A" and isoamyl bromide (Del Zanna a. Guareschi, Atti | Roal Instit. Veneto [5] 6; B. 12, 1609), | Heptyl ether (C,H₁)₂A" (350°). | 8 9519. S.V. 459·6 (Wiens).

§ 9519. S.V. 4596 (Wiens).

Cetyl ether (C₁₆H₃₁)₂A". [58°]. Formed by neating the acid with cetyl alcohol (Tütscheff, Rep. Chim. pure, 2, 463). Plates, sl. sol. alcohol. v. sol. ether.

Ethylene ether C2H4A". [c. 90°]. By heating succinic acid with glycol at 170° there is formed crystalline (CO₂H.C₂H₁,CO₂)₂C₂H₄ melting below 100°, which at 300° yields C₂H₄A" (Lourenço, A. 115, 358). Crystalline, insol. water and ether,

sol. hot alcohol. Decomposed by distillation.

Di-phenyl ether C₂H₄(CO₂Ph)₂. [119°]. (330°). Formed from succinic acid, phenol and POCl, (Rasiński, J. pr. [2] 26, 63). Got also from succinyl chloride and phenol (Weselsky, B. 2, 519). Completely decomposed by slowly heating (Anschütz, C. J. 47, 898). NaSEt gives di-thiosuccinic ether. Pearly plates (from alcohol).

Di-benzyl ether (CH,Ph) A". [42°]. Formed from Ag2A" and benzyl bromide (Zanna a.

Guareschi, G. 11, 255). Laminæ.

Chloride C_2H_4 (CO.Cl)₂ or $C_2H_4 < \stackrel{CCl}{CO} > 0$. Mol. w. 155. (190°-200°). S.G. 1.39. Formed from succinic anhydride and PCl, (Gerhardt a. Chiozza, A. 87, 293).

Preparation.—Succinic acid is heated with PCI, for two days with an inverted condenser in an oil bath. The POCl, is distilled off (below 120°) and the residue shaken with benzoline that has been dried over lime. The benzoline dissolves the rest of the POCl, and the succinyl chloride separates as a lower layer. The operation is repeated until the oil no longer forms phosphoric acid when mixed with water (H. Möller, J. pr. [2] 22, 208).

Properties.—Solidifies at 0°.

Reactions.-1. Reduced to butyrolactone by sodium amalgam (8 p.c. Na) acting upon its

ethereal solution mixed with glacial acetic acid. -2. Bensens and aluminium chloride give C₂H₄<CO^{Ph₂}>O [90°], C₂H₄(CO.C₆H₈)₂ [184°], and a little \$\beta\$-benzoyl-propionic acid (Auger, A. Ch. [6] 22, 312; Bl. [2] 49, 345).-8. ZnEt. gives $C_2H_4 < \stackrel{CEt_2}{CO} > 0$.—4. Na₂S gives succinyl sulphide.-5. PCl, at 230° gives off HCl and the product, after treatment with water, contains C4Cl6O (199°-215°) which solidifies below 0°. Hot conc. H2SO, dissolves C,Cl,O and the product, diluted with water, yields on evaporation hygroscopic crystals, which on sublimation give non-hygroscopic plates of C.Cl.O. [120°] (Kauder, J. pr. [2] 28, 191). Di-chloro-maleic chloride is also a product of the action of PCl, on succinyl chloride .- 6. Chlorine passed into boiling succinyl chloride forms chlorides of fumaric, chlorocinyl chloride forms chlorides of lumaric, chloro-fumaric, and di-chloro-maleïa acids (Kauder, J. pr. [2] 31, 24).—7. C₆H₂,SO₂NBzAg forms C₂H₁(CO.NBz.SO₂C₆H₃)₂ [146°] (G. a. C.).— 8. Phenyl-hydrazine forms the compound C₂H₁(CO.NH.NHPh)₂ [218°] (Freund, B. 21, 2462; Fischer, B. 22, 2728), whence phospene produces C2H4(CO.N2Ph:CO)2[225°]. Sodium phenyl. hydrazine in benzene forms $C_2H_4 < \stackrel{\circ}{CO.NPh}$ [199°], which gives $C_2H_4 < \frac{\text{CO.NPh}}{\text{CO.NAc}}$ [179°] (Michaelis a. Hermans, B. 25, 2751).-9. Cyanamide in ethereal solution forms, on warming, succin-cyanimide C.H.(CO),NCy [138°] crystal-

C₂H₁(CO.NH.CO.NH₂)₂, a powder, v. sl. sol. hot water (Conrad, J. pr. [2] 9, 301). Anhydride C.H. CO O. Mol. w. 100. [119°]. (261°) (Krafft a. Noerdlinger, B. 22, 816). Formation.—1. By rapidly boiling succinic acid. 2. By distilling the acid with P.O. (D'Arcet, A. Ch. [2] 58, 282), with PCl, (Gerhardt a. Chiozza, C. R. 36, 1050), or with BzCl (Kraut, 1070). A. 137, 254).—3. By warming succinyl chloride with dry oxalic acid (Anschütz, A. 226, 16) .-4. By heating succinic acid (100 g.) with POCL (65 g.) at 120° (Volhard, A. 242, 150).—5. By distilling succinyl chloride (180 g.) with succinic acid (137 g.), and crystallising from alcohol (H. Möller, J. pr. [2] 22, 194).—6. By the action of dry Pb(NO₃)₂ (also nitrates of other heavy

lising from alcohol in plates (Möller, J. pr [2] 22, 207).—10. Cyano-acctic ether in Et.O at 100° forms C₂H₄:C₂O₂:CCy.CO₂Et [126°] (Muller, C. R. 112, 1140).—11. Urea at 65° forms the compound

Properties.— Long trimetric needles (from alcohol); a:b:c = 595:1:462 (Bodewig, B. 14, 2788). Sl. sol. water, v. sl. sol. ether. Converted by dry NH, into succinimide. Slowly converted by boiling alcohol into succinic ether. Phenylhydrazine reacts in alcoholic solution, forming CO,H.C,H,.CO.NH.NHPh [120°], converted by heat into C₂H₄<CO>N.NHPh [155°] (Auger,

metals) upon succinyl chloride; PbCl, is pro-

duced, and N2O4 and oxygen evolved; yield c

60 p.c. of theoretical (Lachowicz, B. 18, 2990).

A. Ch. [6] 22, 839; cf. this vol. p. 45) or [158] (Michaelis, B. 25, 2750). Potassium cyanamide forms 'succincyanamic' acid, the compound CO.H.C.H,.CO.NHCy [128°], which is v. e. sol. water, v. sol. alcohol and other, is split up by

dilute soids into succinic soid and cyanamide, and yields the following six salts Na, A" 5aq, K, A" aq, CaA" 4aq, BaA" 2aq, AgHA", and Ag, A" (Möller, J. pr. [2] 22, 193). Urea heated with succinic anhydride at 125° forms succinuric acid CO.H.C.H..CO.NH.CO.NH. [205°] (Pike, B. 6,

Nitrile C₂H.*(CN)₂. Ethylene cyanide. Mol. w. 80. [55°]. (147° at 10 mm.) (F.); (185° at 60 mm.) (Biltz, B. 25, 2541). H.C.p. 546,100. H.F. (from diamond) - 32,000 (Berthelot a. Petit, C. R. 108, 1217). Formed by boiling ethylene bromide (300 g.) with alcohol (500 g.) and KCy (200 g.) for two hours with inverted condenser (Maxwell Simpson, Pr. 10, 574; Geuther, A. 120, 268; Fauconnier, Bl. [2] 50, 214; Nevolé a. Tscherniak, C. R. 86, 1411). Amorphous, sometimes crystalline, solid, v. sol. water, alcohol, and chloroform; sl. sol. ether. Decomposed by distillation under atmospheric pressure. Converted into succinic acid by boiling alcoholic potash. Aniline hydrochloride at 200° reacts, forming di-phenyl-succinimidine C₂H₄ C(NH) NPh (Blochmann, B. 20, 1856). -C₂H₄Cy₂4AgNO₃: tables, sol. water and alcohol, insol. ether.

Amide-nitrile CN.C.H,.CO.NH,. Formed by heating the nitrile with alcoholic potash at 110° (Drouin, C. R. 108, 675). Crystals, sl. sol. Slowly decomposes at alcohol, insol. ether. 210°-220°.

Amide C.H. (CO.NH2)2. Succinamide. Mol. w. 116. [243°]. S. 625 at 9° (Henry, C. R. 100, 943); 11 at 100° (F.). Formed by the action of aqueous NH, on the ether and on the chloride (D'Arcet, A. 16, 215; Fehling, A. 49, 196). Formed also by warming succinimide with alcoholic NH₃ (Menschutkin, A. 162, 165, 187). Needles, insol. ether and alcohol. Decomposed at 200° into NH, and succinimide or by saturating at -15° with gaseous NH3, and heating to 150° in sealed tubes (Roubtzoff, Bl. [2] 45, 250) .-HgC,H₆N₂O₂1¹₂aq. White powder, deposited on cooling from a solution of HgO in hot aqueous succinamide.

Iso-amide $C_2H_4 < \frac{C(NH_2)_2}{CO} > 0$. [6. 95°].

Formed to the extent of 8 p.c. in the preparation of the amide from succinyl chloride and NH3Aq (Auger, A. Ch. [6] 22, 312). Hygroscopic mass. Its aqueous solution gives with AgNO, a pp. of

C₂H₄(CO)₂NAg.

Methylamide C₂H₄(CO.NHMe)₂. Plates (Wallach a. Kamenski, B. 14, 170).

Dimethylamide C.H. (CO.NMe.). [81°]. Formed from succinyl chloride and NHMe, in ether (Franchimont, R. T. C. 4, 202). Crystals (from ether), v. sol. water.

Benzyl-di-amide C,H4(CONH2)(CONHCH,Ph). [189°]. Formed from the benzylimide and ammonia at 100° (Werner, C. J. 55, 633). Minute prisms, sl. sol. ether and hot benzene. Yields the benzylimide when heated.

Di-bensyl-diamide C.H.(CO.NHCH.Ph). [206°]. Formed from succinic ether and benzylamine in alcohol. Thin plates, not decomposed by boiling NaOHAq.

Anilide C₂H₄(CO.NHPh)₂. [227°]. Formed by boiling succinic acid with aniline (Laurent a.

Gerhardt, A. Ch. [8] 24, 179; A. 68, 27; Menschutkin, A. 162, 187). Needles (from alcohol), insol. water. Not affected by boiling alcoholic potash or by nitrous acid. Gives the phenylimide on distillation. Cold fuming HNO₈ converts it into C.H. (CO.NHC₈H. (NO₂)[1:41)₈ [260°] (Hübner, A. 209, 877). Benzoic aldehyde at 180° forms succinic phenylimide and benzyl-

idene-aniline (Schiff, A. 148, 338).

Amide-anilide CO(NH₂).C₂H₄.CONHPh. [181°]. Formed by heating the phenylimide with alcoholic NH₃ at 100° (Menschutkin, A. 162, 182). Broad needles (from water), sl. sol. hot alcohol. Alkaline KOBr followed by heating werff a. Van Dorp, R. T. C. 9, 41).

Di-(a)-naphthyl-di-amide

C₂H₄(CO.NHC₁₀H₁)₂ [285°]. Needles (from HOAo). Converted by fuming nitric acid into C₂H₄(CO.NH.C₁₀H₂(NO₂)₂)₂, [225°], and C₂H₄(GO.NH.C₁₀H₃(NO₂)₄)₂ [256°]. Tetra-phenyl-di-amide

C2H4(CO.NPh2)2. [234°] (Piutti, G. 14, 467).

Needles (from alcohol).

o-Tolyl-diamide C₂H₄(CONH₂).CO.NHC₇H₇. [160°]. Formed by heating the o-tolylimide with alcoholic NH₃ at 100°. Plates.

Di-o-tolyl-diamide C2H1(CO.NHC,H7)2 [100°]. White needles (Bechi, \hat{B} . 12, 25, 321). V. sl. sol. water, m. sol. alcohol.

 $p \cdot Tolyl \cdot di \cdot amide$ $C_2H_1(CONH_2).CONHC_1H_7$. [148°]. Formed by heating the p-tolylimide with alcoholic NH3.

Di-p-tolyl-diamide C.H.(CO.NHC,H.).
[256°]. Plates (from alcohol), sl. sol. hot water
(Bechi, B. 12, 323; Hübner, A. 209, 380). Yields on nitration C2H1(CO.NHC,H8.NO2)2 [217°] and C2H4(CO.NH.C7H5(NO2)2)2

(β)-Naphthalide C2H1(CO.NHC,H1)2. [266°] (Bischoff a. Reebe, B. 25, 3267). Got by heating succinic acid (10 g.) with (β) -naphthylamine (24 g.). Insol. ordinary solvents, sol. H,SO.

Amic acid CO₂H.C₂H₁.CO.NH₂. Succinamic acid. [157°]. Formed by warming succinimide with an equivalent quantity of baryta water (Teuchert, A. 134, 136) or milk of lime (Menschutkin, A. 162, 175). Formed also from nitrosoglutaric acid by heating alone or with Ac,O (Serda a. Wiedemann, B. 23, 3284; Wolff, A. 260, 114). Needles, m. sol. water, insol. alcohol. Decomposed at 200° into water and succinimide. Boiling water forms acid ammonium succinate.

Salts.-KA': very hygroscopic mass (Landsberg, A. 215, 201).—BaA'₂: needles, v. sol. water.—CaA'₃.—MgA'₂ 8aq : trimetric crystals.—MgA'₂ 6aq.—CdA'₂ aq: prisms.—CuA'₂.—PbA'₃. Concentric needles, v. sol. water.—MnA'₂ 5aq.— ZnA'₂. — AgA': monoclinic crystals, v. sol. NH₃Aq.

Ethyl-amic acid CO2H.C2H4.CONHEt. Formed by warming the ethylimide with baryta water (Menschutkin, A. 182, 92). - Ead's: orystals, v. sol. water,

Ethylens-di-amic acid C,oH,sN2O, i.e. C.H.(NH.OO.C.H., CO.H.). Ethylene-disuccin-amic acid. [185]. Formed by boiling the di-imide with baryta (Mason, C. J. 55, 13). Large plates, v. sol. hot water. Does not yield an oxim or a phenyl-hydrazide.—CaA" 8aq: prisms.
—Ag₂A": white amorphous powder.

Bensylamic acid

CO.H.C.H. CO.NHC.H.

[139°]. Formed by boiling the benzyl-imide (2 mols.) with aqueous barium hydroxide (1 mol.) (Werner, C. J. 55, 631). Flat prisms, m. sol. hot water, v. sl. sol. ether.

Phenylamic acid CO2H.C2H4.CO.NHPh. Succinantic acid. [149°]. Formed by boiling the phenylimide with NH₂Aq (Laurent a. Gerhardt, A. Ch. [3] 24, 179) or baryta (Menschutkin, A. 162, 176). Flat needles, v. sl. sol. cold water. Decomposed by heat into water and the phenylimide. Boiling alcoholic HCl forms succinic acid. — CaA', 4aq. — BaA', 3aq. — AgA': crystalline pp.

o-Tolyl-amic acid CO₂H.C₂H₄.CO.NHC₇H₇. [97°]. Got by boiling the o-tolylimide with baryta water (Bechi, B. 12, 322). White needles.—BaA'2 aq.

p-Tolyl-amic acid [157].—BaA', aq. (a)-Naphthyl-amic acid

CO,H.C,H,.CO.NHC,H,. [171°]. Formed by heating the (a)-naphthylimide with KOHAq (Pellizzari, A. 248, 158; G. 18, 323). Needles or plates (from alcohol), v. e. sol. HOAc and benzene

(B)-Naphthyl-amic acid [192°]. Crystals. Di-phenyl-amic acid

CO2H.C2H4.CONPh2. [119°]. Plates (Piutti, G. 14, 468).—AgA': pp.
Phenylene-di-amic acid

C₈H₄(NH.CO.C₂H₄.CO₂H)₂. Formed by heating phenylene-diamine with succinic acid at 200° (Biedermann, B. 9, 1668). Small crystals (from HOAc). Melts above 360°. Converted by KOHAq and MeI into C.H. NMe.O.CO crystallising in plates or tables (containing 1 aq)

(Griess, B. 18, 2410).

Imide CH₂CO NH. [126°] (Erlenmeyer, Z. [2] 5, 175). (288°). H.C. 439,000. H.F. 110,500 (Berthelot a. André, Bl. [3] 4, 229). Formed from succinic anhydride and dry NH₃ (D'Arcet, A. Ch. [2] 58, 294), and also by heating succinamide or ammonium succinate (Fehling, A. 49, 198; Laurent a. Gerhardt, Compt. Chim. 1849, 108; Menschutkin, A. 162, 165, 187; 182, 93). Large efflorescent crystals (containing aq) or octahedra (from acetone) (Bunge, A. Suppl. 7, 118), v. sol. water and alcohol, m. sol. ether. Not attacked by pure HNO_s (S.G. 1.53) (Franchimont, R. T. C. 6, 228). Converted by hot baryta water into succinamic acid, and finally into succinic acid. Alcoholic NH, at 100° forms succinamide. Yields pyrrole on distillation with zinc-dust. KOH (6 mols.) and KBrO (1 mol.), acting for two hours at 60°, form (β)-amidopropionic acid [196°] (Hoogewerff a. Van Dorp, R. T. C. 10, 4). Bromine forms bromo-succinimide [225°] and bromo-maleïmide [152°] (Kisielinski, Sits. W. [2] 74, 561; cf. Kusseroff, A. 252, 158). Chlorine at 160° forms chloro- and di-chloromalete imide. PCl, forms a compound melting You IV,

at 145°-148° (Bernthsen, B. 18, 1047). A solution of bleaching-powder added to a solution of succinimide containing excess of HOAc forms C₂H₄<CO>NCl [148°], which separates from benzene in large crystals, and is reconverted by acids and alkalis into succinimide (Bender, B. 19, 2273). Hydroxylamine at 65° forms NH(CO.C.H.,CO.NH.OH), [171°], crystallising in needles, v. e. sol. water, and yielding a picrate B'C₆H₂N₅O, [266°] (Garny, B. 24, 3434). Methyl cyanate forms C₂H₄ CO.NH₂ CO [149°], while EtNCO forms corresponding O,H10N2O, [950] (Menschutkin, A. 178, 204).

Salts.-KC,H,NO, 1/2 aq. Ppd. by adding alcoholic potash and ether to an alcoholic solution of succinimide (Landsberg, A. 215, 200).tion of succinimide (nandsberg, A. 210, 200).—

KA': needles. V. sol. water and alcohol.—

BaA', 2aq. — BaA', 2½aq. — MgA', 2aq. —

HgA', — NH, HgA'. — ClHgA'. — CyHgA'. —

Cu, A', (OH), 9aq. — Cu, A', (OH), 2aq. — AgA' ½aq.

Needles. Converted by iodine into IC, H, NO, crystallising in dimetric prisms; a:c=1: 873, melting, with evolution of I, at 135°. Silver succinimide is converted by succinyl chloride in ethereal solution into 'trisuccinamide' (C,H,O₂)₃N₂ [83°], crystallising from ether (Gerhardt a. Chiozza, A. 90, 108).—AgA'NH₃: crystalline.

Methylimide C₂H₄:C₂O₂:NMe. (234°). Formed by distilling methylamine succinate. Plates. Got also by the action of conc. H2SO4 on the oxim of \$\beta\$-acetyl-propionic acid (Rischbieth; Bredt a. Boeddinghous, A. 251,

Ethylimide C2H4:C2O2:NEt. [26°]. (234°). Formed by distilling acid ethylamine succinate (M.), and by adding alcoholic EtI to sodium succinimide (Landsberg, A. 215, 212). Long lancet-shaped crystals, v. sol. water, alcohol, and ether. Yields ethyl-pyrrole on distillation over zinc-dust.

Allylimide C.H.:C.O.:NC,H. (245°).
S.G. § 1:1543; ½ 1:1432. Formed by heating succinic acid with allyl thiocarbimide. Liquid, v. sol. water and alcohol.

Ethylene-imide (C,H,:C,O2:N),C,H, [251°]. (395°). Formed by heating succinic acid with the hydrate of ethylene-diamine at 180° (Mason, C. J. 55, 10). Prisms, sol. hot water, v. sl. sol. hot alcohol, insol. ether.

Propylene-imide (C₂H₄:C₂O₂:N)₂C₃H₆. [100°]. Formed from the anhydride and propylene-diamine (Strache, B. 21, 2360). Crystals (from benzene).

Phenylimide $C_2H_4:C_2O_2:NPh.$ cinanil. [156°] (L. a. G.; Kauder, J. pr. [2] 31, 17). [150°] (Hübner, A. 209, 373; Bischoff a. Nastvogel, B. 22, 1807) (above 300°). Formed by heating succinic acid with aniline, and crystallising the product from water and alcohol successively (Laurent a. Gerhardt, A. Ch. [8] 34, 179). Formed also by the action of PCl, on C2H,(CO.NHPh).CO2H in chloroform (Anschütz, 8. 21, 957). Needles, sl. sol. hot water. PCl. in presence of boiling POCl. forms the phenylimide of di-chloro-maleïc acid C. Cl.; C. 20; NPh. Alcoholic NH. forms C. H. (CONH.). CONHPh. Boiling lime water forms C. H. (CO. H.). CONHPh. Fuming HNO forms an o-nitro-derivative [156°]

and the p-nitro derivative [205°-208°]. The salt C.H.:C.O.:NC.H.:SO.Na is got by heating succinic acid with sodium amido-benzene p-sulphonate (Pellizzari, G. 18, 817).

Bensylimide C2H4:C2O2:NCH2Ph. Formed from benzyl chloride, succinimide, and alcoholic NaOH (Werner, C. J. 55, 629). Six-

sided prisms, sol. alcohol.

o-Tolylimide C₂H₄:C₂O₂:NC₆H₄Me. (345° uncor.). Formed by heating o-toluidine with succinic acid (Michael, B. 10, 579; Bechi, B. 12, 25, 321). Needles, v. sol. water.

p-Tolylimids. [150°]. (345°). Needles (from water), sl. sol. cold water. Yields on nitration C₂H₄:C₂O₂:NC₈H₃Me(NO₂)[1:4:2] (Hübner, A. 209, 378).

Tri-methyl-phenyl-imide C2H4:C2O2:NC H2Me2. Succinmesidil. ſ137°1. Formed by heating succinic acid with mesidine (Eisenberg, B. 15, 1018). Pearly plates, sol. alcohol and ether, sl. sol. water.

(a) - Naphthylimide C.H.; C,O.; NC, H, [153°]. Formed by heating succinic acid with (a)-naphthylamine (Hahnemann, B. 10, 1713; Hübner, A. 209, 381; Pellizzari, A. 248, 158). Needles, m. sol. alcohol. Yields a di-nitroderivative [250°]. The sulphonic acid C₂H₄:C₂O₂:NC₁₀H₆SO₃H, prepared from (α)-naphthylamine p-sulphonic acid, yields KA' 2aq (Pellizzari, G. 18, 321).

(β)-Naphthylimide. [180°]. Colourless needles, v. sol. alcohol. Converted by ΚΟΗΑq into CO2H.C2H4.CO.NHC10H7 [192°] (Pellizzari,

A. 248, 159).

Benzimidide C,H,:C,O,:NCPh:NH. [212°]. Formed from acetyl-succinic ether C10H16O5, benzamidine hydrochloride, and NaOHAq (Pinner, B. 22, 2620). Needles, sl. sol. cold acetone and ether, sol. alcohol.

References .- Amido-, Bromo-, Bromo-Amido-, CHLORO-, NITRO-, and OXY-SUCCINIC ACID and DI-IODO-SUCCINAMIC ACID.

Isosuccinic acid v. METHYL-MALONIC ACID.

SUCCINIC ALDEHYDE. Reduction of succinic anhydride, which might be expected to yield the aldehyde, forms instead the isomeric

y-oxy-butyric lactone.

Oxim C.H.(CH:NOH)₂. [173°]. Formed by heating pyrrole with hydroxylamine hydrochloride at 100° and, together with ethylamine, by the action of hydroxylamine on v-ethylpyrrole (Ciamician, B. 17, 533; 22, 1968; 23, 1788). Small white crystals (from alcohol). May be reduced to tetrametlylene-diamine

C.H. (CH.NH₂)₂ [28°]. Phenyl hydrazide C.H.(CH:N.HPh), [125°]. Formed by heating a solution of the oxim (1 pt.) in water (50 pts.) with phenyl hydrazine (5 pts.) dissolved in dilute HOAc (Ciamician, B. 22, 1974; 23, 1784). Small silky plates, v. sol. alcohol. Converted by cold conc. HClAq into a base C₂₀H_{.0}N, [185°], which crystallises from EtOAc in needles, v. sl. sol. alcohol, and gives a deep-blue colour with K2Cr2O, and H2SO.

Succinic semi-aldehyde. Nitrile

CN.CH, CH, CHO. B-Cyanopropionic aldehyde (77°). S.G. 15 89. Formed by heating AgCy (67 g) for ten hours (Chautard, A. Ch. [6] 16, 182). Oil, not solid at -20°, miscible

with alcohol and ether. Reduces Fehling's solution. Does not combine with NaHSO, or phenyl-hydrazine. Decomposed by hot alkalis and acids. Aniline at 350° forms the compound CH,Cy.CH(NHPh),

Succinimidine C.H, N. i.s.

 $C_2H_4 < C(NH) > NH$. Formed, as hydrochloride, together with NH,Cl, by the action of water on succinamidine (Pinner, B. 16, 362, 1657; 18, 2845).-B"HCl: long plates, v. sol. water, sl. sol. alcohol. Converted by acetoacetic ether into crystalline $C_8H_{11}N_3O_2$.— $B''(HNO_3)_2$ $\frac{1}{2}aq$: leaflets (Grabowski, A. 265, 168).— $AgC_1H_uN_3$: ppd. by adding ammoniacal AgNO, to a solution of the hydrochloride.

SUCCINIMIDO-ACETIC ETHER C,H,1NO. i.e. C2H4:C2O2:N.CH2.CO2Et. [67°]. Formed by heating succinimide with alcohol, NaOEt, and CH2Cl.CO2Et (Haller a. Arth, C. R. 105, 280). Needles, v. sol. water, alcohol, and ether. Alcoholic NaOEt forms gelatinous CaH10NaNO4

SUCCINIMIDO-ETHYL ETHER C8H16N2O2 i.e. C.H. (C(NH).OEt). The hydrochloride B"2HCl is prepared by passing gaseous HCl into an ethereal solution of ethylene cyanide (Pinner, B. 16, 359). It is v. sl. sol. alcohol and ether, and decomposed by water into succinic ether and NH Cl. With ammonia it gives $C_2H_1(C(NH).NH_2)_2$.

 $C_2H_4 < CO \longrightarrow NH.$ SUCCINIMIDOXIM

[197°]. Formed by heating ethylene cyanide with alcoholic hydroxylamine at 65° (Garny, B. 24, 3427). White crystals, sol. water. -B'HCl. [98°]. Needles.— $B'C_{6}H_{3}N_{3}O_{7}$. [212°].

Benzoyl derivative

 $C_2H_4 < CO$ NH. [184°]. Formed from the oxim, NaOH, and BzCl. White powder, sol. alcohol, sl. sol. ether.

SUCCINOPHENONE v. DI-PHENYL ETHYLENE

SUCCINOXYL-AMIDO-BENZOIC CARBOXY-PHENYL-SUCCINAMIC ACID.

SUCCINYL-AMIDO-BENZOIC ACID AMIDO-BENZOIC ACID.

SUCCINYL - SUCCINIC ACID v. DI-OXY-TEREPHTHALIC ACID DIHYDRIDE, vol. iii. p. 777.

SUCCISTERENE $C_{15}H_{10}$. [160°]. (above 300°). Occurs in the product of distillation of amber (Pelletier a. Walter, A. Ch. [3] 9, 96). Flat needles, nearly insol. cold alcohol, v. sl. sol. ether.

SUGAR, a term applied to the members of a group of carbohydrates in consequence of the property they possess of being sweet to the taste and of their relationship to the substance to which the term was originally given. The known natural members of this group are not very numerous. They are all easily soluble in water crystallisable, and diffusible. When solutions of them are heated with alkaline solutions of the more easily reducible metals, reduction takes place with precipitation of the lower oxides in some cases, and of the metals in others; some sugars, before exhibiting this property, require to be digested with dilute mineral acids. En zymes also convert some of the non-reducing members into reducing ones. With phenyl

hydrazine they yield phenylhydrazides and phenylosazones. Oxidising agents easily convert them into soids, and reducing agents into alcohols. Some of them undergo fermentation when submitted to the action of beer yeast, i.e. they are decomposed into alcohol, CO2, &c. They yield solutions which are optically active, those of some rotating the plane of polarisation to the right, of others to the left. They give colour reactions with aromatic acids and phenols.

The group may be divided into two classes: (1) those which, when digested with dilute acids. do not yield any other sugar or sugars-the sugars of this class are distinguished by the termination -ose; (2) those which, when diges-ted with dilute acids, do yield some other sugar or sugars-these sugars are distinguished by the termination -on. They are designated according to the number of carbon atoms they contain: thus, pentose containing C, hexose containing Co, &c., and di-penton containing C10, di-hexon containing C12, &c.

The members of the -osc class are: Triose C₃H₆O₃, glycerose

Tetroses C₄H₈O₄, erythrose C₄H₂(C₆H₃)O₄, phenyltetrose

Pentoses C, H, O, arabinose

ribose xylose

CaH, (CH,)Os, rhamnose (methyl pentose)

fucose (ditto)

Hexoses C₈H₁₂O₆, d- l- and i-1 glucose (dglucose = dextrose) $d \cdot l \cdot \text{ and } i \cdot \text{mannose}$

d- l- and i-gulose

d- l- and i-fructose (d-

fructose = lævulose) d- l- and i-galactose

sorbose (sorbinose)

formose lokaose

B-acrose

C.H.1(CH.)O., rhamnohexose (methyl hexose).

Heptoses C, H, O, mannoheptose

a- and β -glucoheptose

galaheptoso

fructoheptose

digitalose

C,H,s(CH3)O, rhamnoheptose (methyl heptose).

Octoses C₈H₁₈O₈, mannoctose

a- and B-glucoctose Nonoses C_pH₁₉O_p, mannononose

glucononose The members of the -on group are:

Di-penton C10H18On, arabinon

Di-hexon C₁₂H₂₂O₁₁, cane-sugar (saccharon) milk sugar, lactose

(lacton) (di-glucon. maltose

amylon)

iso-maltose

melibiose

trehalose

cyclamose

para-saccharose tewfikose (tewfikon)

id, hand i. Fischer's notation, see p. 583,

Tri-hexon C₁₈H₃₂O₁₆, raffinose Hex-hexon C_{3e}H_{e2}O₃₁, gentianose stachyose

Occurrence.—Some of these sugars have been obtained by synthesis, others are products of the action of dilute acids or ferments on more complicated bodies, and others occur naturally. The most important source of the latter is the vegetable kingdom. Little, if anything, is known concerning the formation of the sugars in nature; it is very probable that they are intermediate products of assimilation between CO₂ and H₂O₄ and starch, inulin, cellulose, and such bodies. For an account of the various theories, see textbooks of vegetable and animal physiology. The sugars found in animals are most probably of vegetable origin.

Determination .- Owing to the fact that the sugars possess many properties in common, the presence of a particular sugar can only be definitely proved by its isolation in the pure state. and a determination of its optical activity, reducing power, and other definite distinguishing

properties (v. end of art.).

Molecular Weight.—Until quite recently none of the accepted methods for determining molecular weights were applicable to the sugars. At the present time there are several, chief among which are the physical methods of Raoult (A. Ch. [5] 28, 133; [6] 2, 66-124; [6] 4, 401; [6] 8, 289 a. 317), and De Vries, which are of general application, and the various chemical ones which are of special application. By Raoult's method Brown and Morris (C. J. 1888, 610; 1889, 462), Tollens and Mayer (B.21, 1566), and Tollens, Mayer, and Wheeler (B. 21, 3508), Ekstrand and Mauzelius (Vetensk. Akad. für Handl. 1889. 157), and O'Sullivan (C. J. 1890. 62) have determined the molecular weight of xylose and arabinose to be 150, corresponding to a formula C, H10O; of dextrose, lævulose, galactose to be 180, corresponding to a formula CaH12O6; of arabinon to be 282, corresponding to a formula C10H18O9; of cane sugar, maltose, lactose to be 342, corresponding to a formula $C_{12}H_{22}O_{11}$; and of raffinose to be 504, corresponding to a formula $C_{18}H_{32}O_{16}$. These numbers have been confirmed in the case of the simpler sugars by various chemical methods (see succeeding paragraphs). In the case of arabinose it was first shown to be C,H,O, by Kiliani (B. 20, 339) by the analysis of some of its compounds, its formula previously having been considered to be C.H,2O.

Synthesis.-The first step towards the synthesis of the sugars was made by Butlerow (A. 120, 295; C. R. 53, 145). He obtained a sweet syrup, having the common characteristics of the sugars, by adding lime-water to a hot solution of di-oxymethylene; the product he called methylenitan, and considered its formula to be C, H14Oe. The next step was made by Loew (J. pr. 33, 321), who, having discovered a method for the preparation of formaldehyde (CH,O) in quantity, investigated its condensation by lime-water. He obtained a sweet syrup, which he called formose, and considered it to have a formula C.H,2O. Neither methylenitan nor formose fermented with yeast (see also Tollens, B. 19, 2133). Fischer (B. 21, 989) finds these products to be a mixture of various saccharine bodies. the chief which is a sugar, formose $C_0H_{12}O_4$, yielding an osazone $C_1H_{22}N_1O_4$, m.p. 144°. Another sugar is present in smaller quantities in the condensation products of formaldehyde. It yields an osazone greatly resembling glucosazone, which has been identified with a acrosazone. Later, Loew (B. 22, 475), by the condensation of formaldehyde with lead oxide and magnesis, obtained a sugar which is fermentable. Loew called this methose, but Fischer has shown it to be identical with a acrose.

Acrose was obtained by Fischer (B.20, 1093 and 2566) by acting on acrolein bromide with bases $2C_sH_oOBr_2 + 2Ba(OH)_2 = C_sH_uO_s + 2BaBr_2$. Two isomeric sugars, a-acrose and β -acrose, are

thus produced.

Glycerose yields these two sugars by the action of alkalis. (Glycerose is a sugar C₂H₀O₂, obtained by the action of bromine and soda on glycerol and other methods by Van Deen, J. 1863. 501; Grimaux, C. R. 104, 1276; and Fischer a. Tafel, B. 20, 1088 and 3385; 22, 106. It is probably a mixture of the aldehyde and ketone of glycerol.) The formation of a-acrose from glycerose may be represented CH_(OH).CH(OH).COH+CH_OH-CO.CH_OH=CH_OH.CH(OH).CH(OH).CH(OH).CH(OH).CO.CH_OH. The sugars can only be separated from the products thus obtained as osazones; a-acrosazone is identical with glucosazone in every way except in its action on polarised light.

a-acrosazone

CH₂.OH(CH.OH)₃C—CH.N.NHC₆H₅

й.NH.C₄H.

acted on by furning hydrochloric acid, is converted CH, OH. (CH.OH), CO.COH, into a-acrosone which, when reduced by zinc and acetic acid, , yields a sugar CH2.OH(CH.OH)3.CO.CH2OH, in the form of a sweet syrup; it ferments with yeast, yields lævulinic acid when heated with hydrochloric acid, and is reduced by sodiumamalgam to a hexahydric alcohol α-acritol, which resembles mannitol in every way except that it is optically inactive. By these various reactions so much is lost that from 1 kilo. glycerol only 0.2 g. acritol is obtained. Further, all the bodies obtained in the processes were optically inactive. More knowledge was necessary before the natural sugars could be synthesised. At this stage a new light was thrown on the subject by an observation of Fischer (B. 23, 870) that arabinose carboxylic acid and mannonic acid were identical in every way except that their optical activities, although equal, were opposite in sign, and that they combined to form an optically inactive acid. These three acids were reduced by sodium-amalgam to three sugars resembling one another in all respects except that one of them had a right-handed optical activity, the other an equal but lefthanded one, while the third was optically inactive. They are named l-mannose, i-mannose, and d-mannose; by further reduction they yielded the corresponding hexahydric alcohols I-mannitol, i-mannitol, and d-mannitol.

The sugar obtained from a-acrosazone as

2, 4, and d are very unsatisfactory, and somewhat misleading: but as Fischer has introduced them we must let them stand. A little study will make their meaning dess. above described is identical with lavulose except that it is inactive. If, then, we can decompose this lavulose into d-lavulose and l-lavulose, the synthesis of the natural sugar will be accomplished. This Fischer has done (B. 23, 870). If i-lavulose be submitted to the action of yeast, the lavo- constituent ferments and the residue is dextrorotatory. This is l-lavulose; it is not the natural sugar: that belongs to the d-group, and was destroyed by the ferment.

To obtain the natural sugar from the inactive synthetic one, Fischer proceeded as follows:—i-mannitol, i.e. a-acritol, is oxidised by nitric acid to i-mannose, and this further by bromine-water to i-mannonic acid. By fractional crystallisation of the strychnine or morphine salts it can be mesotomised, the result being d-and l-mannonic salts, which, on being freed from the base, yield by reduction the corresponding mannoses and mannitols. These, by means of the osazones, can be converted into the corresponding lawuloses (see Dextrosazone).

Dextrose and mannose both yield the same osazone; the difference in their constitution must therefore be caused by the position of the group marked with a * in the formula

СН, (ОН).СН(ОН).СЦ(ОН).СН(ОН).•СН(ОН).СОН. Fischer (B. 23, 799 a. 2611) found that by heating gluconic acid with quinoline, part was converted into mannonic acid and part unaltered; and also that mannonic acid, treated in the same way, yielded some gluconic acid. Dextrose may then be obtained by reducing the gluconic acid thus The corresponding reaction with obtained. I-mannonic acid does not take place easily, if at all, but 1-gluconic acid is produced simultaneously with arabinose carboxylic acid (l-mannonic acid) by Kiliani's mode of preparation (see Arabinose). From l-gluconic acid, by reduction, l-glucose, the optical isomer of dextrose, is obtained. The table on next page gives a concise view of the synthesis of dextrose, lævulose, and mannose.

Another sugar, gulose, stereoisomeric with glucose, has been obtained by Fischer (B. 23, 93; 24, 521) by the reduction of saccharic acid, the d-, l- and i- modifications being obtained by the reduction of d-, l- and i- saccharic acids. As these are the products of the oxidation of d- l- and i- glucose, the synthesis of gulose is complete.

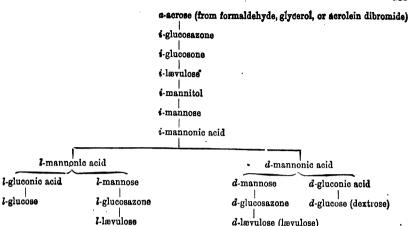
Galactose has not been synthesised up to the present (June 1893), but by the reduction of mucic acid Fischer and Hertz (B. 25, 1247) have obtained i-galactonic acid and i-galactose; i-galactonic acid, by the fractional crystallisation of its strychnine salt, may be mesotomised into d- and I-galactonic acids from which d-and I-galactose are obtained; d-galactose is identical with ordinary galactose.

Arabinose has not been directly synthesised, but its relationship to the synthetical sugars is shown by the fact that the two acids obtained from arabinose by the nitrile reaction are I-mannonic acid and I-gluconic acid (Fischer, B. 23,

2611; 24, 539).

Of zylose the same must be said; but by the nitrile reaction it yields l-gulonic acid (Fischer a. Stahel, B. 24, 528).

Arabonic acid, when heated with quincline, is partly changed into its stereoisomeride ribonic



acid, just as gluconic acid yields gulonic acid; ribonic acid, by reduction, yields the stereoisomeride of arabinose, which it is proposed to call ribose.

The synthetical passage from an -ose sugar to an -on one is said to be accomplished for lactose (lacton) and cane sugar (saccharon) as well as for maltose (amylon).

Lacton. A mixture of dextrose and galactose, is acted on by acetic anhydride, and the resulting products, carefully saponified with alkali, yield lacton (Demole, C. R. 69, 481). This has been contradicted by Berthelot (Bl. [2] 34, 82) and by Herzfeld (4. 220, 219).

Sucron. A body having a dextrorotatory power, and by inversion becoming lævorotatory, was obtained by acting on aceto-chlorhydrose (a derivative of dextrose) with an alcoholic solution of lævulose in the presence of barium carbonate. Another body which was lævorotatory, and became less lævorotatory on inversion, was obtained by acting on aceto-chlorhydrose by sodium lævulosate (Colley a. Vakovitch, Bl. [2] 34, 826).

Isomaltose has been prepared by Fischer (B. 23, 3687) by the action of HCl on dextrose. Dilute acids again hydrolyse it to dextrose, the same product as is yielded by maltose.

Phenyl-tetrose has been prepared synthetically from cinnamaldehyde cyanhydrin; this, by the action of bromine, yielding phenyl-dibromovay-butyronitrile CH.Ph.Br.CH.Br.CH.OH.CN, which, when heated with hydrochloric acid, yields phenyl-bromo-di-oxy-butyrolactone, from which the corresponding acid OH.CH.Ph.CHBr.CH.OH.COOH is easily obtained, and which on reduction yields the sugar OH.CH.Ph.CH(OH).CH(OH).COH.

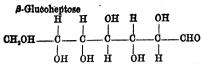
It will not be out of place here to indicate what has been done in the way of converting a sugar into one containing a carbon atom more. To do this, Fischer (B. 22, 2204; 23, 370, 799, 980, 2226, and 3102; Ann. 270, 64) made use of the well-known reaction for proceeding from one alcohol to its next higher homologue by means of the nitrile. Now, in this reaction, where an asymmetric carbon atom is added to the molecule,

d-lævulose (lævulose) Van't Hoff has predicted that two isomeric bodies will be formed which will differ by the arrangement of the groups round the new carbon atoms. Fischer (Ann. 270, 64) has shown that this is so in the case of the glucose homologues, the two acids obtained from glucose being a- and B-glucoheptonic acids; a-glucoheptonic acid is always the principal product of the reaction, and is identical with the dextrose carboxylic acid described by Kiliani (see Dextrose). When the reaction takes place at 20°-25° hardly a trace of the β-acid is formed; but at 40° about 13 p.c. of the latter is obtained. By oxidation these acids yield two penta-oxy-pimelic acids, the α- acid being optically inactive, and by reduction the two sugars a- and β-glucoheptose are obtained.

a-Glucoheptose

separates from its aqueous solution in rhombic prisms, m.p. 180°-190°; they have a faintly sweet taste, dissolve in 10.5 pts. of water at 14°, and are easily soluble in hot water and sparingly in hot alcohol. Its solution is optically active. Freshly-prepared solutions show a slight bi-rotation; for a 10 p.c. solution, $[a]_{1200} = -19.7^{\circ}$. It does not ferment with yeast, but reduces Fehling It is oxidised by slightly less than dextrose. bromine to a-glucoheptonic acid. It yields a hydrazone C,H₁,O₈N₂HC₆H₅, very soluble in water, m.p. 170°, and also an osazone C,H₁,O₅(N₂HC₄H₅), forming yellow needles, m.p. 108° almost involvable in water and difficulty in 195°, almost insoluble in water and difficultly in hot alcohol. Treated with acetic anhydride and zinc chloride it yields a hexacetate, m.p. 156°, and with sodium acetate and acetic anhydride it yields dec-acetyl-diglucoheptose C14H16(C4H2O), O12 m.p. 131°-132°.

By reduction with sodium-amalgam, a-gluco-heptose yields a-glucoheptitol, which crystallises in delicate prisms, m.p. 127°-128°, is optically inactive, easily soluble in water and sparingly in alcohol. It yields a heptacetyl derivative C.H.(C.H.O),O.



is obtained by the reduction of β-glucoheptonic acid, it has not yet been obtained in a crystalline state, it forms a phenyl-hydrazide C,H₁,O_eN₂H.C_eH₃, crystallising from alcohol in slender needles, m.p. 192°; the osazone is identi-

cal with a-glucoheptosazone.

Just as dextrose yields two isomeric glucoheptonic acids, so a-glucoheptose yields two isomeric glucoctonic acids. The a-acid is the chief product, and the amount of \$\beta\$- acid formed varies with the temperature. a-Glucoctonic acid yields a lactone $C_8H_{14}O_8$, sparingly soluble in alcohol and readily in water, m.p. $145^{\circ}-147^{\circ}$ [a]_{D26°} = $-45^{\circ}9$; by reduction with sodium-amalgam it yields a-glucoctose C.H., Os. 2H.O, which crystallises in colourless needles, m.p. 93°. Its aqueous solutions are optically active and show bi-rotation, [a] page = -50.5° for the anhydrous sugar. It yields a phenyl hydrazone C,H₁₀O, (N, IIC,H₃), m.p. 190°, and an osazone C,H₁₁O₆(N, HC,H₃), m.p. 210°–212°, almost insoluble in water. By reduction with sodium-amalgam it yields α-glucoctitol C_sH₁₈O_s, which is casily soluble in water; it forms slender white needles, m.p. 141°. From a-glucoctose two glucononic acids may be prepared. Only one has been examined; this when reduced yields glucononose C, H18O, its phenylhydrazide $C_9H_{19}O_8N_2HC_6H_3$ is sparingly soluble in cold water and alcohol, m.p. 195° – 200° , its phenyl osazone $C_9H_{18}O_4(N_2HC_6H_3)_2$ is sparingly soluble in hot water and alcohol, m.p. 220°-223°. Unlike mannononose, glucononose does not ferment with yeast. By reduction glucononitol is obtained.

Mannoheptose C,H,4O, is obtained by the reduction of mannoheptonic acid. It crystallises from alcohol in fine needles, it has a sweet taste, m.p. 184°-135°. It is easily soluble in water, and does not ferment with yeast; its solution is dextrorotatory and exhibits bi-rotation, the constant value is [a]_D = +68°6°. It yields a difficulty soluble hydrazide C,H₁,O₂N₃H.C₆H₃,m.p. 197°-200°, and an osazone C,H₁₂O₃(N₂H.C₆H₃)₂, m.p. 200°. By reduction with sodium-amalgam it yields a heptahydric alcohol which is identical with the naturally produced body, perseit (Maquenne, A. Ch. [6] 19, 1; C. ½. 107, 583). It combines with hydrocyanic acid, and the compound decomposed by hydrochloric acid yields mannoctonic acid.

Mannoctose $C_8H_{18}O_8$ is obtained by the reduction of mannoctonic acid. It is easily soluble in water, has a sweet taste, and does not ferment with yeast. Its aqueous solutions are laworotatory, $(a|_{D} = -3.3^{\circ}$. It yields a hydrazone $C_8H_{10}O_1N_2H.O_2H_3$, difficultly soluble in water, mp. 212°; and an osazone $O_8H_{11}O_2(N_2H.O_2H)_2$, m.p. 228°. By reduction it yields the octohydric alcohol mannoctitol. It combines with hydrocyanic scid, and the compound decomposed by hydrochloric acid yields mannonononic acid.

Mannononose C, H₁, O, is obtained by the reduction of mannonononic acid. It is easily soluble in water and crystallises from alcohol, mp. about 180°, its solution is destrorotatory, [a] a

= +50° approx. It ferments readily and completely with yeast, and resembles dextrose in many ways. It yields a difficultly soluble hydrazide C_pH₁₀O₂.N₂H.O₂H₃, m.p. 223°, and an osazone, m.p. 217°.

Galactoheptose C,H,O, is obtained by the reduction of galacto-heptoic acid. Its hydrazide (m.p. 199°) is sparingly soluble; so is its osazone

(m.p. 220°).

Fructoheptose is obtained from lavulose by

the same set of reactions.

Rhamnohexose CH₂(CH.OH)₃COH is obtained by the reduction of rhamnohexolactone (Fischer a. Piloty, B. 23, 3102); it does not ferment with yeast, but exhibits all the characters of a sugar; the osazone is obtained in stellate groups of needles, m.p. 200°. On reduction the sugar yields rhamnohextol CH₂(CH.OH)₃CH₂OH; by the action of hydrocyanic acid on rhamnohexose, the lactone of rhamnoheptonic acid is obtained, which on reduction yields rhamnoheptose. The osazone forms yellow needles, m.p. 200°; by the action of hydrocyanic acid, rhamnocotonic acid is obtained. These compounds have the following optical activities:—

Rhamnose, $[a]_D = +8^\circ$. Rhamnohexose, $[a]_D = -61\cdot1^\circ$. Rhamnoheytose, $[a]_D = +8\cdot4^\circ$. Rhamnitol, $[a]_D = +10\cdot7^\circ$. Rhamnohexitol, $[a]_D = +11\cdot6^\circ$. Rhamnohexonolactone, $[a]_D = +83\cdot8^\circ$. Rhamnoheytolactone, $[a]_D = +55\cdot6^\circ$. Rhamnoctonolactone, $[a]_D = -51\cdot2^\circ$.

The reverse of the method of proceeding from one sugar to its next higher homologue—i.e. the production of a sugar containing one less carbon atom than the original one—has been effected by Wohl (B. 26, 730). When dextrose oxim (vide below) is treated with acetyl chloride it yields an acetyl compound from which hydrocyanic acid can be eliminated, and on hydrolysis of the resulting compound a pentose is obtained, which is d-arabinose; l-arabinose (ordinary arabinose) treated in the same way as dextrose yields a tetrose.

As is well known, mucic and saccharic acids are products of the oxidation of the sugars with nitric acid. The action of reducing agents on these bodies indicates their relationship to the sugars and helps to a clearer idea of the synthetical process.

Reduction of mucic acid. Sulphuric acid and zinc-dust reduce mucic acid to i-galactonic acid (Fischer a. Hertz, B. 25, 1247). The lactone crystallises in delicate prisms, m.p. 122–125°. It is optically inactive. By further reduction with sodium-amalgam i-galactose is obtained. This can be prepared as a crystalline mass, m.p. 140°–142°; it yields a hydrazide, m.p. 158°–160° and an osazone, m.p. 195°, which is identical with that obtained from the oxidation product of dulcitol (Fischer a. Tafel, B. 20, 3384).

i-Galactonic acid may be separated into the d- and l- acids by fractional crystallisation of the strychnine salts. The two acids yield respectively d- and l-galactose; d-galactose is identical with ordinary galactose. l-Galactose may also be obtained by the fermentation of i-galactose syrup. The sugar crystallises from alcohol, m.p. 162°-163°, its specific rotatory power is [a] = -78.6°, the phenyl-hydrazide

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nielts at 158°-160° and the osasone at 192°-195°. From this, as well as from other matters connected with the synthetical portion of the work, it will be seen that d-, i-, and l- were intended to mean dextro-, inactive, and lawo-, as indicating the optical activity of the substances to which they are prefixed; but it is obvious the d-body is not always dextro-, nor the l- body lawo-. Hence the unsatisfactoriness already indicated.

Reduction of saccharic acid. Fischer (B. 23, 930; 24, 521) found that the lactone of saccharic acid was easily reduced by sodium-amalgam with formation of glycuronic acid. Thierfelder (H. 15, 71) has shown that this latter is further reduced to an acid $C_6H_{12}O_7$, which reaction Fischer has confirmed, and calls the acid gulonic acid and the corresponding sugar gulose. The relationship of these bodies to the others of the sugar group is shown here:

Dextrose . OH.CH₂(CH.OH), COH. Gluconic acid . OH.CH₂(CH.OH), COOH. Glycuronic acid . COOH.(CH.OH), COH. COOH.(CH.OH), CH.OH. COOH.(CH.OH), CH.OH. COOH.(CH.OH), CH.OH. COOH.(CH.OH), CH.OH. COOH.(CH.OH), CH.OH. COH.(CH.OH), COH.(CH.OH), CH.OH. CH.

Glycuronic acid obtained by the reduction of d-saccharic acid has $[a]_n = +19\cdot 1^n$, m.p. 175°–178°; d-gulonic acid obtained by the reduction of glycuronic acid yields a lactone, m.p. 180°–181°, $[a]_b = +55^\circ$; its phenyl-hydrazide is easily soluble in hot water and hot alcohol, m.p. 147°–149°; d-gulose obtained by the reduction of d-gulonic lactone is a colourless syrup, easily soluble in water and sparingly in absolute alcohol, it is oxidised by nitric acid to saccharic acid, it does not ferment with yeast.

Constitution. Dextrose and galactose are represented by the formula

CH,(OH).OH(OH).CH(OH).OH(OH).OH(OH).COH

and levulose by CH₁(OH).CH(OH).CH(OH).CO.CH₂OH and for the following reasons.

By oxidation dextrose and galactose yield acids containing the same number of carbon atoms as themselves, whilst levulose yields acids containing less carbon atoms than itself; dextrose and galactose yielding gluconic and galactonic acids CH₂(OH){CH(OH)}₂.COOH and by further oxidation saccharic and mucic acids COOH{CH(OH)}₄.COOH respectively; whilst levulose gives rise to trioxybutyric CH₂(OH){CH(OH)}₄.COOH, formic H.COOH, and glycollic CH,OH.COOH acids.

By reduction dextrose and galactose yield respectively mannitol and dulcitol; lævulose also yields mannitol. These yield hexacetyl derivatives, and are reduced by hydriodic acid to secondary hexyl iodide CH₂(CH₂),CHLCH₄ (Wanklyn a. Erlenmeyer, J. 1861. 731; 1862. 480); they are evidently hexahydric alcohols of normal hexane.

All three sugars combine with hydrocyanic acid to form nitriles which when boiled with hydrochloric acid yield different acids C,H₁₄O_s, which are reduced by hydriodic acid to heptoic acids; dextrose and galactose yielding normal heptoic acid CH₁(CH₂). COOH and lævulose yielding methyl-butyl-acetic acid CH₃ CH. COOH (Kiliani, B. 18, 3066; 19, 221, 767 a. 1128). Galactose, dextrose, and lævulose

form oxims or iso-nitroso-compounds by combination with hydroxylamine (Rischbieth, B. 20, 2673; Jacobi, B. 24, 696; Wohl, B. 24, 993). With phenyl-hydrazine, dextrose and galactose yield hydrazides

From the synthetic work above described, it is evident that the aldehyde formula belongs also to mannose, gulose, arabinose, xylose, and ribose, and also their synthetic homologues. Rhamnose, as is evident from its reactions, has also an aldehyde constitution; it appears to be methyl-arabinose.

Sorbose appears to be isomeric with lævulose. By oxidation it yields tri-oxyglutaric acid COOH.{CH(OH)},COOH and other acids, and by reduction it yields mannitol. It combines with hydrocyanic acid. By reduction with hydriodic acid and phosphorus it yields hexyl iodide (Kiliani a. Scheibler, B. 21, 3276).

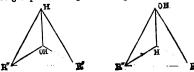
Little is known concerning the -on sugars. Maltose and lactose are probably anhydrides of equal molecules of dextrose and dextrose, and dextrose and galactose respectively; they yield acids (maltobionic and lactobionic) which on boiling with dilute mineral acids are decomposed into dextrose and gluconic acid and galactose and gluconic acid respectively. Both sugars thus appear to contain the dextrose-aldehyde group unaltered. Fischer (B. 21, 2633) has represented lactose as

CH₂(OH), {CH(OH)}, CH

Cane sugar appears to be differently constituted from either maltose or lactose.

It thus appears that the formula $CH_{+}(OH), \{CH(OH)\}, COH$ must be assigned to eight known sugars—i.e. d- and l- glucose; d- and l- gulose, d- and l- mannose, d- and l- galactose (the i- modifications being analogous to racemic acid, i.e. compounds of the d- and l-modifications).

Now, as this formula contains four asymmetric carbon atoms, according to Van't Hoff's theory there will be possible 2'=16 isomers, which in the case of the symmetrical derivatives, as the hexnhydric alcohols and dibasic acids, will be reduced to 10, of which ½2'=8 compounds are grouped in pairs (d- and l-) and ½2\frac{1}{2} = 2 inactive, amesotomic (Fischer, B. 24, 1836 a. 2683; Van't Hoff, La Chimie dans l'Espace and Dix Années dans l'Histoire d'une Théorie). Each of the groups R''——"HoH—"R' may be grouped in two positions represented thus



(the carbon atom being considered to be at the centre of the tetrahedron). For the sake of brevity these two groupings will be written $\begin{array}{ccc} H & OH \\ R'' & C & R' & and & R'' & C & R'. \end{array}$

The sixteen possible modifications of the glucose formula may then be expressed by the following symbols; in the case of the symmetrical derivatives (hexahydric alcohols and dibasic acids) Nos. 11-16 are identical with Nos. 5 to 10:-

Ħ Ħ ÓН Ĥ Since saccharic acid may be obtained either from glucose or its stereoisomeride gulose, then and L saccharic acids must be represented by formulæ corresponding to two of those numbered 5 to 10. Now, 7 and 8 may be eliminated, as they are optically inactive from internal compensation. Nos. 6 and 10 may be excluded for the following reasons: Glucose and mannose yield the same osazone, and consequently differ only in the arrangement of the groups round the asymmetric carbon atom next to the COH group. Other facts which confirm

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Ħ Ħ

QН 0HĦ

15. CH2(OH)

16. CH,(OH)

ÓН QН OH Н

ÓН Ĥ ŎН

ÒН

ÒН

COH

COH

these formulæ are (1) 1-gluconic and 1-mannonis acids are both produced by the nitrile reaction from arabinose; (2) fructose reduced by sodiumamalgam yields mannitol and sorbitol; (3) man-nonic and gluconic acids can be converted, one into the other, by heating with quinoline; (4) all attempts to resolve gluconic and mannonic acids into two components have been unsuccessful.

If saccharic acid has the configuration 6 or 10, then manno-saccharic acid must have the configuration 7 or 8; but the latter are optically inactive, and therefore cannot be the configuration of manno-saccharic acid. Hence dand l-saccharic acid must have a configuration corresponding to 5 and 9; for convenience we may assign 5 to the d- and 9 to the l- bodies.

Now the two sugars corresponding to d-saccharic acid-i.e. d-glucose and d-gulose-must consequently have the configuration 5 and 11; but in order to determine which to assign to one and which to the other, we must consider xylose and arabinose.

Arabinose by the nitrile reaction yields l-glucose and xylose yields l-gulose; now since l-glucose and l-gulose are

then xylose and arabinose must

According to theory, there will be 23 = 8 isomeric pentoses, but when the formula becomes symmetrical, the asymmetry of the centre carbon is destroyed, and there will be only three isomeric pentahydric alcohols and three isomeric trioxy-glutaric acids, of which two are optically active, i.e.:

The same applies to the pentahydric alcohols. As arabitol and the tri-oxy-glutaric acid from arabinose are both lævorotatory, whilst the forresponding compounds from xylose are optically inactive, the formula marked (a) is the formula for xylose, and (b) is the formula for arabinose, (9) and (15) being the formulæ for l-gulose and l-glucose respectively.

& glucose

The other di-basic acids known are mucic acid, which is optically inactive; allomucic acid, formed by the action of pyridine on mucic acid, which is also optically inactive; another isomeride of mucic acid, which is optically active, obtained by treating galactonic acid with quincline and oxidising the product; and iso-saccharic acid. We have as yet not sufficient data to write the constitution of these with certainty.

So far we have considered the sugars in general; we must now turn to a description of the individual members of the group.

Class I. Ose sugars. Arabinese $C_{\nu}H_{10}O_{\nu}$. It does not occur in sature.

Formation.—By the action of dilute acids on metapectic acid, a constituent of bestroot, gum arabic, cherry-tree gum, gedda gum, gum tragacanth, and many other gums (Scheibler, B. 1, 58, 108; 6, 612; Claësson, B. 14, 1271; Martin, Sachsse's Phytochem. Unter. p. 69; Bauer, J. pr. [2] 84, 47; Kiliani, B. 19, 3030; v. Sandersleben, Sachsse, l.c., p. 90; O'Sullivan, C. J. 1884. 41, 1891, 1029; Stone a. Tollens, A. 249, 257; Stone, Am. 12, 435; wheat and rye bran (B. 23, 3110). Owing to the fact that most of the above gums yield galactose besides arabinose, the two were for some time confused (H. Kiliani, B. 13, 2304; 15, 34; Claësson, B. 14, 1270; B. C. 205; Scheibler, B. 17, 1729; E. O. v. Lippmann, B. 17, 2238). Arabinon yields on hydrolysis arabinose alone (O'Sullivan, C. J. 1890. 59).

Preparation.—A dextrorotatory gum, or one yielding little mucic acid when exidised by nitric acid, is selected. A solution containing 30-40 g. per 100 c.c. is heated to 100° in a water bath and digested at that temperature with 2 p.c. sulphuric acid for 10-15 minutes. The solution is then cooled, neutralised with milk of lime, baryta water, or calcium or barium carbonate, and hot alcohol, S.G. 0-83, added as long as a precipitate is formed. The clear abcoholic solution is poured off the pp. which in a short time collects at the bottom, and evaporated in a vacuum to a syrup. After standing a few hours arabinose crystallises out in well-formed rhombic prisms with monoclinic terminations, and is purified by recrystallisation from water.

Formula and synthesis. See general part. Properties.—Arabinose crystallises in fine rhombic prisms out of aqueous solution. The termination and habitat of the crystals vary with the source. From alcoholic solutions it separates in sphenoids. The crystals melt at 160°. Its specific rotatory power is [a]_p = +104.5° for 10 p.c. solution at 20°C.; in more concentrated solutions it is higher, [a]p = + 110° being observed for nearly saturated solutions. Freshly-prepared solutions possess bi-rotation, an angle of [a]_D = 156.7° having been observed Scheibler, Lc.; O'Sullivan, Lc.; E. O. v. Lipp-mann, Lc.; Bauer, L. V. 36, 304; Tollens, A. 257, 160; Groth, B. 6, 615; Griess a. Harrow, B. 20, 3111). The specific gravity of aqueous solutions does not increase regularly with the strength, being less in proportion for high concentrations than for low ones. The S.G. of a solution confaining 10 g. in 100 c.c. at 15.5° is 1.0385-1.0384.

Action of acids. The action of boiling dilute mineral acids destroys much of the opticity and K. of arabinose in a short time (O'Sullivan, 1884, 55). The first products of the change have not been studied. When, however, the action is continued for a considerable time, no lavulinic acid is produced, but furfural is present in large quantities (Ganz, Stone, a. Tollens, B. 21, 2148; 23, 3791). Chalmont a. Tollens (B. 24, 694) obtained 52·7 p.c. furfural by precipitating the distillate from the products of action of acids with phenylhydrazine acetate. Formic and aceto-propionic acids and humus substances are also present (Conrad a. Guthzeit, B. 18, 2905).

Reduction.—Treated with sodium-amalgam in acid solutions, arabinose yields arabitol, a body resembling sorbitol, m.p. 102°. This body

does not reduce Fehling's solution, and is optipally inactive (Kiliani, B. 20, 1233)

Oxidation .- By oxidation with nitric acid arabinose yields arabonic acid (lævorotatory trioxyglutaric acid), and by violent oxidation at an elevated temperature oxalic acid (Kiliani, B. 21, 8006). Bromine also oxidises it to arabonic acid C.H., O., m.p. 89° (Bauer, J. pr. [2] 34, 47; C. C. 1877, 732; Kiliani, B. 19, 3031; 20, 345). It is oxidised by alkaline solutions of metallic oxides, 100 c.c. of Fehling's solution being reduced by 0.4303 g. arabinose, and 100 c.c. of Sachsse's solution being reduced by 0.4375 g. arabinose (Bauer, L. V. 36, 304). Its K = 108 110 (O'S., .c.), i.e. 100 pts. of it reduce as much CuO as 108-110 pts. dextrose.

Fermentation.—Arabinose does not seem to be capable of fermentation with yeast (Stone a. Tollens, l.c.; Scheibler, l.c.; v. Lippmann, B. 17, 2238); with Bacillus ethaceticus it ferments with the production of ethyl alcohol, acetic, formic, and carbonic acids, and hydrogen (Frankland a. MacGregor, C. J. 1892. 737).

Compounds with cyanogen. By the nitrile reaction arabinose yields a mixture of l-gluconic and 1-mannonic acids (Kiliani, B. 19, 3029; 20, 282, 339, 2710; Fischer, B. 23, 2611; 24, 539). The first product of the action of HCy on arabinose seems to be a compound of both bodies. HCl converts this into a crystal-line amide C_cH₁₈NO_s, which on treatment with baryta yields the acids just mentioned.

Hydrazine compounds. Arabinose yields with phenylhydrazine, just as dextrose (q.v.) does, an osazone, m.p. 157°-158° (Scheibler, B.

17, 1729; Kiliani, B. 20, 345).

Compounds with diamines. With o-diamidobenzene, arabinose yields arabinose-o-diamidobenzene C.H. (NH), C.H.O. It is a neutral body, not reducing Fehling's solution, and is dextrorotatory, m.p. 235° with decomposition; it withstands boiling with dilute hydrochloric acid or potash, and yields a hydrochloride and hydrobromide. Arabinose-m-p-diamido toluene C₆H₃(CH₃)(NH)₂:C₅H₈O₄, m.p. 238°, and arabino γ diamido benzoio acid COOH.C₆N₂:(NH)₂:C₅H₈O₄ + 2H₂O, m.p. 235°, have also been obtained (Griess a. Harrow, B. 20, 3111). Arabinose gives colour reactions with orcinol and phloroglucinol (Wheeler a. Tollens, A. 254, 314; 260, 304).

Ribose. Fischer a. Piloty, B. 24, 4214.

When certain carboxylic acids of the sugar group are heated with quinoline or pyridine, they are converted with stereo-isomeric acids.

When arabonic acid OH.CH₂(CH.OH)₃.COOH is treated in this manner it yields a new acid COOH.(CH.OH), CH,OH, which the authors name ribonic acid; ribonic lactone crystallises from solution in ethyl acetate in long prisms, m.p. 72°-76°, does not reduce Fehling's solution, and is easily soluble in water, alcohol, and acetone. Its specific rotatory power is $[\alpha]_{D20^0} = -18$. Its phenylhydrazide forms colourless needles, m.p. 162°-164°. Ribonic acid may be converted into arabonic acid by heating with quinoline.

By reducing ribonic lactone with sodiumamalgam, it yields the new sugar ribose, which forms a phenylhydrazide crystallising from alcohol in colourless crystals, m.p. 154°-155°; ribose-osazone is identical with arabinose-

osazone. By oxidation ribonic acid yields trioxy-glutaric acid, which differs from the tri-oxyglutaric acid obtained by the oxidation of xylose, but which is also optically inactive. By the further reduction of ribonic lactone, a pentahydric alcohol was obtained which has been found to be identical with the naturally occurring adonitol, obtained from Adonis vernalis (Fischer, B. 26, 636).

Xylose. C₅H₁₆O₅. It does not occur free in

Formation.—It is obtained by the action of dilute boiling acids on xylan or wood gum (Koch, B. 20, ref. 145; Wheeler a. Tollens, B. 22, 1046; A. 260, 289; Winterstein, H. 17, 381; Stone a. Test, Am. 15, 195), on the carbohydrate from the epidermis of Psyllium gallicum (Bauer, A. 248, 140), on vegetable amyloid (Winterstein, Z. P. C. 17, 353), on brewer's grain (Stone a. Tollens, A. 249, 227; 271, 55), on jute (Wheeler a. Tollens, l.c.), and other vegetable bodies (Voswinkel, C. C. 1891, 2, 655; Hebert, Ann. Ag. 16, 358; 18, 261; Stone a. Lotz, B. 24, 1657; Allen a. Tollens, B. 23, 137; Bertrand, Bl. [3] 5,

Preparation.—Xylose may be prepared by extracting straw or any other of the above-mentioned materials by 5 p.c. soda, precipitating the wood gum from the solution by alcohol, and hydrolysing this by boiling with dilute sulphuric acid. The digested solution is treated in the same way as described in the case of arabinose, and the xylose may be easily purified by crystallisation from water.

The formula and synthesis have already been

discussed in the general part.

Properties. - Xylose is easily soluble in water; 100 pts. of water at 20.3° dissolve 117 pts. of xylose; it is insoluble in absolute alcohol, 90 p.c. alcohol will dissolve in 10 c.c. 0.4 g. sugar at 19° (Bertrand, Bl. [3] 7, 499). Its solutions are optically active, freshly-prepared solutions having about four times the constant eptical activity (Parcus a. Tollens, A. 207, 160). For a 10 p.c. solution at 20° $[a]_D = +19.3^\circ$ (Parcus a. Tollens, l.c.; Bertrand, l.c.). Schulze a. Tollens (A. 271, 40) give the formula $[a]_D = +18.095 + 0.06986p$ at $15^\circ - 20^\circ$, where p = percentage of xylose in solution. Xylose frequently crystallises in prisms belonging to the ortho-rhombic system. Its solutions are not fermentable by yeast. It reduces Fehling's solution, K = 109.6, agreeing in this respect very closely with arabinose (Bertrand, l.c.). Boiled with acids it yields about 50 p.c. furfural (Günther a. Tollens, B. 23, 1751; Chalmont a. Tollens, B. 24, 694; Bertrand, l.c.).

It is reduced by sodium-amalgam to a pentahydric alcohol xylitol (Bertrand, Bl. [3] 5, 554; Fischer a. Stahel, B. 24, 528). It is oxidised by bromine to xylonic acid (Bertrand, l.c.; Allen a. Tollens, A. 260, 306); it is oxidised by nitric acid to inactive tri-oxy-glutaric acid C, H,O, (Fischer, B. 24, 1836). By the nitrile reaction xylose yields l-gulonic acid, the stereo-isomeride of l-gluconic acid (Fischer a. Stahel, B. 24, 528; Fischer, B. 23, 2625; Fischer a. Curtis, B. 25, 1025).

With phenyl hydrazine it yields an osazone m.p. 160°. Warmed with phloroglucinol and hydrochloric acid, it gives a cherry-red coleura-

tion, just as arabinose does under the same conditions (Tollens a. Mayer, B. 21, 3508; Wheeler a. Tollens, B. 22, 1046).

Isodulcite. *hamnodulcite Rhamnose.

 $C_6H_{12}O_5.H_2O.$ Preparation.—Rhamnose is obtained, together with other bodies, by the action of hot dilute acids on quercitrin, hesperidin, xanthorhamnin, naringin, and frangulin (Rayman a. Kruis, Bl. [2] 48, 632; C. C. 1888, 6; Hlasiwetz a. Pfaundler, A. 127, 362; Liebermann a. Hörmann, A. 196, 323; Kruis, A. 196, 333; Berend, A. 196, 328; Rigaund, A. 90, 292; Will, B. 18, 1316; 20, 297 and 1186; Dehn, Zeit. d. Ver. 15, 562; Rayman, Bl. [2] 47, 668; Tanret, Bl. 49, 20; Thorpe a. Miller, C. J. 1892. 8).

Properties .- Rhamnose forms fine crystals, which have a sweet taste, and a composition corresponding to the formula CoH12O3.H2O; by careful drying it loses water and then melts at 90°-110° (Websky, B. 18, 1318; Hirschwald, A. 196, 330). It is easily soluble water, and its solutions are dextrorotatory, $[a]_D = +9^{\circ}$. Freshlyprepared solutions show bi-rotation (Schnelle a. Tollens, A. 271, 61). In alcoholic solutions the optical activity decreases as the proportion of alcohol to water increases, until the solution becomes lævorotatory (Rayman a. Kruis, C. C. 1888. 6). It reduces Fehling's solution, 1 c.c. being reduced by 0.0052-0.0055 g. rhamnose (K = 91-96) (Rayman a. Kruis, l.c.). Its solution does not ferment with yeast.

Action of acids. Boiled with moderately strong acids furfural is evolved (Maquenne, C. R. 109, 603). Concentrated nitric acid converts it

into a nitrate.

Oxidation .- Nitric acid oxidises rhamnose to tri-oxy-glutaric acid (Will a. Peters, B. 22, 1697). Malin (A. 145, 197) obtained an acid CoH10Oo. Bromine water oxidises it to rhamnonic acid CaH12Oa, which is obtained in the form of the lactone $C_0H_{10}O_3$, m.p. 148° (Will a. Peters, B. 21, 1813; Rayman, B. 21, 2046). With bromine and silver oxide it is oxidised to acetaldehyde and acetic acid (Herrig, Chem. Zeit. 1887, Rep. 145; M. 8, 227).

Reduction .- Sodium-amalgam reduces rhamnose to rhamnitol CH3(CH.OH)1.CH2OH, which crystallises from alcohol or acetone in triclinic prisms, m.p. 121°, and has a sweet taste (Fischer

a. Piloty, B. 23, 3102).

Compounds .- With phenylhydrazine rhamnose yields a hydrazide $C_sH_{12}O_s:N_sHC_sH_s$, m.p. 159°, and an osazone $C_1H_{12}N_sO_s$, m.p. 180° (Will, B. 20, 1186; Fischer a. Tafel, B. 20, 1089, 1091 a. 2566). With aniline it forms a compound C.H. O.NC.H., m.p. 118° (Rayman a. Kruis, l.c.). With ammonia and ethylaceto-acetate it forms rhamnodiasine $C_{18}H_{32}O_8N_2$, m.p. 186° (Rayman a. Chodounsky, B. 22, 304 and 3247).

Rhamnose combines with hydrocyanic acid to produce rhamnonamide. The lactone C,H12O6 crystallises in needles, melting-point 168°; this is reduced by hydriodic acid and phosphorus to normal heptoic acid (Fischer a. Tafel, B. 21, 1657 a. 2178). Rhamnose hexoic acid lactone is reduced by sodium-amalgam to a sugar (Fischer, B. 22, 2204; Fischer a. Tafel, B. 23, 8102). Sodium rhamnose C₂H₁₂O₂Na, is precipitated by adding sodium ethylate to an alcoholic solution of rhamnose (Liebermann a.

Hamburger, B. 12, 1186). With benzoyl chloride tri- and tetra- rhamno-benzoates are formed: with acetic anhydride rhamno-tetracetate (Rayman, B. [2] 47, 668). From thermo-chemical considerations rhamnose appears to be methylxylose (Stohmann a. Langbein, J. pr. [2] 45, 805). Fucose C.H,2O, is obtained by the hydrolysis

of fucus. The sugar forms microscopic needles. Its solution has a sweet taste and is levorotatory, $[\alpha]_{p} = -77^{\circ}$. With phenyl-hydrazine it forms a hydrazide, melting-point 170°, and an osazone, melting-point 159° (Bieler a. Tollens, A. 258, 110; Günther a. Tollens, B. 23, 2585). Fucose appears to be methyl-arabinose (Stohmann a. Langbein, l.c.).

Dextrose. d-glucose, glucose, starch-, corn-, grape-, honey-, diabetic-sugar. (Ger. Krümmelzucker, Traubenzucker; Fr. Sucre de raisin.)

C. H12O. and C. H12O. + H2O.

Occurrence.-Dextrose is widely distributed throughout the vegetable kingdom, being usually accompanied by lavulose and cane sugar. The most important sources are honey, most fruits, the sap of plants, seeds. It occurs in the animal kingdom in the liver, blood, and other parts of the body, and in diabetic urine (S. Sachsse, Die Ch. und Phys. der Farbst. Kohlenhydrate u. Protein subst., Leipzig, 1877; F. Mack, J. 1869, 892; Girard, B. 17, 17c; Neubauer, Fr. 12, 39; Gorup-Besancz, B. 4, 906; Petit. B. 6, 1313; v. Schneider, A. 162, 235; Report on Sorghum and Cornstalles, Dep. of Agr., Report No. 35, Washington, 1881; Hermann a. Tollens, A. •230, 50; Vogel, B. 15, 2271; Fischer a. Bödecke, A. 117, 111; De Bary, Hoppe-Seyler's Medic. Ch. Unt. p. 72; Hoppe-Seyler, Handb. d. phys. Ch. Ana., 1883, 301; Klason, B. 19, 2541; Welmer, Inaug. Diss., Göttingen, 1886, 40; O'Sullivan, C. J. 1886, 58; Welmer a. Tollens, B. 19, 707; Seegen a. Kratzschmer, Pf. 22, 206; Kütz, Pf. 24, 52; Boussingault, C. R. 91, 639; J. Sieben, B. C. 1885, 134; Hermann a. Tollens, A. 230, 50; Müller, Ann. Agronom. 13, 88; Seegen, Pf. 37, 348; 39, 121; 40, 48; Cuisinier, C. C. 1886, 614; H. Thoms, B. 21, 1916a; Reali, G. 17, 325; Maquenne, A. Ch. [6] 17, 495).

Formation .- By the action of acids and ferments on the following glucosides: amygdalin (Schmidt, A. 119, 92; Hesse, l.c., 176, 112); populin (v. Lippmann, B. 12, 1648b); ruberythria acid (Liebermann a. Bergami, B. 20, 2247); salicin (Schmidt, A. 119, 97; Hesse, l.c., 176, 112); lupinin (B. 11, 2200b); hesperidin (Tanret, Bl. 49, 20); phlorizin (Rennie, C. J. 1887, 636). Other glucosides yield dextrorotatory, reducing, fermentable, and crystallisable sugars, but there is not sufficient evidence to prove with certainty that they are dextrose. These are: esculin (Rochleder a. Schwarz, A. 87, 186; Zwenger, i.c., 90, 76); arbutin (Hlasiwetz a. Grabowski, Ar. Ph. 141, 329); coniferin (Tiemann a. Har-

mann, B. 7, 608).

By the action of dilute acids the following carbohydrates yield dextrose, alone or with other glucoses. Some of them are also hydrolysed to dextrose by ferments:

a- and B- amylan yield dextrose.

Cellulose yields dextrose (Flechsig, H. 7, 523; Lindsay a. Tollens, A. 267, 370).

Glycogen yields dextrose.

Lichenin vields dextrose.

Tunicin Starch Dextrin Maltose

Lactose vields dextrose and galactose. Cane sugar yields dextrose and lævulose. Raffinose yields dextrose, levulose, and

galactose.

Preparation .- Dextrose can be prepared from any of the substances above mentioned, but it is in many cases difficult to obtain it in any quantity in the pure state. Starch and sucrose are the bodies usually employed, and we find that lactose can also be used with advantage.

(a) A white saccharum (the commercial glucose obtained by the action of acids on starch) with an optical activity approaching that of dextrose is selected. This is scraped as fine as possible, and treated with boiling ethyl alcohol 8.G. 820. On cooling, the clear saturated solution is separated from the undissolved syrup and a little previously prepared dextrose added to it. Crystallisation soon begins and continues for some time pa crop of fairly pure dextrose is thus obtained. Further purification can be effected by melting the crystals in 8-10 p.c. boiling water and adding dry boiling methyl alcohol until a slight cloud is produced. Anhydrous dextrose in a state of great purity separates abundantly from this solution. Or the saccharum is melted in 5 or 6 p.c. water, allowed to crystallise, the crystals pressed and further purified by treatment with methyl alcohol as described.

(b) A 25 p.c. aqueous solution of crystallised sucrose is taken and heated to 50°-55° and 2-3 p.c. pressed brewers' yeast stirred in (Tompson, E. P. 8686, 1884), the temperature is maintained for 2-3 hours, when the sucrose is completely inverted—that is, converted into dextrose and lævulose. The solution is then evaporated in a vacuum to a syrup, S.G. 1.5 or thereabouts. On standing for a short time this solidifies to a crystalline mass; it is washed with cold alcohol. S.G. 830, and the residue dissolved to saturation in alcohol of the same strength. Dextrose soon begins to crystallise out; the crystals can be further purified by dissolving in

methyl alcohol and recrystallisation.

Sucrose may also be inverted by digestion with sulphuric acid, the acid separated by baryta water, and the filtrate from the barium sulphate evaporated to a syrup and treated in the way mentioned. Inversion by yeast yields the best result. Soxhlet (J. pr. [2] 21, 242) recommends that inversion be effected by alcoholic hydrochloric acid. 480 c.c. of strong hydrochloric acid are mixed with 12 litres of alcohol, S.G. 810, in a glass vessel, the mixture heated 45°-50°, 4 kilos. powdered sucrose stirred in, and the whole maintained at that temperature for two hours. When cool a little previously prepared anhydrous dextrose is added, and in a few days there is an abundant crystallisation of dextrose. This can be purified by crystallisation from methyl alcohol. Should any colour be developed, the aqueous solution is treated with animal charcoal and again concentrated in a vacuum. Under such sircumstances it is better to begin again, for if proper care be taken no colour need be produced.

An aqueous solution containing 25 p.c.

lactose and 3 p.c. sulphuric soid is digested in a water-bath for three hours, care being taken by continued agitation that no colour is developed, the sulphuric acid is separated by baryta water, and the filtrate concentrated to a syrup containing 76-80 p.c. solid matter. On standing this solidifies, and after a few days is treated with boiling methyl alcohol; this dissolves out the dextrose, leaving the galactose undissolved; the former soon crystallises from the saturated methyl alcohol. A recrystallisation yields the pure body in moderately large, well-defined crystals.

Hydrous dextrose CaH12Oa.H2O can be obtained from any of the above preparations by dissolving in 12 to 20 p.c. water, and allowing to crystallise. If honey is used as a source of dextrose, any sucrose it may contain should be inverted by yeast or acids, and the residue obtained by evaporation crystallised from methyl alcohol as in the case of inverted sucrose. pure product may be obtained in a few crystallisations.

Formula and synthesis. See first part on the sugars generally.

Properties .- Dextrose crystallises out of 93-95 p.c. ethyl or methyl alcohol in the anhydrous state. Anhydrous crystals may also be obtained by special treatment from concentrated aqueous solutions at 30°-35°. As a rule aqueous solutions deposit crystals containing one molecule of water of crystallisation. Anhydrous dextrose crystallises in rhombic, hemibedric forms; the axial relationship is a:b:c=0.704:1:335. Hydrated dextrose forms hemimorphous crystals; the elements are a:b:c = 1.7350:1:1.9080, $\beta = 97^{\circ} 59'$ (F. Becke, M. 10, 231). Well-defined crystals of both varieties are difficult to obtain; usually the first separates as a powder and the second in cauliflower-like masses; both dissolve easily in water, the first with evolution of heat. Hydrated dextrose dissolves easily in strong ethyl and methyl alcohol, but the anhydrous sugar is almost insoluble in them. It is insoluble in ether and hydrocarbons, slightly soluble in aniline, acetic acid, and acetic ether. Hydrated dextrose easily loses its molecule of water of crystallisation when exposed in a vacuum over sulphuric acid, or when heated gently. The anhydrous sugar melts at 1440-146° (Hesse, A. Ch. 176, 106); its specific gravity is, according to Guerin-Varry a. Heintz, 1.386; according to Bödecker, 1.5384 (v. Lippmann, Zuckerarten, p. 12). Dextrose is not so sweet as cane sugar. Behr (B. 15, 1106) finds it } as sweet, and T. Schmidt (B. C. 1887, 405) that 1.53 pts. of dextrose are as sweet as 1 part of cane sugar. An aqueous solution of 10 g. dry dextrose in 100 c.c. of solution at 17.5° has a specific gravity of 1-0381 (water at $17\cdot5-1$) (Salomon, B. 14, 2710). This is fairly accurate, K=100. Its solutions rotate the plane of polarisation of a ray of polarised light to the right. According to Hesse a. Tollens (B. 17, 2284), the amount of rotation for the D line is expressed by the formula $[\alpha]_D = 52.5 + .018796P + .00051688P^*$ for anhydrous dextrose, and

[s]_D = 47·73 + 015584P + 0003888P? for hydrated dextrose, in which P is the percentage of the two varieties respectively in solution. In solutions containing 10 p.c. dry sugar and theresbouts, the

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factors $[a]_p = 52.7$ and $[a]_1 = 58.8$ are sufficiently accurate, but probably a shade too low. These values are not materially affected by the temperature. The presence of some inactive bodies in the solution appears to have some effect (Pribram, M. 9, 395); bodies such as potash, soda, lime, &c., which act on dextrose reduce its optical activity; other bodies, such as urea, do not alter it (N. Wender, B. 24, 2200). Freshlyprepared solutions have a greater optical activity than those which have stood a few hours. F. Urech (B. 17, 1547) has observed a rotation 2.19 times greater than the constant value. Parcus a. Tollens (A. 257, 160) observed an angle of $[a]_D = 105 \cdot 16$ in a 10 p.c. solution $5\frac{1}{9}$ min. after commencing solution. This phenomenon is called bi-rotation; the optical activity quickly falls, and the constant value is reached in about six hours in the cold and immediately on boiling. bi-rotation is also immediately destroyed by potash (O'Sullivan a. Tompson, C. J. 1890, 920), or ammonia (Schulze a. Tollens, A. 271, 49). Dextrose when produced by the inversion of cane sugar at a low temperature is set free in the birotatory state (O'Sullivan a. Tompson, l.c.). Only crystallised dextrose exhibits this phenomenon; fused dextrose does not show it (Hesse, A. 176, 113). A solution of dextrose in strong alcohol retains its bi-rotation (?) The dispersive power of dextrose solution is practically the same as that of quartz (Hoppe-Seyler, Fr. 3, 1866, 412). The ratio between the specific rotatory power for the C and D lines respectively is 1:1.258 (Grimbert, J. Ph. [5] 16, 295 and 345). The heat of combustion of dextrose is +677.2 cal., and the heat of formation +300.8 cal. (Berthelot a. Recoura, C. R. 104, 1571).

Action of heat. When the dry sugar is heated to 170°, a molecule of water is eliminated and dextrosan C.H.O. is produced, which may be reconverted into dextrose by the action of water and dilute acids. If the temperature is raised to 200°, gas, water, and volatile acids are given off, and if the heating be continued without raising the temperature, a brownish black mass is finally left. This substance is soluble in water and constitutes the colouring matter (caramel) sused in beer, wine, cooking, &c. Should the temperature be raised, carbon monoxide, dioxide, and methane are evolved, and aldehyde, furfural, acetone, metacetone, propionic, acetic, and formic acids distil over, and a black carbonaceous mass is left. If the hydrate be heated for a considerable time in a closed tube a fluid is obtained which absorbs oxygen and nitrogen (?) from the air (Thénard, C. R. 52, 795).

Action of acids. Dextrose is dissolved by strong sulphuric acid without blackening, dextrose-sulphuric acid being formed (Péligot, A. Ch. [2] 67, 170); from this solution alcohol precipitates a compound of diglucose with alcohol (Musculus a. Meyer, B. 14, 850). Similar compounds are produced by the action of chlorosulphotic acid (Claësson, J. pr. [2] 20, 1). A mixture of sulphuric and nitric acids converts dextrose into a nitro-compound (Carey Lea, Bl. [2] 10, 415). Dextrose phosphoric acid is said to exist (Amato, B. 4, 418). Several acetyl derivatives have been described. Dextrose discotate Callago (Callago), and dextrose triacetate

C_cH_sO_s(C_cH_sO_s)_s are amorphous, soluble in water, alcohol and ether (Schützenberger a. Naudin, Bl. [2] 12, 107, 204; Liebermann a. Hörmann, B. 11, 1619; Herzfeld, B. 13, 265). Dextrose pentacetate C_cH_sO(C_sH_sO_s)_s is prepared by the action of acetic anhydride and zinc chloride on dextrose, m.p. 111-112 (Erwig a. Koenigs, B. 22, 1464, 2207). Didextrose octoacetate C₁₂H₁₄O₂(C₂H₂O₂), is prepared by the action of acetic anhydride and sodium acetate on dextrose, m.p. 134 (Herzfeld a. Erwig a. Koenigs, l.c.). Dextrose-monochlorhydrintetracetate is formed by the action of acetyl chloride on dextrose (Culley, C. R. 70, 401). Tri-, tetra-, and penta-benzyl (C₆H₁(C₇H₅O)₅O₆) dextroses are obtained by the action of benzoic chloride and potash on dextrose (Skraup, M. 10, 389; Kueny, H. 14, 330; Panormoff, J. R. 23, 375). Compounds of dextrose with other organic acids have been prepared (Berthelot, A. Ch. [3] 54, 74; Gm.-K. 7, 764; v. Lippmann, Zuckerarten, p. 40; Baumann, B. 19, 3218; Colley, C. R. 76, 436). If dextrose is boiled with dilute sulphuric acid the specific gravity of the solution gradually increases for some time, apparently from the fixation of the elements of water. On continued boiling the solutions become coloured, brown humus substances, acetopropionic and formic acids, are produced (Malaguti, A. Ch. [2] 59, 407; Tollens a. Grote, A. 175, 181; 206, 207; Wohl, B. 23, 2084). Dilute hydrochloric acid produces similar results, but more rapidly. Gummy bodies are also produced (Grimaux a. Lefèvre, C. R. 103, 146). See also Conrad a. Guthzeit (B. 18, 439; 19, 2569) and Wehmer a. Tollens (B. 19, 707).

Action of alkalis. Alkalis give a brownish colour with dextrose solution, quickly on heating, slower in the cold, with production of acetal, acetone, and lactic, acetic, and formic acids. Other bodies of unknown composition are also formed, such as glucinic, saccharumic and japonic acids. When potash is used oxygen is absorbed. With calcium hydroxide, saccharin or calcium saccharinate is also produced; this is not one of the products of the action of potash (Emmerling a. Loge, B. 14, 1005; 16, 838; Henry, B. 14, 2272; Breuer a. Zincke, B. 13, 638; Rochleder a. Kawalier, J. pr. 94, 403; Hoppe-Seyler, B. 4, 346; Kiliani, B. 15, 700; Nencki a. Sieber, J. pr. [2] 24, 498; Péligot, A. Ch. 30, 75; Mulder, A. Ch. 36, 260; Reichardt, Z. 1870. 401; v. Lippmann, Zuckerarten, p. 22; Péligot, B. 13, 196; Scheibler, B. 13, 212; Kiliani, B. 15, 701; Cuisinier, v. Lippmann, Zuckerarten, p. 25; Scheibler, B. 16, 2434). Thénard (C. R. 52, 444) obtained bitter bodies containing 10-19 p.c. nitrogen, by acting on dextrose with ammonia; they absorb oxygen from the air, and resemble certain nitrogenous humic acids. Tanret (Bl. [2] 44, 102) obtained two volatile bases: a-glucosine C.H.N. b.p. 136° and \$-glucosine C,H10O2 b.p. 160°, by heating dextrose with strong ammonia. Heated with aniline, dextrose anilide is produced (Schiff, A. 140, 123; Sorokin, B. 19, 298).

Reduction.—Nascent hydrogen reduces dextrose in alkaline solutions to mannitol, but not in neutral or acid solutions (Linnemann, A. 128, 186; Dewar, Z. 1870. 418; Bouchardat, Bl. [2] 16, 38; Krusemann, B. 9, 1466). Under the most

favourable conditions the yield does not exceed 10 p.o. If the reduction be carried on at a high temperature other fatty alcohols are formed. Meunier (C. R. 111, 49) obtained sorbitol by reducing dextrose with sodium-amalgam.

Oxidation .- Gluconic acid C.H.,O, is produced by oxidising dextrose with mercuric oxide (Heffter, B. 22, 1049; Herzfeld, A. 245, 27) or with chlorine or bromine and subsequent treatment with silver oxide (Hlasiwetz a. Habermann, A. 155, 122; 156, 253; Kiliani, A. 205, 182; Kiliani a. Kleeman, B. 17, 1298; Herzfeld, A. 220, 335, 358), or by the action of Bacterium aceti (Brown, C. J. 1886. 179; Boutroux, C. R. 1880. 236). Oxygen has no action on dextrose in neutral or acid solutions, but it is absorbed by alkaline solutions. Ozone oxidises dextrose to saccharic and formic acids (Renard. A. C. 5, 17, 289). Platinum black acts similarly (Loew, B. 23, 865). Nitric acid oxidises dextrose to saccharic acid C_sH₁₀O_s, and finally to oxalic, formic, and carbonic acids (Liebig, A. 113, 1; Heintz, P. 51, 183; Hornemann, J. pr. 89, 304; Kiliani, A. 205, 172; Guérin-Varry, A. 8, 31; Sohst a. Tollens, Z. 11, 99). Iodine when acting on alkaline solutions of dextrose yields a little iodoform (Lieben, A. Suppl. 7, 228; Hermann a. Tollens, B. 18, 1335; Millon, C. R. 21, 828). Alkaline solutions of many metallic oxides oxidise dextrose, in some cases being reduced to the metal, in others to lower oxides. Potassium ferrocyanide, potassium permanganate, indigo, picrio acid, litmus, &c., oxidise dextrose also. The chief products are formic, oxalic, glycollic, and carbonic acids. Some of these reactions are employed for the quantitative estimation of dextrose (Tollens, B. 16, 921; Herzfeld, Zeitschr. d. Ver. d. Rüben-zucker-Ind. 37, 337; Habermann a. Hönig, B. 15, 2624; Worm-Müller a. Hagen, Pf. 22, 325; B. 13, 2096 a. 2442; Herzfeld a. Bruhns, Zeitschr. d. Ver. d. Rübenzucker-Ind. 36, 110; Reichardt, A. 127, 297; Felsko, A. 149, 856; Beyer, A. 131, 353; Claus, A. 147, 115; Smolka, B. 20, 167; M. 8, 1).

Fermentation.—Under the influence of

Fermentation.—Under the influence of various species of saccharomyces and other organisms, dextrose ferments, yielding alcohol and carbon dioxide as the chief products, glycerol, succinic acid, and small quantities of other bodies are formed at the same time. Bacteria decompose dextrose in other ways, one yielding chiefly lactic acid, another butyric, another cel-

lulose, &c. (v. FERMENTATION).

Compounds with acids (v. Action of acids). Compounds with bases. Potassium and sodium dextrose $C_bH_{11}KO_a$ and $C_bH_{11}NaO_a$ are prepared by adding potassium or sodium ethylate to a solution of dextrose in strong alcohol. A white, bulky precipitate is obtained, which is very hygroscopic, and decomposed by water (Hönig a. Rosenfeld, B. 10, 871; Franchimont. B. 10, 994). The compounds with the alkaline earths are differently constituted, being apparently a combination of the sugar and base. They are formed by mixing alcoholic solutions of the base and sugar, or by precipitating their mixed aqueous solutions with alcohol. Lime forms C₄H₁₂O₆,CaO.H₂O, C₆H₁₂O₆,CaO, 2C,H,O,BCaO.H,O, 2C.H.2O.3CaO.2H.O. 4CaH12Oa.8CaO, and similar compounds are

formed with baryta, strontia, and magnesis. Neither lead acetate nor subacetate precipitate aqueous dextrose solutions, but lead oxide yields compounds similar to those with lime &c. (Brendeche, Ar. Ph. [2] 29, 84; v. Lippmann, Zuckerarten, p. 45; Péligot, J. pr. 15, 105; Franchimont, B. 12, 1939). Alkaline dextrose solutions dissolve copper hydroxide, and from these solutions soda or potash in proper proportions precipitates compounds of copper oxide and dextrose of varying composition (Guignet, C. R. 109, 528; Worm-Müller a. Hagen, Pf. 22, 325; Fileti, B. 8, 441; Salkowski, B. 12, 704). The compound C₆H₁₂O₈·22nO.3H₁O is formed by adding an alcoholic solution of dextrose to an ammoniacal solution of zinc oxide (A. C. Chapman, C. J. 1889. 576). Dextrose forms amorphous compounds with nickel, chromium, and iron oxides (Chapman, C. J. 1891. 323).

Compounds with metallic salts. Dextrose forms well-defined crystalline compounds with sodium chloride and bromide; their formulæ are 2C₂H₁₂O₂.NaCl.H₁O, which crystallises from diabetic urine, C₂H₁₂O₃.NaCl, C₅H₁₂O₃.2NaCl, 2C₆H₁₂O₃.NaBr (Pasteur, A. Ch. [3] 31, 92; Erdmann a. Lehmann, J. pr. 13, 111; v. Lippmann, Zuckerarten, p. 45; Städeler, C. C. 1854. 930; Hönig a. Rosenfeld, B. 10, 872; Stenhouse,

A. 129, 286).

Compounds with cyanogen. By digesting an aqueous solution of dextrose with hydrocyanic acid solution, the following reaction takes place: $C_6H_{12}O_8 + HCN + 2H_2O = C_7H_{13}O_8NH$, (Kiliani, B. 19, 767). To prepare this compound Kiliani gives the following directions: 100 g. crystalline dextrose are dissolved in 30 g. water, and an equivalent quantity of 60 p.c. hydrocyanic acid is added and digested for six days at the ordinary temperature; after twenty-four hours' further digestion at 35°C. all smell of hydrocyanic acid had disappeared, and the liquid smelt of ammonia. The ammonium salt thus obtained is converted into a barium one by boiling with baryta, and the free acid obtained by removal of the barium by sulphuric acid. Fischer (A. 270, 64) dissolves 5 kilos. dextrose in 25 litres 3 p.c. hydrogen cyanide solution, adds 10 c.c. ammonia solution, and digests the solution at 25°C. for six days, boils with baryta (6.7 kilos.) dissolved in water (20 litres) until all the ammonia is expelled, the hot liquid acidified with sulphuric acid, and boiled to expel hydrogen cyanide, neutralised with baryta. and filtered. The filtrate is concentrated. This syrup contains the lactones of a-heptonic acid and B-heptonic acid. After standing some weeks nearly the whole of the a-lactone will have crystallised out; the mass is triturated with alcohol of 80 p.c.; the filtrate yields a further crop of a-lactone, and the mother-liquor contains the B-lactone. This may be obtained by neutralising with brucine; the brucine 8-heptonate crystallises out, and is purified by recrystallisation; the brucine may be separated by precipitation with baryta, and the barium salt decomposed by sulphuric acid.

a-Glucohepto-lactone forms rhombic crystals readily soluble in water, and has $\{a\}_b = -55^\circ 3$; boiled with concentrated hydriodic acid it yields a heptolactone, b.p. $216^\circ - 230^\circ$ at 717 mm., with partial decomposition. About an equal quantity

of rormal heptoic acid is also produced (Kiliani, B. 19, 1128). By digestion with nitric acid S.G. 1·2 at 40° for 24 hours, a-glucoheptoic acid is oxidised to normal penta-oxy-pimelic acid (Kiliani, B. 19, 1916); this melts at 143°, is easily soluble in water, difficultly in alcohol, and soluble in ether. a-Gluco-heptonic acid yields a hydrazide C.H₁₁O,N₂H₂O₆H, m.p. 171°-179° (Fischer, B. 22, 2732).

β-Gluco-heptonic lactone crystallises in delicate needles, m.p. 151°-152°, reduces Fehling's solution, and is very soluble in water; its sp. rot. power is [α]₁₀₀° = -67·7°. Its phenylhydrazide C,H₁₃O,N,H₂Ph crystallises from alcohol in yellowish leaflets, and melts at 150°-152°. Heated with pyridine (4 lactone, 4 pyridine, and 20 water) in a sealed tube for three hours it is

converted into the a- acid.

Hydrazine compounds. A concentrated solution of dextrose yields, with phenylhydrazine, dextrose phenylhydrazine C₁₂H₁₈N₂O₅; this forms fine crystals, melting at 144°-145°. When heated with an aqueous solution of phenylhydrazine, hydrochloride, and sodium acetate on the waterbath, yellow crystals of phenylglucosazone $C_{18}H_{22}N_1O_4$ are formed (Fischer, B. 20, 824). Phenylglucosazone can be prepared by heating on the water bath 1 pt. dextrose, 2 pts. phenylhydrazine hydrochloride, 3 pts. sodium acetate, and 20 pts. water; after 10-15 minutes' heating the separation of osazone commences, and after $1\frac{1}{3}$ hours the precipitate amounts to about 85-90 p.c. of the weight of dextrose taken. It is purified by recrystallisation from alcohol. Another method which gives satisfactory results is to heat a mixture containing 1 g. sugar in 100 c.c. water and 5 c.c. of a solution containing in 1 litre 400 g. phenylhydrazine and 400 g. glacial acetic acid. According to Maquenne's (C. R. 112, 799) numbers, the yield is low, but by increasing the strength of the sugar solution and keeping up the quantity of the phenylhydrazine acetate solution in proportion, it is materially increased. It is insoluble in water; not very soluble in cold, but fairly easily in boiling alcohol. It melts at 204°-205° with decomposition, and so in m.p. determinations it is important that the heating be done as quickly as possible. It reduces Fehling's solution, and is leworotatory (Fischer, B. 17, 579). It dissolves in cold fuming hydrochloric acid, with a dark-red colouration, the osazone group O.H., HN.; C:C:N., HC. H., being thereby converted into the group .CO.CO. This reaction is common to all the osazones of the sugars, and Fischer (B. 21, 2631) has called the compounds thus obtained -osones. Dextrosone reduces Fehling's solution on boiling, and does not ferment with yeast; with phenylhydrazine acetate it again yields phenylglucosazone. The osazone is reduced by zinc and acetic acid to iso-glucosamine, which yields lævulose by treatment with nitrous acid (Fischer, B. 19, 1920; 20, 2569). The osone yields compounds with methyl phenylhydrazine and ortho-diamines (Fischer, B. 22, 87). By proceeding in the same way o-tolyldettrosazone C₂₂H₂₅N₁O, m.p. 201° and p-tolyl-dextrosazone C₂₂H₂₂N₁O, have been prepared (Raschen, A. 239, 229). Diphenyl-hydrazine combines with the sugars in alcohol solution; sparingly soluble crystalline hydrazones are

formed, which are resolved into their constituents by concentrated hydrochloric acid. The dextrose compound $C_aH_{12}O_sN_a(C_aH_a)_2$ melts at 161° (Stahel, A. 258, 242). Roder (A. 236, 229) has prepared phenyldextrosazone carboxylic acid.

Compounds with aromatic amines. trose - o - diamido - benzene C_sH₁(NH)₂.C_sH₁₀O₅ and anhydro - dextrose - o - diamido - benzene $C_{\mu}H_{\mu}N_{\sigma}C_{\mu}H_{\mu\sigma}O_{\mu} + 2H_{\mu}O$ are formed by the interaction of dextrose and o-phenylene-diamine in acid solution. Di-dextrose-o-diamido-benzene is obtained when the reaction takes place in neutral solution. They are all crystalline bodies, soluble in water, and having a bitter taste. The first one does not reduce Fehling's solution, the last two do (Griess a. Harrow, B. 20, 281 and 2205); o-tolylene-diamine gives a similar compound (Hinsberg, B. 20, 495). Dextrose-ydiamido-benzoic acid is obtained by mixing boiling aqueous solutions of dextrose and γ-diamidobenzoic acid (Griess a. Harrow, l.c.). aniline dextrose forms a crystalline anilide m.p. 147° (Schiff, A. 154, 30; Sorokin, B. 19, 513; J. R. 1887, 377). Dextrose forms compounds with aldehyde, acetone, benzaldehyde, chloral, &c. (Schiff, A. 244, 19; Heffter, B. 22, 1050).

Dextrose-oxim $C_6H_{13}O_6N$ is formed by the combination of dextrose and hydroxylamine. It forms colourless, microscopic crystals, m.p. $136^\circ-137^\circ$; very soluble in water, sparingly soluble in alcohol, and insoluble in ether. It reduces Fehling, and is levorotatory, having $[a]_{1000} = -2 \cdot 2^\circ$ (Jacobi. 24, 696).

[a]_{Dmo} = $-2\cdot2^\circ$ (Jacobi, B. 24, 696).

On warming an alkaline solution of dextrose with pieric acid a blood-red colour is produced (Braun, Fr. 4, 185). It to crystallised diazobenzene suiphonic acid be added soda, dextrose solution, and a little sodium-amalgam, a red colouration is produced in a short time (Penzold a. Fischer, B. 16, 657).

Many aromatic alcohols give a colouration with dextrose and other carbohydrates in the presence of sulphuric acid. If two drops of a 15-20 p.c. alcoholic solution of (a) naphthol be added to a dextrose solution, and one part of concentrated sulphuric acid, a violet colouration will be produced, changing to bluish violet.

Optical isomerides of glucose, gluconic acid and saccharic acid (E. Fischer, B. 23, 2611).

I-Gluconic acid. I-Mannonic acid can be converted into l-gluconic acid by heating with quinoline, but it is most conveniently prepared from arabinose by treatment with hydrogen cyanide and baryta (Kiliani, B. 19, 3029); I-mannonic and l-gluconic acids are formed simultaneously. The greater portion of the I-mannonic acid may be separated as lactone, and the remainder may be separated from the I-gluconic acid by crystallising out the calcium I-gluconate.

i-Gluconic acid is obtained by mixing the l- and d- acids, or from i-mannonic acid by quinoline.

l-Glucose is formed by reducing l-gluconic lactone with sodium-amalgam; it resembles dextrose closely, but does not ferment with yeas; $[a]_{\rm b} = -51.4^{\circ}$; its derivatives also resemble the corresponding ones of dextrose very closely.

i-Glucose is prepared by mixing i- and d-glucose or reducing i-gluconic acid.

I-Secenaric acid is prepared by exidising I-gluconic acid with nitric acid.

i-Saccharic acid is prepared by oxidising i-gluconic acid or by mixing l- and d- saccharic acid.

Lævulose. d-Fructose, lævoglucose, fruit sugar; $C_aH_{12}O_a$.

Occurrence.—Lævulose is widely distributed in the vegetable kingdom, being found, together with dextrose, in many parts of plants, in honey, &c. (v. Dextrose).

&c. (v. Dextrose).
Formation.—The following carbohydrates
yield levulose, either alone or accompanied by
other sugars, when acted on by dilute acids:

Cane sugar yields dextrose and lævulose. Raffinose yields lævulose, galactose, and dextrose.

Inulin yields lævulose.

Irisin (O. Wallach, A. 234, 364), lævulan (v. Lippmann, B. 14, 1509), triticin (Reidemeister, C. C. 1880, 808), scillin (Riche a. Remont, J. Ph. [5] 2, 291), sinistrin (Schmiedeberg, B. 12, 704), lævulin or synanthrose (Dieck a. Tollens, A. 198, 228; Ville a. Joulie, Bl. [2] 7, 262; Popp, A. 156, 185; Müntz, C. R. 227, 679), and inuloid (Popp, A. 156, 190) also yield lævulose. Lævulose is formed by the oxidation of mannitol (Cotton, Bl. [2] 33, 546; Gorup-Besanez, A. 118, 273; Bodenbender, Zeit. d. Ver. 14, 812; Renard, A. Ch. [5] 17, 316), by the fermentation of mannitol by B. aceti and B. xylinum (A. J. Brown, C. J. 1886, 184; 1887, 641); from phenylglucosazone by reduction to isoglucosamine, and thegee by the action of sodium nitrite; from glucosone by reduction with zinc and acetic acid (Fischer, B. 22, 87, 2566).

Preparation.-Inulin is heated with very weak sulphuric acid for some hours, after which the sulphuric acid is carefully precipitated by baryta water and the filtrate decolourised by charcoal and evaporated on the water bath to a This is treated several times with absolute alcohol, which removes the water, and the syrup which remains put on one side for some time in a closed flask, when fine needles make their appearance, and in time the whole solidifies (Jungfleisch a. Lefranc, C. R. 93, 547; also Crookewitt, A. 45, 184; Krusemann, A. 282, 26; Wohl, B. 23, 2084). A 10 p.c. solution of cane sugar is carefully inverted with hydrochloric scid (20 c.c. to a litre of solution) at 60°. The solution is cooled to -5° , 6 g. of slaked lime added for each 10 g. sugar, the temperature allowed to rise to 2°, and the line lavulose carefully pressed from the rest of the solution and washed repeatedly with water. It is finally suspended in water, decomposed by oxalic acid, and the filtered solution evaporated in vacuo to a syrup which, when treated with absolute alcohol as above described, yields crystals of lævulose (Girard, Bl. [2] 33, 154; Dubrunfaut, C. R. 42, 901; 69, 438).

Formula and synthesis. See general part. Properties.—Lævulose forms colourless, fine, shining needles, belonging to the rhombic system, the axial ratio is a:b:c=0.80067:1:0.90674; they are slightly biaxial as regards their action on polarised light; they have a composition corresponding to the formula C_sH₁₂O_s, melt at 95°, and lose water at 100°. According to Hönig a. Jesser (M. 9, 562), the crystals con-

tain water of crystallisation and have a formula 2C,H12O,H2O. If free from alcohol they are not deliquescent in the air (Hönig a. Schubert, M. 8, 529; Jungfleisch a. Lefranc, l.c.). The sugar is almost insoluble in cold absolute alcohol. and soluble in a boiling mixture of alcohol and ether (Diech a. Tollens, A. 198, 228). With regard to the specific rotatory power of levulose there are many and varied statements; all those based on the factors of unpurified solutions obtained by the inversion of inulin or cane sugar are worthless, as lævulose is extremely easily decomposed by acids (Jungfleisch a. Grimbert, C. R. 108, 144), and many apparent discre-pancies may be explained by the fact that the optical activity varies very much with the temperature. Jungsleisch a. Grimbert (C. R. 107, 390) found for crystallised lævulose $[a]_D = -101.38^{\circ} - 0.56t + 0.108 (p-10)$, where t is the temperature and p the weight of levulose This formula holds for in 100 c.c. solution. temperature 0°-40° and for concentrations betemperature 0'-40° and for concentrations below 40 p.c. The $[a]_j = -108^\circ$ (c=10 g. sugar in 100 c.c.), calculated from $[a]_j = -24.5$ for invert sugars, and $[a]_j = +58.5$ for dextrose agree very well with the numbers of Jungfleisch a. Grimbert. Hönig a. Jesser (M. 9, 562) give $[\alpha]_1 = -111.38$, c 10, $t = 20^\circ$ for a carefully crystallised preparation. Herzfeld a. Winter (B. 19, 390) give for 20 p.c. solution at 20° [a]_D = -71.4° ; but these determinations cannot be for the pure body. Freshly-prepared solutions of crystallised lævulose have a greater sp. rot. power than after standing a short time; Parcus a. Tollens (A. 257, 160) found for a 10 p.c. solution at 20° observed in a 200 mm. tube, $[a]_p = -104.02^\circ$ six minutes after commencing solution, which sank to a constant value $[a]_D = -92.25^{\circ}$ in 35 minutes. This cannot have been pure lævulose. K = 100; but Soxhlet makes it 92-93 (J. O'Sullivan, C. J. 1892, 408).

Action of heat and acids. Lævulose is exceedingly easily decomposed by heat and acids. Its aqueous solutions colour exceedingly quickly if heated for any length of time. Wohl (B. 23, 2084) found that by the action of minute quantities of acid on a hot concentrated solution of lævulose, a dextrin-like body was produced which was reconverted into levulose by boiling with dilute acids. This instability accounts for the many different numbers which have been given for the sp. rot. power and for the fact that the opt. act. of invert sugar does not in all cases correspond with that of a mixture of pure lævulose and dextrose in equal quantities. On boiling with dilute sulphuric or hydrochloric acids, acetopropionic, formic, and other acids are produced Jungfleisch a. Grimbert, C. R. 108, 144; Grote a. Tollens, A. 175, 181; Sieben, Zeitschr. d.

Ver. 34, 237; Conrad a. Guthzeit, B. 19, 2569).

Action of alkalis. Alkalis quickly decompose lavulose, especially on warming; caustic sods and baryta yield lactic acid among other products (Sorokin, J. R. 1885, 368). Sodium lavulose C.H., NaO. is produced by acting on an alcoholic solution of lavulose with sodium ethylate (Hönig a. Rosenfeld, B. 12, 45). Lime yields a compound C.H.,O.,CaO.H.,O., which is soluble in 137 parts cold water (E. Péligot, C. R. 90, 153; Herzfeld a. Winter, B. 19, 390); and 2(C.H.,O.)3CaO, which torms needles soly.

ble in 338 parts cold water (Dubrunfaut, A. Ch. [8] 21, 169). Similar compounds are formed with potash, baryta, lead oxide, and bismuth oxide (Herzfeld a. Winter, B. 9, 890, and v. Lippmann, Zuckerarten, p. 68). If a solution of levulose be boiled with lime, saccharin is formed (Scheibler, B. 13, 2212).

Reduction.—Lævulose in alkaline solution is reduced by nascent hydrogen to mannitol, and more easily than dextrose (Scheibler, B. 16, 8010; H. Krusemann, B. 9, 1465; Herzfeld, A. 244, 274). Fischer (B. 23, 3634) finds that equal parts of mannitol and sorbitol are produced.

Oxidation .- Mercuric oxide and baryta boiled with an aqueous solution of levulose yield formic, glycollic and normal trioxybutyric acid (Börnstein a. Herzfeld, B. 18, 3353). Bromine water in the same way yields normal trioxybutyric acid (Hönig, B. 19, 171; Herzfeld a. Winter, B. 19, 390; C. C. 1886, 271). Lævulose by oxidation always yields an acid containing less carbon atoms than itself (Herzfeld a. Börnstein, C. C. 1886, 187; Herzfeld a. Winter, C. C. 1886, 271; B. 19, 390). Chlorine and bromine with silver oxide oxidise lævulose to glycollic acid (Hlasiwetz a. Habermann, A. 155, 130; Kiliani, A. 205, 175). Nitric acid yields oxalic acid, tartaric acid, glycollic acid, formic acid, a little saccharic acid, malic acid, acetic acid, and racemic acid (Dragendorf, Materialien zu einer Monographie des Inulins; Kiliani, A. 205, 162; Hornemann, J. pr. 89, 283).

Fermentation.-Lavulose ferments easily with yeast, with formation of alcohol and carbonic acid &c., but rather slower than dextrose, so that towards the end of a fermentation of invert sugar the solution is always levorotatory (Bourquelot, A. Ch. [6] 9, 245; C. R. 101, 958; C. R. 100, 1404 and 1466; Maumeno, C. R. 100, 1505; 101, 695; Leplay, C. R. 101, 479; Gourgon a. Dubourg, C. R. 110, 865).

Compounds with acids. Chlorosulphonic acid gives a tetra-sulphate (Claesson, J. pr. [2] 20, 1 a. 18). Acetyl chlorido yields an aceto-chlorhydrin (Colley a. Wachowitsch, B. 13, 2390; Bl. [2] 34, 326). With acetic anhydride, acetic acid, and zinc chloride levulose yields pentacetyl levulose (Erwig a. Koenigs, B. 23, 672). Benzoyl chloride yields pentabenzoyl lævulose, m.p. 85° (Skraup, M. 10, 389).

Compounds with bases. See Action of alkalis above.

Compounds with metallic salts. Compounds with potassium or sodium chloride have not been described. A compound with lead chloride is known (Herzfeld a. Winter, B. 19, 390).

Compounds with cyanogen. By treatment with strong hydrocyanic acid, lævulose yields a cyanhydrin $C_1H_{13}O_4N$, this crystallises from water in tabular monoclinic crystals, m.p. 110°-115°, and has a slight dextrorotatory power; fuming hydrochloric acid converts it into the lactone of fructoheptonic acid C,H12O,, and this, heated with hydriodic acid and phosphorus, yields a heptolactone $C_1H_{12}O_2$, b.p. 220°, which does not solidify in a freezing mixture. When the lactone is further treated with hydriodic acid and phosphorus an acid is obtained boiling at 210°. which is identical with methyl-butyl-acetic acid as synthetically prepared (Kiliani, B. 18, Vol. IV. 8966; 19, 221 and 1914; Kiliani a. Düll, B. 23, 449). Tetra-oxy-butane-tri-carboxylic acid COOH.(CH.OH), C(OH)(COOH); is obtained by oxidising fructoheptonic acid by nitric acid (Düll, B. 24, 348).

Hydrazine compounds. Lævulose yields an esazone which appears to be identical with, and is prepared in the same manner as, dextrose

osazone (q.v.).

Anilides. By heating an aqueous solution of lavulose with aniline, an anilide is formed nelt at 147° with partial decomposition (Sorokin, B. 19, 513; J. R. 1886, 129; 1887, 877). With hydroxylamine lavulose combines to form lævulosoxim (Wohl, B. 24, 993). It strongly resembles dextrosoxim in appearance, m.p. 1180 it is levorotatory, and reduces ammoniacal silver solutions on warming, whilst dextrosoxim does so in the cold.

Galactose. Lactose. CaHiaOa. does not occur in nature.

Formation.—By the action of dilute acids on many carbohydrates and similar substances of vegetable and animal origin. Lactose yields dextrose and galactose (Pasteur, C. R. 42, 347; Fudakowski, B. 9, 42; C. C. 1877, 6). Raffinose yields levulose, galactose, and dextrose. a-Galactin, B-galactin, paragalactin, lactosin, agar-agar, carragheen moss, plum gum, peach gum, gum arabic, gedda gum, and many other similar vegetable substances, yield galactose amongst other products of their hydrolysis (Müntz, Bl. [2] 37, 409; A. Ch. [6] 10, 566; C. R. 94, 453; 102, 624, 681; A. Meyer, B. 17, 690; Bauer, J. pr. [2] 30, 375; L. V. 1888, 33 a. 214; Hädicke, Bauer a. Tollens, A. 238, 302; Kiliani, B. 13, 2304; 15, 36; v. Lippmann, B. 17, 2238; Scheibler, B. 1, 58; 6, 612; 17, 1729; O'Sullivan, C. J. 1884, 41; 1391, 1029; Hädicke a. Tollens, A. 238, 308; Schulze a. Steiger, B. 19, 827;
20, 290; L. V. 36, 391; Schulze, B. 25, 2213;
Maxwell, Am. C. J. 12, 51 a. 265; v. Lippmann, Deutsche Zuckerind., 1887, 455; B. 20, 1001; Stone, Am. 12, 435). Galactose is also produced by the long-continued action of dilute sulphuric acid on certain nitrogenised constituents of the brain (Thudichum, Ann. of Chem. Med. [2] 209: Thierfelder, Z. P. C. 14, 209; Brown a. Morris, C. J. 1890, 57). This sugar was called by the discoverer cerebrose; B. a. M. proved it to be galactose.

Preparation .- A solution of lactose (milksugar) containing in every 100 c.c. 25 g. dry lactose; 2 to 3 grams H.SO, is digested in a flask on the water-bath for 25 to 3 hours, the water being kept boiling all the time and care being taken by continual shaking of the flask to avoid colouring. The acid is, on cooling the solution, carefully neutralised with baryta water and the BaSO, separated by filtration. On evaporating the filtrate to a strong syrup in a vacuum solidification takes place in a short time. The solid crystallised mass is digested several times with dry methyl alcohol; this dissolves out the dextrose and other products of the action of the acid on lactose and the hydrolysed sugars, and leaves galactose as a white crystalline powder. This is dissolved in the least possible quantity of boiling water, again allowed to solidify, and again treated with boiling methyl alcohol. If

the whole of the lactose hydrolysed, and it ! generally is under the conditions indicated, the residue is white, nearly pure, galactose. It can be rendered pure by recrystallisation from water. If the crystals are allowed to form slowly from solutions not too concentrated they are distinct and well-defined (Rendell, N. Z. 4, 163; Soxhlet, J. pr. 2, 21, 269). The sugar can also be prepared from certain gums of the arabin group. For this purpose the most suitable are those having a lavorotatory power and yielding the larger percentage of mucic acid on oxidation with nitric acid. The dextro-gums also yield the sugar, but in less quantity (O'Sullivan. C. J. 1884, 41; 1891, 1029). A solution of the gum selected—gum arabic, Turkey, Levantine or East India gum - is made containing about equal weights of water and gum; this is heated in a flask in a water-bath as high as the boiling bath will take it, and 5 grams H,SO, diluted to 15 c.c. added for every 100 c.c. of the gum solution employed. The mixture is digested for 30 to 35 minutes, then rapidly cooled, and alcohol, S. G. 0.83, added as long as a pp. is produced. This pp. is again dissolved in water, and again ppd. One or two fepetitions of this process frees the pp. from arabinose. A solution of the same strength as that above described for the original gum is then made of the pp. and heated as high as the boiling water of a water-bath will take it, and then for every 100 c.c. of the solution 5 grams H,SO, diluted to 15 c.c. added. At the end of about 8 hours' digestion the solution is cooled, carefully neutralised with baryta water, and alcohol, 0.82, added as long as a pp. is thrown out. The alcoholic solution becomes clear on standing; it contains galactose, and on concentration in a vacuum yields crystals of the body in a fairly pure state. They may be completely purified by washing with methyl alcohol, recrystallising the residue from ethyl alcohol, and finally from water.

Formula and synthesis. See general part.

Properties.—Galactose crystallises in hexagonal plates, m.p. $163^\circ-164^\circ$ (after drying at 100°) (E. Bourquelot, J. Ph. [5] 13, 51), or, according to v. Lippmann (B. 18, 3335), in microscopic six-cornered prisms and needles, m.p. 168° . Galactose is easily soluble in water, almost insoluble in methyl alcohol. Solutions of galactose rotate a ray of polarised light to the right, the specific rotatory power for the D line being given by the formula $[a]_{\mathbf{p}} = 83^\circ-883 + 0^\circ-0785P - 0^\circ-209^\circ$ (Meissl, J. pr. [2] 22, 97); this formula agrees well with numbers found by other observers. Freshly-prepared solutions exhibit the phenomenon of bi-rotation (Pasteur, J. pr. 68, 428). Parcus a. Tollens (A. 257, 160) observed an angle of $[a]_{\mathbf{p}} = 117^\circ-48^\circ$ in a 10 p.c. solution at 20° , 7 minutes after commencing solution. K=100, and varies slightly with the conditions of determination.

Action of acids. By prolonged heating with dilute acids, galactose yields aceto-propionic and formic acids (Kent a. Tollens, A. 227, 228; B. 17, 668; Conrad a. Guthzeit, B. 18, 2905; sulphuric acid and chloro-sulphuric acid yield galactose-sulphuric acids (Hönig a. Schubert, M. 7, 455; Classon, J. m. 21, 20 a, 180.

M. 7, 455; Claësson, J. pr. [2] 20 a. 18).

Action of alkalis. Alkalis colour galactose yellow; the action of milk of lime produces saccharin (Cuisinier, v. Lippmann, Zuckerarten).

Fusion with KHO gives rise to acetic and exalic acids.

Reduction. — By reduction with sodiumamalgam, galactose yields dulcitol and other alcohols (Bouchardat, A. Ch. [4] 27, 79).

Oxidation.—Bromine oxidises galactose to galactonic acid (lactonic acid) C₆H₁₂O₇, isomeric with gluconic acid (Hlasiwetz a. Habermann, A. 122, 96; Kiliani, B. 13, 2307; 18, 1551; Bauer, J. pr. [2] 30, 379); which when heated loses 1 mol. water, and is converted into the lactone; it yields with phenylhydrazine a hydrazide which melts at 200°-205° with decomposition (Fischer a. Passmore, B. 22, 2731). Nitric acid oxidises galactose to mucic acid, isomeric with saccharic acid. As mucic acid is only slightly soluble in water, the yield of mucic acid, which is normally 75 to 78 p.c., is sometimes made use of for the estimation of galactose; but the yield varies considerably with the condition of experiment (Pasteur, C. R. 42, 349; Kent a. Tollens, A. Ch. 227, 228). Neutral or alkaline solutions of cupric hydroxide are reduced by galactose; carbonic, formic, glycollic, and lactic acids are produced (Habermann a. Hönig, M. 5, 208).

Fermentation.—According to Kiliani (B. 13, 2305) and Koch (B. 20, Ref. 145), galactose does not ferment with yeast, whilst v. Lippmann (B. 17, 2238; 20, 1001), Bourquelot (C. R. 106, 283), and Pasteur find that it does ferment. Stone a. Tollens (A. 249, 257; B. 21, 1572) find that it ferments with beer yeast as well as with Mucor racemosus, but slower than dextrose. Certain bacteria yield lactic acid (Pranzmovaski a. v.

Tieghem, B. 12, 2087).

Compounds.—Galactose yields a crystalline compound with sodium chloride (Fudakowsky, Bl. [2] 30, 433). With a solution of baryta in methyl alcohol, galactose yields the compound $(C_eH_{11}O_e)_e$ Ba. BaO (Fudakowsky, l.c.). With acetic anhydride, a pentacetate is produced C_sH₂O(C_sH₃O_s), m.p. 62°-66° (Fudakowsky). According to Erwig a. Koenigs (B. 22, 2207) this body melts at 142°, crystallises in rhombic prisms, reduces Fehling's solution, is dextrorotatory, and differs in all its properties from Fudakowsky's galactose pentacetate. With aniline, galactose forms an anilide, crystallising in long triclinic prisms, and levorotatory (Sorokin, J. R. 1887, 377; B. 19, 298). With hydroxylamine, galactose yields the oxim C₆H₁₂NO₆, the crystals melt at 175°-176°, and are easily soluble in water and weak alcohol (Rischbieth, B. 20, 2673). With ortho-diamido-benzene, galactose yields galactose-o-diamido-benzene C_eH₄(NH)₂·C_eH₁₀O₃, melting at 246° with decomposition. Galactose-y-diamido-benzoic POSITION. GREACIOSE-7-Hammo-serizoro Local COOH.C₀H₃(NH)₂·C₀H₁₀O₃+H₂O crystallises in needles (Griess a. Harrow, B. 20, 3111). With hydrocyanic acid, galactose yields galactohep-tonamide C,H₁₈NO,, m.p. 194°; it is converted into the barium salt of galactoheptonic acid C,H,O, by digesting with baryta. The free acid melts at 145° and orystallises in slender needles; it is reduced by hydriodic acid and phosphorus to the lactone of Lormal γ-oxyheptoic acid (b.p. 231°) and a very small quantity of normal heptoic acid (Maquenne, C. R. 106, 286; Kiliani, B. 21, 915; 22, 521 a. 1385). With phenylhydrazine, galactose forms galactose-phenylhydrazide, crystallising in colourless

needles, m.p. 158°, and galactose-osazone, m.p. 198°-194° (Fischer, B. 20, 821). Fischer's first determination of the melting-point (B. 17, 579) was 182°, Scheibler (B. 17, 1731) gave 171°, and other observers have given lower numbers; this may be accounted for by the fact that unless the osazone be heated up very quickly it decom-poses before it fuses. By the action of hydrochloric acid it yields galactose-osone (Fischer, B. 22, 87). Galactose also yields a diphenylhydrazide, m.p. 157° (Stahel, A. 258, 212). Galactose forms a penta-benzoate C.H.O(C.H.O.)

Suppose the supplier of

m.p. 165° (Skraup, M. 10, 389).

Sorbose. Sorbinose C₈H₁₂O₆. Sorbose is obtained from the juice of the mountain ash after allowing it to stand for some time. It is doubtful if it exists in the fresh juice as a free sugar, but it is probably formed by the decomposition of a glucoside (Pelouze, A. Ch. [3] 35, 222; Boussingault, C. R. 74, 939; Delffs, B. 4, 799; Byschl, J. pr. 62, 504; Freund, M. 11, 560). The expressed juice of the unripe berries of the mountain ash is allowed to ferment for eight or ten months, the clear solution is filtered from the organisms by which the fermentation was effected, and evaporated to a syrup, when the scrbose crystallises out on standing. It forms colourless rhombic crystals easily soluble in water. Its solutions are laworotatory: for 10 p.c. solution, $[\alpha]_D = -43.4^{\circ}$ (Wehmer a. Tollens, B. 19, 708). It is oxidised by chlorine and silver oxide to glycollic acid; it behaves with bromine water like lavulose, being practically unaltered (Kiliani a. Scheibler, B. 21, 3276); nitric acid oxidises it to oxalic, aposorbic and tartaric acids. By more careful oxidation with HNO. Kiliani a. Scheibler (l.c.) obtained trioxy-glutaric acid. Copper hydrate oxidises it to carbonic and formic acids and other bodies, amongst which is possibly glyceric acid (Dessaignes, J. pr. 89, 313; Hlasiwetz a. Habermann, A. 155, 129; Habermann a. Hönig, M. 5, 208). Hydriodic acid reduces it to hexyl iodide (Kiliani a. Scheibler, l.c.). It reduces Fehling's solution, and is coloured yellow by alkalis. Sorbose ferments slowly with beer yeast (Stone a. Tollens, A. 249, 257). By prolonged heating with dilute acids it is decomposed, yielding, amongst other bodies, lævulinic acid (Wehmer a. Tollens, l.c.). With phenyl-hydrazine it yields an osazone $C_{18}H_{22}N_4O_4$, m.p. 164° , which is almost insol in water, but fairly easily soluble in alcohol, from which it crystallises in fine microscopic needles (Fischer a. Tafel, B. 19, 1920; 20, 217 and 2566; Fischer, B. 20, 828).

Mannose. Seminose C.H 12O. This sugar

does not occur free in nature.

Formation .- It is obtained by the action of dilute sulphuric acid on the so-called reserve cellulose (Reiss, B. 22,609, 3218) and on salep juice (Tollens a. Gans, A. 249, 256), and by the oxidation of mannitol (Fischer a. Hirschberger, B. 21, 1805; 22, 1155 a. 3218; Carlet, J. 1860. 250; Gorup-Besanez, A.118, 257; Dafert, B. 17,

227).

Preparation. — Sifted ivory nut shavings (1 pt.) are digested with 6 p.c. hydrochloric acid (2 pts.) for six hours on the water-bath, filtered hot, and the residue pressed and extracted with water. The brown solution contains the sugar. It may be obtained as hydraside by adding phenyl-hydrazine acetate, and this is decomposed by hydrochloric acid with reproduction of the sugar (Fischer a. Hirschberger, B. 22, 365 a. 3218).

Properties.—Mannose is precipitated from its alcoholic solution by ether; the syrup, on keeping under absolute alcohol, solidifies to a hard colourless mass which shows no sign of crystalline structure. Its solutions are dextrorotatory, $[\alpha]_D = 13.0^{\circ}$ approx.; they are reduced by Fehling's solution, 1 c.c. of this solution being reduced by 4.307 mgm. mannose, i.e. K = 110°-112°. It is fermented by yeast.

Reduction .- Mannose is reduced by sodiam-

amalgam to mannitol.

Oxidation.- Mannose is oxidised by bromine to mannonic acid, the lactone of which (CaH10Os) crystallises in colourless needles, readily soluble in water and less in alcohol; it is dextrorotatory in aqueous solutions, $[a]_D = 53.8^\circ$, and forms a phenylhydrazide $C_{12}H_{18}N_2O_8$, m.p. 214° _ 216°. Its optical isomeride, l-mannonic acid, is obtained by the nitrile reaction from arabinose. Oxidised with nitric acid, manno-saccharic acid is obtained (Easterfield, C. J. 1891, 306; Fischer, B. 24, 539). It crystallises in colourless needles. m.p. 180° - 190° , and $[\alpha]_{p} = 201.8^{\circ}$. With ammonia it yields a monamide, and with phenylhydrazine a mono- and di-phenylhydrazide. Kiliani's metasuccharic acid is its optical isomeride (1-mannosaccharic acid) (Fischer, l.c.).

Action of acids. Hot hydrochloric acid has little action on mannose, but if the heating be continued for some time, humus substances are

formed.

Action of alkalis. Alcoholic potash precipitates a flocculent hygroscopic substance

from solutions of the sugar.

Compounds. - Lead acetate and ammonia produce a precipitate which becomes yellow on keeping. With phenylhydrazine it yields a sparingly soluble hydrazide, C₁₂H₁₈N₂O₃, crystallising in yellow slender prisms, m.p. 195°–200°, le vorotatory in dilute hydrochloric acid solution. By heating the hydrazide with excess of phenylhydrazine hydrochloride, sodium acetate, and water, it yields an osazone C18H22N,O4 crystallising in yellow needles, which is identical with phenylglucosazone. With di-phenyl-hydrazine it yields a di-phenyl hydrazide, m.p. 155°. With hydrocyanic acid it yields a compound which is easily decomposed, yielding mannose-heptonic acid; its lactone C.H.O. crystallises in needles, m.p. 148°-150°; by reduction with hydriodic acid normal heptoic acid is obtained. With hydroxylamine mannose yields an oxim C_eH₁₃O_eN, m.p. 184° (Reiss, *l.c.*; Fischer a. Hirschberger, B. 22, 1155). Aceto-chloro-mannose is obtained by the action of acetyl chloride (Fischer, l.c.).

Phlorose C_aH₁₂O_a. This has been shown to be identical with dextrose (Rennie, C. J. 887,

636; Fischer, B. 21, 988).

Crocose C₆H₁₂O₈. Kayser (B. 17, 2232) a. Rochleder a. Mayer (J. pr. 74, 1) obtained a dextrorotatory sugar by heating saffron (from Crocus electus or yellow shoots of Gardenia grandiflora) with dilute sulphuric acid. It forms rhombic crystals, which only reduce half as much copper oxide as dextrose. According to Fischer (B. 21, 988), it yields, with phenylhydrazine, an osazone identical with phenyl glucosazone,

Lokaose C.H. O. is obtained from lokao or Chinese green by boiling with dilute sulphuric acid, lokaonic acid yielding lokanic acid and lokaose $C_{42}H_{48}O_{27} = C_{38}H_{36}O_{21} + C_6H_{12}O_6$. Lokaose forms minute acicular crystals, and is distinguished from dextrose by being optically in-active and having a lower reducing power (K=50) (R. Kayser, B. 18, 3417).

Tabakose is said to exist in tobacco (Att-

field, Ph. 541).

Digitalose C.H., O, is obtained, together with dextrin, by the action of strong hydrochloric acid on digitalin; oxidised with bromine it yields digitalonic lactone C,H,O,; hence the formula of the sugar (Kiliani, Ar. Ph. 230, 250;

B. 25, 2116),

Aromatic sugar. Phenyltetrose (Fischer a. Stewart, B. 25, 2555). Cinnamaldehyde cyanhydrin, when dissolved in chloroform and bromine added, yields phenyl-dibromo-oxy-butyronitril CHPhBr.CHBr.CH(OH)CN; this when heated with hydrochloric acid yields phenylbromodioxybutyrolactone

CHPh CH, Br CH.OH, from which the acid CHPh.CHBr.CH(OH).COOH is easily obtained; on reduction this yields phenyltetrose OH.CHPh.CH(OH),CH(OH),COH. It yields a

phenylhydrazide, m.p. 154°. For Acrose, Formose, Glycerose, see Synthesis

of the Sugars.

CLASS II. The '-on' sugars.

(a) Dipentose. Arabinon, diarabinose, or arabinbiose C₁₀H₁₈O₉. A product of the partial hydrolysis of a series of gum acids. A 25 p.c. solution of any of the strongly rotating gum acids is heated to boiling, and 2 g. sulphuric acid for every 100 c.c. solution, previously diluted with 4 to 5 volumes water, added. At the end of 10 to 15 minutes' digestion the solution is quickly cooled and alcohol, sp.gr. '830, added as long as a precipitate forms. The clear alcoholic solution contains arabinon and arabinose, and some arabinon is taken down with the precipitate; and on again dissolving it in a little water and reprecipitating with alcohol, the arabinon often appears on the surface of the syrup in spherocrystals, and the alcoholic supernatant liquid contains it in quantity. It is easily soluble in water and methyl alcohol. Dilute ethyl alcohol also dissolves it, but absolute alcohol precipitates it as a syrup from a strong methyl alcohol solution. Ether also precipitates it. Its solutions are dextrorotatory, $[a]_D = +202^\circ$ (c. 6.466), there appears to be an increase with the concentration; it reduces Fehling's solution; K = 58 (K = 57.5 if2 mols. sugar reduce 9 mols. CuO). D=3.95. It tastes sweet, and is easily diffusible. acids hydrolyse it, the sole product being arabinose,

 $\mathbf{C_{10}H_{18}O_9 + H_2O} = 2\mathbf{C_5H_{10}O_8}$ Arabinon Arabinose

(O'Sullivan, C. J. 1890, 59).

(b) Dihexoses.

Cane sugar. Saccharon, sucrose C₁₂H₂₂O₁₁.
Occurrence. — Cane sugar is widely distributed throughout the vegetable kingdom, and is frequently accompanied by dextrose and lævulose. The most important sources are the sugar-cane (Saccharum officinarum); the sugar-beet (Beta vulgaris); the sugar-maple (Acer saccharinum) and Sorghum saccharatum (Girard, C. R. 102, 108; Centrbl. f. Agric. Ch. 1886. 683; Berthelot, C.R. 59, 583; A. Ch. [3] 55, 289; Buignet, A. Ch. [3] 61, 233; Maxwell, L. V. 36, 15, Am. 12, 265; Reports of the Department of Agriculture, Washington, No. 6; The Sugar Industry of the United States, by Wiley, 1885; The Literature of the Sugars, H. L. Roth, London, 1890; Gössmann, A. 104, 335; Hermbstädt, Gehlen's J. f. Ch. Ph. Min., 8, 589 (1809); Boier, Jahresb. f. Zuckerfabr. 5, 139; Balland, J. Ph. [4] 25, 97; Corenwinder, C. R. 83, 1238; A. v. Wachtel, B. C. 1880, 344; Stone, B. 23, 1406; Wiley, C. N. 51, 88; Ann. Agronom. 11, 392; Schulze a. Seliwanoff, L. V. 1887. 403; Washburn a. Tollens, B. 22, 1047; Stingl a. Morawski, M. 7, 176; 8, 82; Déon, Bl. [2] 32, 125; Reali, G. 17, 325; Schulze, L. V. 1887, 403, 408; v. also the references under the heading Dextrose. Occurrence, and many others throughout the range of chemical literature)

Formation.—Icery (A. Ch. [4] 5, 350) and Jackson (C. R. 46, 55) found that in the early period of vegetation of many plants, invert sugar only occurs, and that cane sugar is formed later. Leplay (C. R. 46, 444) confirms this observation in the case of sugar-cane. Barley contains from 0.8 to 1.6 p.c. cane sugar, whereas germinated barley (malt) contains from 2.8 to 6.0 p.c. cans sugar; the starch of the endosperm being converted into cane sugar for the use of the growing plant (Kuhnemann, B. 8, 202, 387; Kjeldahl, Res. du C. R. des Travaux du Lab. de Carlsberg, 1881, 189; O'Sullivan, C. J. 1886, 58). Brown a. Morris (C. J. 1890, 516) found that the cane sugar of germinated barley was chiefly localised in the embryo, whilst maltose appears in the endosperm; they consider that starch is first converted by diastase into maltose in the endosperm, and then, being transferred to the embryo, is converted into cane sugar for the purpose of growth. Colley a. Vakovitch (Bl. [2] 34, 326) may have obtained cane sugar by acting on barium lævulosate with acetochlorhydrose, but the evidence is not satisfactory. Aubert a. Giraud (D. P. J. 257, 298) state that by passing an electric current through acidified starch-paste at 100°C. cane sugar may be manufactured (?).

Preparation .- (For the commercial preparation of cane sugar see Thorpe's DICTIONARY OF APPLIED CHEMISTRY.) The best samples of commercial cane sugar consist of almost the pure sugar. Dry, clean, glassy sugar-candy is sufficiently pure for most purposes. Absolutely pure saccharon may be obtained by careful crystallisation from warm aqueous solutions; or a cold, clear saturated solution made with carefully-purified distilled water is mixed with an equal volume of purified ethyl alcohol, S.G. 820, with continual stirring. On standing, saccharon crystallises out in pure glassy crystals.

Properties .- Cane sugar forms fine large monoclinic hemihedral crystals, S.G. $\frac{17.5}{17.5}$ 1.58047 (Schröder, B. 12, 562; Gerlach, D. P. J. 172, 31 and 286; Joule a. Playfair, C. J. 1, 130), which do not contain water of crystallisation. It is easily soluble in water; 100 parts of a solution saturated at 0° contain 65.0 pts. saccharon, at 20° 67 pts., and at 40° 75.8 pts. (Scheibler,

2. 7. 22, 255). A large number of figures have been given to represent the relation between the quantity of sugar in solution and the specific gravity thereof (v. Lippmann's Zuckerarten; Brown a. Heron, C. J. 1879, 644; Périer, C. R. 108, 1202), and much apparent contradiction exists on the subject; but the bulk of this disappears when the processes by which the figures were obtained are inquired into. The general agreement is with the numbers of Balling, confirmed, within the limits of error, by Scheibler a. Mategczek (Z. V. 15, 586; 24, 827; 27, 32) and others. These are:—

Per cent. saccharon	Sp. gr. sol.
in sol.	17:60
5	1·01970
10	1.04014
20	1.08329
40	1.17943

The relation is sometimes more convenient when expressed as weights in measure. If a vessel be made to hold 100 g. H₂O at 15.5°, and such is the 100 c.c. vessel most generally in use, then a solution containing

20 g. saccharon in this 100 c.c. = sp. gr. 1.07686 10 1.03857 •• .. 5 1.01931 ,, •• 1.00386 Hence, if the sp.gr. of a pure cane sugar is known the amount of sugar in the 100 c.c. can be arrived at broadly by dividing the S.G. -1.000bv ·00385. This number multiplied by 1000 has been called the D of the sugar. D = 3.85 for saccharon. The use of the number gives too low an indication for the higher specific gravities and too high a one for the lower ones, being almost accurate for solutions containing between 10 and 20 g. sugar per 100 c.c. It is a useful, practical factor when its meaning and value are understood, being at most 3 per 1000 incorrect.

Concentrated sugar solutions possess a higher boiling-point than water, an 80 p.c. solution boils at 112°, a 90.8 p.c. solution at 130° (Gerlach, D. P. J. 172, 31 and 286).

Solutions of pure cane sugar crystallise quickly, but if foreign matters are present the crystallisation is very much slower, and the forms of the crystals vary with the character of the impurity; some impurities entirely prevent crystallisation. These facts play a most important part in the refinery (see art. in Dictronary of Applied Chemistry and v. Lippmann's Zuckerarten, p. 115). Solutions of cane sugar are highly diactinic (Hartley, C. J. 1887, 59). Cane sugar is soluble in methyl and ethyl alcohol, acetone, and glycerin in proportion to the amount of water they contain, being almost insoluble in them when they are anhydrous (Scheibler, Z. V. 22, 246; B. 5, 343). Solutions of cane sugar and the fused sugar are optically active, rotating the plane of polarisation to the right; crystallised sugar is not optically active. The oldest value given for specific rotatory power is [a]₁ = +78.8° = [a]₀ = +66.6° (24:21.67:78.8°:66.6°).

This is only an approximate average number, much of the same value as the D described

above. It is the apparent specific rotatory power, and may be called the working value. Tollens (B. 17, 1757), Schmitz (B. 10, 1419), Girard a. de Luynes (C. R. 80, 1355), and Calderon (C. R. 83, 393), from numerous observations worked out an absolute value. Tollens gives $[\alpha]_{\rm p} = 66.386 + 0.015035 {\rm P} - 0.0003986 {\rm P}^2$. P is the p.c. of sugar; Schmitz's numbers are $[\alpha]_D = 64\cdot156 + 0\cdot051596q - 0\cdot00028052q^2$, where q = p.c. of water. The optical activity diminishes with the concentration of the solution, so that for a 100 p.c. solution (i.e. for the dry sugar, if the curve follows the same course as the observations) the specific rotatory power is $[a]_0 = 64^\circ$ approximately, while very weak solutions, as 1 p.c. for example, it is $[a]_p = 67^\circ$ (Pibram, B. 20, 1849; Nasini a. Villavecchia, Gaz. 22, 1, 97). The temperature of observation has but a very slight influence on the optical activity (Dubrunfaut, A. Ch. [3] 18, 99; Andrews, M. S. [4] 3, 1366). The specific rotatory powers of solutions of the sugar in mixtures of water and ethyl alcohol, methyl alcohol, and acetone respectively are slightly greater than that of aqueous solutions; if the latter be taken at $[a]_D = 66.67^\circ$ they are respectively $[a]_D = 66.83^\circ$, 68.63° , and 67.40° (Tollens, B. C. 1881,570). The optical activity of fused sugar is less than that of its solutions, and diminishes according to the length of time it has been kept fused. This is, no doubt, due to the presence of decomposition products. The specific rotatory power of aqueous solutions is altered by the presence of most foreign substances; alkalis and alkaline earths diminish it (Thomsen, B. 14, 1649; v. Lippmann, Zuckerarten, p. 157; Farnsteiner, B. 23, 3570). Lead acetate does not appear to have any influence, while ammonia increases the rotation (Ost, N. Zcitsch. f. Rübenz .-Ind. 9, 42). The dispersion of cane-sugar solutions is almost the same as that of quartz, so that the rotation of the plane of polarisation caused by a sugar solution may be almost completely neutralised by a plate of left-handed quartz of the correct thickness. Grimbert (J. Ph. [5] 16, 295) gives $[a]_0 = 66.45^\circ$ and $[a]_0 = 52.85^\circ$, so that the dispersive power for these two wave-lengths is 1.257. The refractive index for sugar solutions has been determined for seven lines of the spectrum (Obermeyer, Landolt-Börnstein, Physikalisch-chem. Tabellen, Berlin, 1883, p. 213; Kanonnikoff, B. 16, 3047). Gladstone (C. J. 1891, 589) finds the molecular refraction of cane-sugar solutions to be 118.7 for the A line, and the molecular dispersion be-

tween A and H lines 4.73.

Action of heat. Dry cane sugar melts at 160°, and solidifies ou cooling, if care be taken and the temperature does not exceed 160°, to a colourless, glassy mass; but if the temperature be maintained the fused mass becomes slightly coloured, and on cooling yields the substance known as barley-sugar, this ofter a time becomes crystalline; but even with the greatest care it seems impossible to fuse the sugar without producing some decomposition. With the appearance of the colour dextrose and lævulosan are probably the chief products; but although much work has been done on the subject, the exact nature of the alteration is not settled. A little furfural is formed at times (Gélis, A. Ch. [3] 57, 234; C. R. 51, 331; Schiff, B. 20, 540). When the tempe

¹ Z. V.=Zelischrift des Vereins für die Rübensucker in-Entirie des deutschen Reichet.

rature is raised to 200° distinct decomposition sets in, caramel is formed, gases are evolved, and finally a residue of charcoal remains. Among the gases are carbon dioxide, carbon monoxide, marsh gas, ethylene, acetylene; among the volatile products are water, acetone, formic, acetic, and propionic acids, aldehyde, furfural, acrolein, benzoic aldehyde, and a bitter substance assamur (Völckel, A. 85, 59; 86, 63; 87, 303; Fremy, A. 15, 278; Schiff, B. 20, 540; A. 238, 380; Reichenbach, A. 49, 3). Caramel has the same composition as cane sugar, less one or more molecules of water. It is soluble in water and partly soluble in alcohol, and probably consists of a mixture of several bodies. Baryta and basic lead acetate give precipitates with it. It combines with aniline, reduces some metallic salts, and yields an acid with chlorine. It is largely used as a colouring matter in cookery, brewing, &c. (Gélis, A. Ch. [3] 52, 386; 65, 190 a. 496; Graham, A. Ch. 65, 190; Péligot, A. Ch. [2] 67, 172; Völckel, A. 75, 59; 85, 74; Pohl, J. pr. 82, 148; Schiff, B. 4, 908; Wachtel, Org. d. Centr.-Ver. 17, 930).

It seems proved that when dry saccharon is heated at 100°, even for a long time, no change takes place, and, as has been said, the sugar can be heated to the melting-point, 160°, without producing any marked decomposition, but it would appear that rapid heating to this temperature can produce a mixture of dextrose and lævulosan, without any change in weight. If, however, a mixture of 100 pts. of the sugar and about 5 pts. water is heated at 150° for some time. a mixture is produced which contains little or no unaltered saccharon, but which consists, in part at least, of a sugar said to be optically inactive, and to be a compound of bi-rotating dextrose and lævulose. Other bodies must also be present, probably dextrose and lævulose. The compound sugar is, no doubt, present, but inasmuch as it has never been isolated it cannot be said with certainty that it is inactive (Morin, C. R. 86, 1033; Berzelius a. Mitscherlich, J. Ph. 3, 4, 216). The so-called inactive sugar is easily converted by boiling with water into dextrose and lævulose. Neutral aqueous solutions of saccharon are slowly inverted on boiling. They are, however, stable in the cold, if sterilised, and can be concentrated under diminished pressure at 50°-60° without undergoing much change (Kreuster, Z. V. 25, 521; Béchamp, A. Ch. [3] 54, 28; Morin, C. R. 86, 1,083; Horsin-Déon, Bl. [2] 32,121; Gunning, Z. V. 27, 895). By heating to 150°-200° in a sealed tube, humus substances, formic acid, pyrocatechin, and other bodies are formed (Löw, Z. 1867, 510; Hoppe-Seyler, B. 4, 15).

Action of acids. All dilute acids, even carbonic acid, hydrolyse (invert) cane sugar, causing the assimilation of one molecule of water and the production of equal quantities of dextrose and lævulose,

Saccharon Dextrose Levulose $O_{18}H_{20}O_{11}+H_{2}O=C_{8}H_{12}O_{4}+C_{6}H_{12}O_{5}$. This mixture is called invert sugar. The experiments made on this phenomenon may be classified under two headings: (a) the action of different acids acting under the same conditions on the sugar solutions; (b) the action of the

same acids under varying conditions.

regard to those coming under the first heading, Ostwald's experiments are the most complete (J. pr. [2] 29 385; 30, 98 a. 225; 81, 807; Koral, J. pr. [2] 34, 109). He examined the action of thirty-two acids, and finds that there is a close relation between the constants of inversion and the affinities of the acids. See also Fleury (D. P. J. 219, 436; J. Ph. [4] 22, 423). With regard to reactions coming under the second heading, it is found that inversion proceeds more rapidly in hot solutions than in cold ones (several formulæ have been given to express this relation, v. Arrhenius, Zeit. phys. Ch. 4, 226; Urech, B. 20, 1836); that increase in the percentage of acid increases the rapidity of inversion; that, the percentage of acid to water being constant, increase of volume decreases the time; and that the percentage of acid to sugar being constant, increase of volume (dilution) increases the time (Löwenthal a. Lenssen, J. pr. 85, 321 a. 401; Urech, B. 13, 1696; 15, 2130; B. C. 1881, 570; 1883. 501). The presence of neutral salts sometimes increases and sometimes diminishes the rapidity of inversion; for a detailed account see Spohr (J. pr. [2] 32, 32 and 33, 265). If the heating be long continued, or if too strong acids be used, most of the lævulose and part of the dextrose is destroyed, and humus substances, acetopropionic and formic acids are produced Mulder, J. pr. 21, 219; Malaguti, A. 17, 52; Stein, A. 30, 82; Conrad, B. 11, 2178; Tollens, B. 14, 1951; Sestini, L. V. 26, 235; 27, 163; Conrad a. Guthzeit, B. 18, 439; 19, 2569 a. 2814; Tollens a. Grote, A. 175, 181, 206, 237 a. 233. The inversion of cane sugar cannot be carried out by heating with acids without destroying some lævulose (q. v.), unless the temperature and quantity of acid be kept within welldefined limits (Jungfleisch a. Grimbert, C. R. 108, 144; Wohl, B. 23, 2084). Nicol (Fr. 14, 180) and Clerget (A. Ch. [3] 26, 175) give instructions for the preparation of pure invert sugar. According to the latter, 5 c.c. of strong hydrochloric acid is added to 50 c.c. sugar solution, containing 8.175 g. saccharon, and heated for ten minutes at 68°. Under these conditions the sugar is completely inverted, and the products are unacted upon. They are identical in optical activity and cupric reducing power with the sugar obtained by the action of invertase (see Action of ferments) under the most favourable conditions. There is no doubt that invert sugar is a mixture of lævulose and dextrose in equal quantities (Jungfleisch a. Grimbert, C. R. 108, 144; 107, 390), as its properties agree in every particular with that of a mixture of these two sugars in molecular proportions. Concentrated sulphuric acid dissolves cane sugar at the freezing temperature, without the production of colour, but slight heating causes it to swell up to a black, frothy mass; a blue fluorescent body is formed (Simmler, C. C. 1862, 378). Other acids act in a similar way (Gmelin-Kraut, Hand

buch d. Ch.; van Kerckhoff, J. pr. 69, 48).

Action of alkalis. Dilute alkalis do not act on cane sugar in the cold, and but slowly on neating (Michaelis, J. pr. 56, 430). By heating with potassium hydroxide and but little water, decomposition takes place, carbon dioxide, acetone, and formic, acetic, propionic, and oxalic acids are formed (Gottlieb, A. 52, 122). Potash

or baryta under certain conditions yield a large quantity of lactic acid (Schützenberger, Bl. [2] 25, 289). Milk of lime and strontia also decompose cane sugar by prolonged heating (Fremy, A. 15, 278; Benedict, A. 162, 303; Niedschlag, Deutsche Zuckerind. 1887. 159; Pinner, B. 16.

Oxidation. Cane sugar is easily oxidised by almost all the common oxidising agents. Free oxygen does not act on it, but in the presence of platinum black it does; ozone also oxidises it (Gorup-Besanez, A. 110, 103). Chlorine or bromine yields gluconic acid, glucos, and other substances (Reichardt, B. C. 1880, 559; Grieshammer, A. Ph. [3] 15, 193); the same reaction takes place in the presence of lead or silver oxide (Hlasiwetz a. Habermann, A. 155, 128; Herzfeld, A. 220, 353). Iodine and potassium carbonate yield a little iodoform (Millon, C. R. 21,828). The more powerful oxidising reagents... such as strong chromic acid, chlorate of potash. strong sulphuric acid, &c .- act so violently as to cause explosions. Strong nitric acid acts very energetically; dilute nitric acid yields sacchario and oxalic acids; anhydrous nitric acid, or a mixture of strong nitric and sulphuric acids, yields mixtre of strong introducts supported acids, yields a nitrate (Sobero, C. R. 24, 247; Schönbein, P. 70, 104; Carey-Lea, Bl. [2] 10, 415; Tollens, B. 15, 1828; Salkowski, B. 15, 1738; Heintz, A. 51, 185; P. 61, 315; Reinsch, Jahrb. f. Pharm. 18, 337; Hornemann, J. pr. 89, 304; Tollens, Chem. Zeit. 11, 1178). Fehling's solution is not reduced by cane-sugar solution, neither are alkaline solutions of other oxides, except ammoniacal silver solutions, which are reduced slowly in the cold and quicker on warming; but many neutral or acid metallic solutions are reduced (Tollens, Z. V. 82, 712; B. 15, 1828; Salkowski, B. 15, 1738). Dilute chromic acid oxidises cane sugar to oxalic, formic, and carbonic acids; potassium permanganate yields carbonic acid and water; by careful oxidation in the cold, oxalic and formic acids are also produced (Heyer, Ar. Ph. [3] 20, 336 a. 430; Brunner, B. 12, 549). Maumené (Bl. [2] 22, 2; 30, 99) says that three acids, di-, tri-, and hexa-pinic acids C2H4O4, C₂H₂O₃, and C₆H₁₂O₃, are formed under certain

conditions. Action of ferments. Cane sugar is not directly fermentable by organised ferments, with the exception of Monila candida; it requires first to be hydrolysed (inverted), and for this purpose every organism which has the power of assimilating cane sugar produces an organised ferment or enzyme called *invertase*, which first inverts it (Bernard, Lecons de Physiologie Exper., Paris, 1856; Hansen, Meddelelser, 1888, 2, 143; Brown, O. J. 1886. 173). The action of invertase was first studied by Kjeldahl (Meddelelser, 1881, 3, 186); O'Sullivan and Tompson (C. J. 1890, 834) have exhaustively investigated the subject. They find the change follows the same time curve as a catalytic reaction; the time necessary to perform a given percentage of hydrolysis varies directly with the amount of invertage; the most favourable concentration of the sugar solution is 20-25 p.c., and the most favourable temperature 55°. Hydrolysis proceeds slowly at the freezing-point; it ceases at about 65°; alkalis immediately stop the reaction, whereas very minute quantities of acid

aid it. Invertase is uninjured by the reaction, and is capable of inverting about twenty-two times its weight of cane sugar per minute for an unlimited period. The dextrose formed is in the bi-rotatory state; on standing, the invert'sugar has the same optical activity as that obtained by the careful action of dilute acids. See also Barth (B. 11, 474), Mayer (B. C. 1881, 784; 1882, 850), Müller (Ann. Agronom. 12, 481), Tamman (Zeit. phys. Ch. 3, 25). Invertase acts at a temperature higher than is sufficient to kill the yeast whence it is derived. For production of alcohol. acids, &c., under the influence of organised ferments, see FERMENTATION.

Compounds with acids. Nitrosaccharon $C_{12}H_{18}(NO_2)_4O_{11}$ is prepared by treating the powdered sugar with a mixture of strong H_4SO_4 and fuming HNO, in the cold (Schönbein, P. 70, 167; Sobero, C. R. 24, 247). It is a white doughy mass, insoluble in water, soluble in alcohol and ether. Boiling water decomposes it;
Li.p. 20°. It is explosive.

With arsenious acid a compound

C12H22O11.As2O3 is said to be produced. The composition is improbable.

By the action of acetic anhydride and glacial acetic acid, or acetic anhydride and sodium acetate, a series of acetates have been obtained. In these the group CoH,O takes the place of H. We have the monoacetate $C_{12}H_{21}(C_2H_2O)O_{11}$ (Schützenberger a. Naudin, Bl. 12, 206); the (Herzfeld, N. Z. 3, 155); the hexacetate (Schützenberger, Bl. 12, 204; C. R. 61, 485); and the octacetate (Herzfeld, B. 13, 267; Démole, C. R. 89, 481), all more or less resinous substances. diminishing in solubility in water in proportion to the number of acetyl groups they contain, and increasing in solubility in alcohol and ether with the same change in composition. The octacetate is said to crystallise in needles, m.p. 67°. They are all decomposed by the action of acids and alkalis into acetic acid and the products of the inversion of saccharon. It is probable that by careful treatment with alkalis in equivalent quantities (sufficient to neutralise the acetic acid formed) saccharon is again produced. Benzoyl chloride yields with saccharon (Baumann, B. 19, 3220; Skraup, M. 10, 389).

Compounds with bases. By mixing sodium

ethylate with a solution of cane sugar and precipitating with alcohol, a compound C₁₂H₂NaO₁₁ is obtained (Pleisser a. Tollens, A. 211, 285). A similar potassium compound has been prepared (Soubeyran, A. 43, 223; Brendeche, An. Ph. [2] 29, 73). Cane sugar combines with many bases, forming saccharates which are decomposed into the sugar and carbonate by carbon dioxide, and are but slightly soluble in water. The most important of these are barium saccharate $C_{12}H_{22}O_{11}$ BaO, strontium saccharate $C_{12}H_{22}O_{11}$ SrO, and $C_{12}H_{22}O_{11}$ 2SrO, the former produced by mixing solutions of its constituents; it crystallises with $\delta H_{2}O_{1}$, the latter obtained by bringing together its constituents obtained by bringing solution. Calcium saccharates: C₁₂H₂₂O₁₁.8CaO 3aq is but slightly soluble in water; C₁₂H₂₂O₁₁.2CaO 2aq and C₁₂H₂₂O₁₁.2CaO are soluble in water and decomposed partly by Calcium saccharates:. boiling into the tri-saccharate and free sugar,

 $C_{12}H_{22}O_{11}.CaO + 2H_2O_1$ C₁₂H₂₂O₁₁.2CaO, (C₁₂H₂₂O₁₁)₂8CaO have also been described. Lead acetate alone does not precipitate cane sugar; lead acetate and ammonia yield $C_{12}H_{18}Pb_2O_{11}$ and $C_{12}H_{18}Pb_2O_{11}$; iron and copper yield saccharates; it is doubtful if magnesia forms one (Soubeyran, A. 43, 223; Stromeyer, Ar. Ph. [3] 25, 229; Brendeche, Ar. Ph. [2] 29, 73; Péligot, J. pr. 13, 379; 15, 76; A. [3] 54, 377; Landolt a. Degener, Z. V. 32, 325; Scheibler, B. 15, 2945; 16, 985; v. Lippmann, Organ d. Centr. Ver. 18, 37; B. 16, 2764; Benedict, B. 6,413; Harperath, Chem. Zeit. 1886. 323; Boivin a. Loiseau, C. R. 58, 60; also old editions of Watts' Dict.). Ammonia gas at 150° forms brown amorphous bodies; solutions of ammonia yield similar bodies (Thénard, C. R. 52, 444; Payen a. Schützenberger, Jahresber. f. Zuckerfabr. 1861-62, p. 191, 192; Laborde, J. 1874, 883).

Compounds with metallic salts. Several compounds of saccharon with sodium chloride, bromide, and iodide have been prepared (Péligot, A. 30, 71; Maumené, Bl. 15, 1; Gill, C. J. 1871, 269). Such compounds are C₁₈H₂₂O₁₁.NaCl.2H₂O; 2C₁₂H₂₂O₁₁.3NaCl.4H₂O; C₁₂H₂₂O₁₁.NaBr.1½H₂O;and2C₁₂H₂₂O₁₁.3NaL.3H₂O; the latter is a very stable and definite compound, and is, like the others, easily prepared by boiling a mixture of the sodium salt and saccharon in equivalent quantities, and allowing the solution to stand in a quiet place over sulphuric acid. These bodies form distinct and definite crystals. No definite compounds of the halogen salts of potassium and ammonium with saccharon have been described, but there can be little doubt. from the work of Gill, that such are obtainable. Lithium salts seem to give lithium compounds. Compounds of saccharon with sodium-acetate. nitrate, iodate, and phosphate are not obtainable (Gill, l.c.). A double salt of copper sulphate and saccharon, C12H22O11.CuSO4.2aq crystallises from a saturated solution of the constituents (Barreswil, J. Ph. [3] 7, 29). The sodium mercury chloride compound crystals on the slow evaporation of a solution of its constituents in weak alcohol (Boullay, Bl. 12, 292). A borax compound 3C₁H₂O₁, Na₂B₄O₂, 4H₂O has also been described (Stürenberg, Ar. Ph. 18, 279). Many other compounds have been described, but they present no material interest.

Saccharon, like many other organic substances, prevents the precipitation of many metals from their solutions by ammonium, sodium, and potassium hydroxide; in some cases the prevention is complete, in others only a portion of the metal is retained in solution (Lussaigne, C. R. 14, 691; Groth, J. pr. [1] 92, 175; Pellet J. Fabr. 18, 22).

-, the assimilation no accharon yields only

With phenyroduction of equal (q. v.). ulose and devices, milk Isoulose and dextrose compound L Lactose. Lacton, lactobiose Callong known. C₁₂H₂₂O₁₁·H₂O(a) and C₁₂H₂₂O₁₁(γ). ichras Sapota) It occurs in the milk of the mam constitutes It occurs in the milk of the mam stose constitutes in the fruit of Sapotillier (, sheep, goats, and (Bouchardat, Bl. [2] 16, 26). Lith B-5 p.c. of the milk of women. To de Sucre.

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cows, 6 p.c. of asses' milk, and a slightly greater proportion of mare's milk (Fleischmann, Das Molkereiwesen, Braunschweig, 1875; Kühne, Lehrb. d. physiol. Ch. p. 573).

Preparation.—Skim milk, or, better, milk from which the fat has been separated by mechanical means, is coagulated with rennet and the whey digested for some time with calcium carbonate (chalk) and aluminium hydroxide. The insoluble matter is then filtered out and the filtrate concentrated in a vacuum to a syrup; this, on standing, yields crystals of lactose. During concentration some matter becomes insoluble; this should be filtered out before final concentration. The crystals are purified by repeated re-crystallisation from solutions concentrated at the temperature of boiling water; on cooling C1.H2O11.H2O crystallises. This is lactose a. If the saturated solution is evaporated rapidly on the water bath with continual stirring, small crystals of C12H2.O11 are obtained; lactose y. These are not hygroscopic. If the a modification is dried at 130° a hygroscopic mass is left, which is known as the β modification. There are said to be other modifications, but in solution after boiling they all have the same optical activity and are identical (Enling a. Rüf, B. C. 1882, 346; Centbl.

f. Ag. Ch. 1885, 130; J. Kunz, Ph. [3] 15, 443).
Properties.—Ordinary lactose forms large, rhombic, hemihedral crystals, having a sp.gr. 1.53-1.54 (Schröder, B. 12, 562) and containing 1 mol. H.O. which is lost by drying at 130°. It is soluble in six parts of cold water and in two and a-half or less of boiling water, from which on cooling it slowly crystallises. Its solutions rotate the plane of polarisation to the right, and its specific rotatory power for the D line is [a]_b = $52 \cdot 53^{\circ} + (20 - t) \times 0.055$ (Schmöger, B. 13, 1927; Hesse, A. 176, 98; Erdmann, J. 1855, 661; Denigès a. Bonnans, J. Ph. [5] 17, 363 a. 411). The variation with the concentration is very little, and, as is obvious from the above formula, the effect of temperature is slight. These numbers for the $[a]_D$ are calculated for the crystals $C_{12}H_{22}O_{11}$. H₂O. For the dry sugar $C_{12}H_{22}O_{11}$ I have found $[a]_D = 55.5^\circ$ with a Jellet-Cornu instrument (Schmidt a. Hans, Ch.), sodium flame, and absolutely the same number $[a]_1 = 61.6^{\circ}$ with a Soleil-Scheibler, taking 100 divs. = 38.4°.

 $(24:21.67::61.6^{\circ}:55.5^{\circ})$. $55.5^{\circ}-5.25$ p.e. = 52.59: my observations were made at 15.5°, Schmöger's at 20°. Freshly-prepared solutions of crystallised lactose exhibit the phenomenon of bi-rotation, the angle immediately after solution being in the proportion of 8:5 to the constant value (Urech, B. 16, 2270; Dubrunfaut, C. R. 42, 228; Schmöger, l.c.; Parcus a. Tollens, A. 257, 160). The rotatory power does not vary with the concentration. The dispersive power-that is, the ratio between the specific rotatory powers for the C and D lines—is 1:1.259 ([α]₀ = 41.58) (Grimbert, J. Ph. [5] 16, 295 a. 345). The modification γ when freshly dissolved in water exhibits the phenomenon of semi-rotation—that is, the specific rotatory power is only about § of the normal, to which it attains on standing a few hours (E. O. Erdmann, Fortschritte der Physik, 1855, 13; B. 13, 2180; Schmöger, B. 13, 1915). The modification β on solution has immediately the normal optical activity; the presence of alkali lowers the

activity (Schmöger, L.c.; Urech, B. 17, 1543). Schmöger give the specific gravity of solutions, containing given percentages of the crystals from which by calculation we get D=3°956 for a solution containing 2.5 g. dry sugar in 100 c.c. at 20°, 3°921 for a 10 g. solution and 3°913 for a 15 g. one. My observations are, temporature 15°5°:—

1 gram in 100 c.c. sp.gr. $\frac{155}{155}$ 1·0040; D = 4·00 5 grams, 1-0199; D = 3·98 10 , 1-0397; D = 3·97 20 , 1-0785; D = 3·93

D=3·99 for solution below 10 g. per 100 c.c. at 15·5°. The K=79·2 for dry sugar, i.e. 0·5723 anhydrous lactose reduce 1 g. CuO from Fehling's solution (Jones, Analyst, 1889, 81). According to Soxhlet 0·5 g. sugar=74 c.c. Fehling's solution, hence K=74; in this case 1 g. CuO=0·127 lactose: by weighing the precipitated CuO as Cu by Allihn's method, 1 g. sugar=1·736 CuO, or 1 g. CuO=0·5760 g. sugar, K=78·8, agreeing with the number given by Jones. According to Roderwald a. Tollens (B. 11, 2076) the working number 1 g. CuO=0·5795 g. anlydrous sugar. I am inclined, when the conditions hereafter to be described are followed, to place the K at 78·9, i.e. 1 g. CuO=0·5768 g. sugar. In this case 7·5 mols. CuO are reduced by 1 mol. sugar.

Action of heat. Hydrous crystallised lactose (a) remains constant at 100°; above this water is slowly given off, and at 130° the dehydration is complete without decomposition if the water is climinated slowly. Anhydrous lactose commences to colour at 170°-180°, loses water, and forms the so-called lactocaramel C_oH₁₀O_s, which is easily soluble in water but insoluble in alcohol, and yields compounds with lead and copper oxide. Lactose melts at 203·5° to a brown liquid, and by further heating it is decomposed with separation of carbon (Lieben, J. pr. 68, 409). Heated in a scaled tube with water to 90°-100° it is coloured, and more so at 180°-200°, when a glucose is produced which may be precipitated by alcohol, and, by further heating, carbonic acid, a little pyrocatechin, and other bodies are formed (Vohl, A. 105, 334; Hoppe-Seyler, B. 4, 16; Munk, H. 1, 357).

Action of acids. By heating with dilute acids lactose is hydrolysed (inverted), yielding galactose and dextrose

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

Lactose Dextrose Galactose

one molecule of water being taken up. The reaction takes some hours to complete; during the hydrolysis the reducing power and optical activity increase (Pasteur, G. R. 42, 223; Fudakowski, B.8, 559; 9, 42; 278 and 1602; 11, 1069; Bourquelot, N. Ztschr. f. Rubenz-ind. 16, 71; Kent a. Tollens, A. 227, 221; Rindell, N. Ztschr. f. Rubenz-ind. 4, 163). The chief products of the reaction are as stated, but the conditions have not yet been described by which the optical activity and K of the resulting substances will exactly correspond with those of a mixture of equal parts of galactose and dextrose. Other bodies are undoubtedly produced. By the continued action of acids for several days, aceto-propionic and formic acids are produced (Tollens a. Roderwald, A. 206, 231; Conrad a. Guthzeit,

B. 19, 2575). Concentrated sulphuric acid does not blacken lactose in the cold.

Compounds with acids. A mixture of sulphuric and nitric acids give lactose pentanitrate $C_{12}H_{17}(NO_2)_5O_{11}$, insoluble in water but soluble in alcohol and ether, m.p. 139.2° and exploding when struck by a hammer on an anvil; lactose tri-nitrate C₁₂H₁₈(NO₂)₃O₁₁, very slightly soluble in water, but easily in alcohol and ether, m.p. 37° ; and lactose tetranitrate $C_{12}H_{18}(NO_2),O_{11}$, m.p. 80° – 81° (Gé, J. R. 1882, 253; B. 15, 2238). With chlorosulphonic acid lactose yields dextrosetetra-sulphonic acid chloride (Claesson, J. pr. [2] 20, 1 and 18). Organic acids act very slowly on lactose, but by prolonged action they yield ethers of lactose or of dextrose and galactose (Berthelot, Chim. org. 2, 279, 295). A series of acetates, beginning with the mono-body and ending with the octo-one, have been described. C12H11(C2H3O)8O11 is obtained by boiling lactose with an excess of acetic anhydride or by heating a mixture in the proper proportions of the sugar, acetic anhydride, and fused sodium acetate at 100° (Herzfeld, B. 13, 265). This body is insoluble in water and in ether, soluble in benzene, acetic acid, and in alcohol. It crystallises from a mixture of alcohol and acetic ether. $[\alpha]_D = +31^\circ$ in alcoholic solution. The mono- and di- acetate are obtained by incompletely decomposing the octo-acetate by alkalis (Démole, C. R. 89, 481). Tetracetate is formed at the same time as the octo- acetate, when lactose is boiled with acetic anhydride (Schützenberger a. Naudin, Bl. 12, 208). It is easily soluble in water, $[a]_p = +50^\circ$. Hexacetate C12H16(C2H2O)O11 crystallises from a mixture of alcohol and acetic ether in white needles, m p. 86° (Herzfeld, N. Z. R. 3, 156). It is doubtful whether or not lactose is reproduced when these bodies are saponified by treatment with alkalis. There seems to be no reason why it should not be so, if the alkali is carefully employed.

Action of alkalis. Hot alkalis colour solutions of lactose yellow to brown, and form lactic acid, pyrocatechin, and other products (Hoppe-Seyler, B. 4, 347; Nencki a. Sieber, J. pr. [2] 34, 503; Urech, B. 17, 1543). Fused with KHO it yields carbonic, oxalic, and a little succinic acids (Hlasiwetz a. Barth, A. 138, 76).

Compounds with alkalis. Lactoseates are formed by the action of potash or soda on lactose in alcoholic solutions, or by adding alcohol to the mixed aqueous solutions. They are amorphous, easily decomposed precipitates having a composition expressed by the formulæ C₁₂H₂₁NaO₁₁ and C₁₂H₂₁KO₁₁ (Fremy, A. 15, 278; Hönig a. Rosenfeld, B. 12, 45). Calcium, barium, and lead lactoseates are obtained by dissolving the base in lactose solution and precipitating with alcohol. The long-continued action of lime produces isosaccharin and metasaccharin (Cuisinier, M. S. [3] 12, 520; Kiliani, B. 16, 2625). By heating with ammonia, brown, amorphous, nitrogenous products are obtained (Thénard, C. R. 52, 444). Aniline yields two crystalline compounds, C₁₀H₁₀NO₂₁ and C₁₀H₁₀NO₂₀, which reduce Fehling's solution (Sachsse, B. 4, 835; L. V. 16, 441).

Oxidation.—Oxygen and ozone have no action on lactose in the cold; hot solutions are oxidised by oxygen in the presence of platinum black (Gorup-Besanez, A. 110, 86 a. 103; Reiset

a. Millon, A. Ch. [3] 8. 295). Alkaline permanganate solutions oxidise lactose easily (Laubenheimer, A. 164, 288). Chromic acid yields aldebyde (Guckelberger, A. 64, 98). Nitric acid hyde (Guckelberger, A. 64, 98). Nitric acid first inverts lactose and then yields mucic and saccharic acids; from 86 to 40 p.c. of mucic acid is produced; by long-continued heating tartaric and oxalic acids, &c., are obtained (Liebig, A. 113, 1; Dubrunfaut, C. R. 42, 228; Kent a. Tollens, A. 227, 227). Alkaline solutions of copper oxide are reduced by lactose, and from amongst the products of the reaction Bödecker a. Struckmann (A. 100, 264) isolated gallactinic acid $C_{14}H_{10}O_{9}$; pectolactinic acid $C_{16}H_{16}O_{12}$, lactic and glycollic acids are also produced (Habermann a. Hönig, B. 17, 351). Silver oxide oxidises lactose solutions with production of oxalic, glycollic, and lactonic (galactonic) acids (Kiliani, B. 13, 2307). Chlorine or bromine in the presence of silver oxide yield lactonic (galactonic) acid C₂H_{1,2}O₂ (Barth a. Hlasiwetz, A. 119, 281; 122, 96). By very careful oxidation with bromine water Fischer a. Meyer (B. 22, 361) have obtained lactobionic acid C12H22O12; it is a colourless, strongly acid syrup, easily soluble in water, but only sparingly in alcohol. It does not reduce Fehling's solution; it decomposes metallic carbonates, forming salts. The calcium $(C_{12}H_{21}O_{12})_2Ca$, barium $(C_{12}H_{21}O_{12})_2Ba$, lead (C12H21O12)Pb, and other salts may be prepared in this way; they are insoluble in alcohol, but soluble in water. When heated with dilute mineral acids, lactobionic acid is decomposed into galactose and gluconic acid. With iodine and sodium bicarbonate lactose yields a little iodoform (Millon, C. R. 21, 828).

Fermentation.—There is no known enzyme capable of inverting lactose; it does not ferment with yeast (Berthelot, A. Ch. [3] 50, 332 a. 362; Fitz, B. 11, 42). It easily undergoes lactic acid fermentation, especially in milk (Fitz, l.c.; Richet, C. R. 86, 550; Schmidt-Mülheim, B. 15, 2631). It undergoes alcoholic fermentation in kumys or kefir fermentation (Struve, B. 17, 314; Vieth, A. 12, 2), and also under the agency of certain bacteria (Rotondi a. Zechini, see v. Lippmann, Deutsche Zuckerind. 1887, 1091).

Phenylhydrazine yields lactose phenylhydraside C₁₁H₂₂O₁₆N₂, soluble in water and alcohol, insoluble in ether and levorotatory, and lactose osazone C₂H₂₂N₄O₃, crystallising in yellow needles; soluble to some extent in hot water, and m.p. 200° (Fischer, B. 17, 583; 20, 830; 20, 2566). By the action of hydrochloric acid it yields lactose osone (Fischer, B. 21, 2631).

Maltose. Maltobiose, Anylon, C.,H.,O.,;
C.,H.,O.,,H.,O. De Saussure (Bibl. Britannique,
56, 1814, 333; P. 1819, 29, 58) may have obtained this sugar when studying the products of
the spontaneous decomposition of starch-paste
when exposed to the air at 20°-25°. GuérinVarry (A. Ch. 60, 32; 61, 66) described accurately
how the body could be prepared in the crystallised state and some of its properties, but failed
to recognise it as a distinct substance; Jacquelain (A. Ch. 68, 167) added nothing to Varry's
work; Dubrunfaut (A. Ch. [3] 21, 78) prepared
the body according to Varry's method, observed
that it was less soluble in alcohol than dextrose,
and had an optical activity three times as great,
46, [a] = 58 × 3 = 174, a figure so high as to lead

one to believe that he had not a pure body in his hands. He recognised it as a distinct body, and called it maltose; he, however, looked upon it as a glucose, triglucose; O'Sullivan (C. J. 1872, 576; 1876, 478) showed that it was not an 'ose' but an 'on' sugar, and from this and a fuller description of its characters gave it a place among chemical entities.

Occurrence.—It is present in some commercial glucoses and in beer (Valentin, J. S. A. 24, 404); probably in bread; in ame, a rice-extract prepared in Japan (Yoshida, C. N. 43, 29), and in germinated cereals to the extent of 1 to 2 p.o. (O'Sullivan, C. J. 49, 58). After feeding with amylaceous substances it is found in the intestinal canal, but the blood of the mesenteries contains only dextrose. If injected into a vein it is found in the urine; if injected subcutaneously, it is partially converted into dextrose (Phillips, B. C. 1882, 127). Some of the reducing sugars of blood may be maltose.

Formation.—Diastase converts starch and the dextrins into maltose (O'Sullivan, L.c.). The ferment of saliva, ptyalin, of the pancras, and of the liver, act in the same way (Nasse, J. Th. 1877, 62; Musculus a. v. Mering, Z. 2, 403). The same ferments act on glycogen, maltose being amongst the products; dextrose is present when saliva is employed (Kütz, Pf. 24, 8). All mineral acids and many organic acids act on starch and glycogen; maltose is amongst the products.

Preparation .- 100 g. purified starch are mixed as completely as possible with 300 c.c. water at 40°, and then poured with continuous stirring into 2 litres of boiling water. The paste is cooled to 60° and the extract from 20 g. pale malt added to it; the mixture is kept at 60°-63° for four or five hours, and the solution may be allowed to cool and stand for a few days. At the end of that time it is evaporated, best in a vacuum, to 200 c.c., and then boiled with 2 litres alcohol, sp.gr. 820. On cooling and standing, the clear liquid is decanted off the undissolved syrup and put aside in a corked flask; at the end of six days the sides of the flask will be found to be covered with a crystalline crust of maltose. Or the undissolved syrup may be treated with strong alcohol as long as any matter is taken up, the whole of the clear alcoholic solutions are mixed, the alcohol distilled off and the residue concentrated to a syrup; this on standing in a cool place becomes filled with crystals of maltose, especially if a few crystals from a previous preparation be stirred in. These may be washed with dry methyl alcohol; if this is used hot, a portion of the crystals dissolves and the solution soon yields much sugar. The crystallisation is hastened by adding half a volume of ethyl alcohol (.810 sp.gr.) or a little ether with some crystals of a previous prepara-tion (O'Sullivan, *l.c.*; Schulze, *B.* 7, 1047; Soxhlet, *J. pr.* [2] 21, 277; Herzfeld, *A. Ch.* 220, 209; Cuisinier, J. 1884, 1803). The body may be purified by recrystallisation from methyl alcohol or water.

Properties.—Maltose crystallises out of water in plates which contain $C_{12}H_{22}O_{11}.H_{2}O$; out of alcohol (sp. gr. 810) it crystallises in crusts and at times in cauliflower-like or warty aggregations which contain $C_{11}H_{22}O_{11}$. The hydrous body easily parts with its water at 100° in a

ourrent of dry air. The anhydrous body is but slightly soluble in strong ethyl alcohol; it is more soluble in methyl alcohol. The hydrous body dissolves more freely in both solvents. Both bodies are very soluble in water, but less so than dextrose. The solution is optically active, and the activity for a solution containing 10 g. in 100 c.c. is 15°-20° less when freshly prepared than after standing. The activity becomes constant in ten to twelve hours in the cold or immediately on boiling (Meissel, J. pr. [2] 25, 120).

The specific rotatory power for dry maltose is $[a]_1 = 154^\circ - 155^\circ$, $[a]_D = 139^\circ - 140^\circ$ at $15\cdot 5^\circ$ in solutions containing 10 g. per 100 c.c. and under (O'Sullivan, C. J. 35, 771; 45, 5); Meissel (J. pr. [2] 25, 114) gives the formula $[a]_D = 140\cdot 735 - 01837 P - 095 T$ to represent the specific rotatory power of dry maltose at 0°, in which P = percentage of maltose in solution and T the temperature of observation. On calculating the value of the sugar in a 10-g. solution at 15·5° from this formula we get $[a]_D = 138\cdot 9$ (v. also Soxhlet, L.c., and Herzfeld, A. 220, 206). The dispersive power, Le. the ratio of $[a]_D : [a]_C$, is 1·262 (Grimbert, J. Ph. [5] 16, 295). A solution of maltose containing 10 g. dry substance in 100 c.c. at 15·5° has a sp. gr. $\frac{1550}{1550} =$

1.0395. Maltose reduces alkaline copper solution. O'Sullivan $(C.\ J.\ 35,\ 771)$ gives its reducing power $K=62.5,\ i.e.\ 62.5$ parts dextrose reduce as much copper oxide as 100 parts of maltose. Soxhlet $(\hat{J}. pr. 21, 227-317)$ says 0.5 g. maltose in 1 p.c. solution = 64.2 c.c. undiluted Fehling solution (1 c.c. = 005 g. dextrose), i.e. K = 64.2, and 67.5 c.c. if the solution is diluted with four times its volume of water, i.e. K=67.5. He further states that 100 parts of dry maltose = 113 parts Cu, hence 141 parts CuO; from this, we have K = 63.94. There appears to be fair evidence that the K varies within certain limits according to the mode of manipulation, but when we see that the K should be 63.17 if it be supposed that 1 molecule malfose reduces 6 molecules CuO, and that the observed numbers closely approach this, we may take it that this is the true number when errors of manipulation are avoided. If the Cu2O be separated, the filtrate treated with acid gives a further reduction with Fehling's solution which, if added to the first, equals the reduction of dextrose (Herzfeld, A. B. 589, 220). Alkaline mercuric cyanide solutions are also reduced by maltose. Copper acetate is not reduced by it (Barfoed, Org. Analysis, 214); dextrose reduces this reagent. When maltose reduces copper oxide, glycollic and a mixture of acids of unknown composition are produced (Habermann a. Hönig, M. 5, 208).

Maltose is hydrolysed to dextrose according to the equation $C_{11}H_{21}O_{11} + H_{21}O = 2C_{2}H_{12}O_{2}$ by the following reagents: the mineral acids and many organic ones; pancreatic secretion and portions of the small intestine (Brown a. Heron, C. N. 42, 63; Bourquelot, C. R. 97, 1000 and 1822); a ferment developed in Aspergillus niger and in Mucor mucedo; the former contains also a ferment capable of inverting sucrose, the latter yields only the one (Bourquelot, Lo.). Under the action of ordinary beer yearts maintenance of the second contains a second con

ose ferments, i.e. is broken down into carbonis acid, alcohol, &c., apparently without being previously inverted. Other organisms yield lactic acid and other products; v. FERMENTATION.

Maltose withstands the hydrolytic action of sulphuric acid with five times the power of sulrose; 3 hours' digestion with a 3 p.c. solution gives complete inversion (Meissel, l.c.). 0.5 p.c. solution of lactic acid does not hydrolyse it, even at 110°; 1 p.c. oxalic acid acts at that temperature; carbonic acid at 100°, and under a pressure of six atmospheres, is without action (Bourquelot, J. de l'Anat. et de la Physiol. 22, 161-204; Urech, B. 18, 3074).

Nitric acid converts maltose into saccharic acid and finally oxalic acid. Chlorine does not act on it as energetically as it does on dextrose or sucrose; the product is neither gluconic nor glycollic acids (Meissel, l.c.). Herzfeld (B. C. 1883) obtained an acid which he called maltonic acid, by the action of bromine on maltose; this is probably identical with Fischer and Meyer's (B. 22, 194) maltobionic acid C₁₂H₂₂O₁₂, which they prepared by acting on maltose in aqueous solution with bromine in the cold for two or three days. This acid is broken down into dextrose and gluconic acid by digestion with sulphuric acid. Treated at 110° with acetic anhydride and acetic acid, maltose yields monacetyl maltose $C_{12}H_{21}(C_2H_3O)O_{11}$ (Yoshida, l.c., a. Steiner, G. N. 43, 52); with sodium acetate and acetic anhydride the octacetyl derivative C12H14(C2H3O)5O11 is produced, the optical activity of which is $[\alpha]_D = 81 \cdot 18^\circ$ (Herzfeld, A. 200, 206). With benzyl chloride it yields penta-benzyl maltose, m.p. 110°-115° (Skraup, M. 15, 359).

Sodium $C_{12}H_{21}NaO_{11}$, calcium $C_{12}H_{22}SrO_{11}H_{2}O$, and barium $C_{12}H_{22}SrO_{11}H_{2}O$, strontium $C_{12}H_{22}SrO_{11}H_{2}O$, and barium $C_{12}H_{22}SrO_{11}H_{2}O$ maltose are prepared as easily decomposable amorphous precipitates when alcoholic solutions of maltose and the corresponding bases are mixed (Herzfeld, *l.c.*). Compounds with the alkaline chlorides or bromides have not been prepared.

When 1 part maltose, 2 parts phenylhy-drazine hydrochloride, 3 parts sodium acetate, and 15 parts of water are heated together for 1½ hours, phenylmaltosazone crystallises out on cooling in fine yellow needles, m.p. 190°–191°. The equation C₁,H₂,O₁, +2N,H₂,C,H₃=C₂,H₂,N₁,O₂+2H₂O+H₃ represents the reaction. Only 30 p.c. of the maltose employed is obtained as osazone (Fischer, B. 17, 583). With y-diamido-benzoic acid, maltose yields malto-y-diamido-benzoic acid according to the equation

The body crystallises in white microscopic needles or narrow plates; its barium salt is a gummy mass (Griess a. Harrow, B. 20, 2212).

Isomaltose. Fischer (B. 23, 8687) prep ared a saccharon by the polymerisation of dextrose. Previous attempts in this direction had been made by Musculus (Bl. 18, 66), Muscu us a Meyer (C. R. 92, 528), Hönig a. Schuber M. 7, 455), and they obtained by the action of strong sulphuric acid a dextrin-like body $C_0H_{10}O_{20}$

SKA SUGAR.

which slightly reduced Fehling's solution, did not ! ferment with beer yeast, and was reconverted into dextrose by the action of dilute sulphuric acid. Grimaux a. Lefèvre (C. R. 103, 146) obtained a like result by evaporating in vacuo dextrose with dilute hydrochloric acid. Gautier (Bl. 22, 145) obtained a body $C_{12}H_{22}O_{11}$ by the action of hydrochloric acid on an alcoholic solution of dextrose; this body reduces Fehling's solution but slightly, does not ferment with beer yeast, and could not be reconverted into dextrose. Grimaux and Lefèvre considered that in their product they could detect maltose by the osazone. Scheibler a. Mittelmeier (B. 23, 8075; 24, 301) isolated an unfermentable syrup from commercial glucose which reduces Fehling's solution and yields an osazone $C_{2}H_{2}N_{*}O_{p}$, m.p. 152°-153°. They find it is only produced when the heating with acid has been prolonged, and that it may be prepared by the action of acids on dextrose. This body has been previously named gallisin (Cobenzl, Roseneck a. Schmitt, B. 17, 1000 and 2456; Anthon, D. P. J. 151, 213; Mehring, Deutsche Vierteljahrsschrift für öffentl. Gesundheitspflege, 14, Heft 2). Fischer's substance also yielded the same osazone, m.p. 150°-153°; he calls the body isomaltose, and prepares it as follows: One hundred g. glucose (commercial dextrose) are digested with 400 g. hydrochloric acid solution sp. gr. 1·19 at 10°-15° for 15 hours. Alcohol throws out of the solution a small precipitate, which is not formed if the temperature of the reaction is kept below 10°. To the clear solution an excess of ether is added, when a colourless amorphous precipitate is obtained which is filtered out and washed with a mixture of alcohol and ether. This body is dissolved in water, neutralised, boiled to expel alcohol and ether, and fresh beer yeast added. After 18 hours all the dextrose is destroyed (?); the solution has still a high reducing power, and contains isomaltose and other bodies.

The isomaltose is separated as osazone; the solution is heated with phenylhydrazine acetate in the water-bath for 11 hours. A little glucosazone separates and is filtered out, and on cooling the filtrate deposits a yellow precipitate consisting of a mixture of glucosazone and isomaltosazone; the mother-liquor, by further heating and similar after-treatment, yields more osazone. The whole of the osazone obtainable is boiled with 100 c.c. water and the solution filtered, the filtrate contains isomaltosazone, which is deposited on cooling in needles; $2\frac{1}{9}g$, of this are obtained from 100 g. glucose, the actual yield is, no doubt, considerably higher than this. By the action of hydrochloric acid the osazone is converted into the osone, which, when boiled with 4 p.c. hydrochloric acid, yields glucosone and glucose.

Lintner claims to have found isomaltose amongst the transformation products of starch by diastase (Woch. Brauerci, 9, 245), and in wort and beer (Zeit. ges. Brauw. 1891, 281), but it is very doubtful if this is the same body as that above described. Schiffer (C. C. 1892, 2, 825) has also isolated isomaltose from the diastase transformation products of starch. But the whole evidence is unsatisfactory, as the factors upon which the identity of the bodies can be recognised are not stated. Lintner and Düll (Zeit. ges. Brauw. 1892, 145) prepare it as fol-

lows: 250 g. potato starch are mixed with 500 c.c. diastase solution at 55° containing 0.5 g. diastase (J. pr. 34, 378) and 2 litres water at 75°C. After complete solution another 0.5 g. diastase is added, and the reaction allowed to proceed for three hours at $65^{\circ}-69^{\circ}$. $[a]_{D} = 170^{\circ}$. for matter in solution. The solution is evaporated to a syrup, saturated with 80 p.c. alcohol, and poured into hot alcohol. Sufficient alcohol must be used so that every 100 parts of 80 p.c. alcohol do not contain more than 10 pts. dry substance. After cooling, the clear solution is decanted and the alcohol distilled off. The residue is diluted to a 20 p.c. solution and yeast added in order to destroy the maltose; this is found to take place in about 20 hours. The fermented solution is filtered, decolourised with animal charcoal, evaporated to a syrup, and precipitated with 85 p.c. alcohol; there must be 100 c.c. of 85 p.c. alcohol for every 5 g. of dry substance. The solution is evaporated and the syrup treated in the same way, but with 99 p.c. alcohol and so that 100 c.c. of alcohol are present for every 3 g. dry substance. The clear alcoholic solution contains isomaltose and but a trace of dextrin, which may be removed by fractionating with alcohol. In this way 20 p.c. of the starch is obtained as isomaltose.

Lintner (Zeit. ges. Brauw. 1892, 6) finds the reducing power of iso-maltose to be 84 p.c. of that of maltose, i.e. K = 53.1, and its optical activity to be $[a]_D = 139^\circ$. He has not been able to crystallise it, and finds it under certain conditions fermentable by yeast and converted by diastase into maltose (Zeit. ang. Ch. 1892,

Trehalose. Mycose C₁₂H₂₂O₁₁.H₂O.
Occurrence.—It has been isolated from ergot of rye (Wiggers, A. 1, 173; Mitscherlich, 56, 15); trehala-manna, the hollow cocoons of the larvæ of an insect (Larinus maculatus) (Berthelot A. Ch. [3] 53, 232; 55, 272 and 291); and from various fungi (Müntz, C. R. 76, 649). Berthelot at first considered it a new sugar and called it trehalose, but afterwards found it was iden. tical with the mycose of Mitscherlich, and the Saccharum spermodiæ of Wiggers.

Preparation. - Any one of the materials mentioned is extracted with boiling alcohol of moderate strength; the alcohol is distilled off the clear solution. The residue is taken up with water and precipitated with basic lead acetate. The precipitate is washed with water and pressed: it is then suspended in water and submitted to a current of H.S. The clear filtrate from the lead sulphide is evaporated to a syrup, when the sugar crystalliscs and can be purified by recrystallisation. I may say that I do not find this mode of treatment answer very well; the filtrate from the PbS is, no doubt, clear, but the precipitate with the lead salt is bulky and unwieldy. I much prefer in this case, as in others of the same kind, fractional precipitation with alcohol; a few experiments will show the strength of alcohol best suited to holding or precipitating the sugar. (See also Apping.)

Properties.—The sugar crystallises in rhombs (C₁₂H₂₂O₁₁H₂O); it gives up its water at 100°, m.p. 109°; it is sweet, easily soluble in water and boiling alcohol, insoluble in ether. Specific rotatory power in squeous solutions

 $[a]_j = 199^\circ$ (Berthelot); $[a]_j = 192 \cdot 5^\circ$ (Mitscherlich); $[a]_D = 197 \cdot 28^\circ$ (Apping). These factors are unsatisfactory, and cannot be relied on to identify the sugar. It does not reduce Fehling's solution. Acids convert it very slowly into dextrose (Berthelot), there being no other product; but considering that five hours are required for complete hydrolysis, it is not possible that only pure dextrose could be formed. With strong nitric acid it yields a nitro- compound; with weaker acid no mucic acid is formed, but saccharic acid and finally oxalic acid. With acetic and butyric anhydrides it yields compounds identical with those produced from dextrose. Maquenne (C. R. 112, 947) says acetic anhydride yields $C_{12}H_{14}(C_1H_2O)_*O_{11}$. Alkalis do not act on it. On adding basic lead acetate, or an ammoniacal solution of the acetate, to its solutions a lead compound is precipitated. It appears to slowly undergo alcoholic fermentation in contact with beer yeast, but this has not been established with certainty. Phenylhydrazine does not form a compound with trehalose (Fischer, B. 17, 583).

Agavose C₁₂H₂₂O₁₁ (?) is obtained from the

juice of Agava americana; it is crystalline, soluble in water, and optically inactive (?). It is hydrolysed to a sugar or mixture of sugars $[a]_j = -14\cdot 4^\circ$. It reduces Fehling's solution; $K = 62\cdot 5$, agreeing nearly with maltose in this respect. It does not yield mucic acid on treatment with nitric acid. It is probably fermentable under the influence of some saccharomyces and yields alcohol, &c. (Michaud a. Tristan, Am.

Cyclamose $C_{12}H_{22}O_{11}$. A sugar obtained from Cyclamon europeaum, having a lavorotation $[a]_D = -15 \cdot 15^\circ$ or $-11 \cdot 4^\circ$; it is hydrolysed by dilute acids, when the lavorotation increases to

 $[a]_{\rm D} = -66.54^{\circ}$ (Michaud, C.N. 53, 232).

Parasaccharose $C_{\rm D}H_{\rm c2}O_{\rm H}$. This, together with another uncrystallisable sugar, is said to be obtained from cane sugar by the action of a yeast (Jodin, C. R. 53, 1252). It crystallises easily, and is easily soluble in water and difficultly in alcohol. It is dextrorotatory, having $[a]_1 = 108^\circ$, and it reduces Fehling's solution; K = 50 (about). Hot dilute sulphuric acid does not act on it, whilst hot dilute hydrochloric acid diminishes the optical activity and increases the K. On long digestion the solution becomes brown, and finally complete decomposition takes place.

Melibiose C₁₂H₂₂O₁₁ is obtained by the careful hydrolysis of raffinose by acids or invertase (see Raffinose). Its specific rotatory power is $[a]_b = +126:8^\circ$. It forms a hydrazide $C_{11}H_{12}O_{12}O_{13}$

a. Mittelmeier, B. 23, 1489). Invertuse converts it into galactose and dextrose.

Tewfikose C₁₂H₂₂O₁₁ occurs in the milk of the gamoose (Bos Bubulus). It is prepared by precipitating the milk by 4 p.c. acid mercuric nitrate (Wiley, Am. 6, No. 5 (?), neutralising the filtrate with NaHO, filtering out the precipitate, separating the mercury from filtrate by H.S. and concentrating the slightly acid solution to the crystallising point. A slight precipitate formed during evaporation must be separated. It is purified by two or three recrystallisations.

reduces Fehling's solution; K=73.6, hence less than lactose; if 7 molecules CuO were reduced by 1 molecule of sugar, the K would be 73.4, a near approximation; and D = 3.94 for the crystals, hence they are anhydrous. Acids hydrolyse it very easily, the only product being dextrose (Pappel a. Richmond, C. J. 1890, 758). The substance is, no doubt, an '-on' sugar C12H22O11, and is, like amylon, di-dextrose, and should not therefore yield mucic acid on treat-ment with nitric acid.

(c) Trihexoses. Raffinose C₁₈H₂₀O₁₆5H₂O, first obtained from a Tasmanian Eucalyptus manna by Johnston (C. J. 1, 159). This was the melitose of Berthelot (A. Ch. [3] 46, 66), who now says (C. R. 103, 533) that this term should be applied only to a loose combination of raffinose with eucalin, which is decomposed by re-crystallisation. From the evidence it would appear that the body first described as melitose was impure raffinose, and that the impurity even was not eucalin. It occurs also in cotton seed (Berthelot, *l.c.*; Ritthausen, *J. pr.* [2] 29, 357; Böhn, *J. pr.* [2] 30, 37); in beetroot (Loiseau, *C. R.* 82, 1058; Tollens, *A.* 232, 169; *B.* 18, 26; Rischbieth a. Tollens, *A.* 232, 172; *B.* 18, 2611); in beet juice (v. Lippmann, B. 18, 3087); in barley (O'Sullivan, Sumbal, B. 18, 3091; in bate-budg Richardson a. Crampton (B. 19, 1180); and again in Eucalyptus manna (Tollens, A. 232, 201); probably also in Soja beans. Loiseau considered it a product of the refining process, but v. Lippmann that it was ready formed in beet juice.

Preparation. - A molasses containing a fair quantity of railinose is selected, and the chief part of the cane sugar removed as monostrontium saccharate; on heating the solution raffinose and cane sugar bistrontium saccharates are precipitated. The compounds are decomposed by CO₂ and the sugar solution obtained again precipitated with strontia, when the cane sugar is precipitated as monostrontium saccharate, and raffinose remains in solution and may be purified by crystallisation (Scheibler, B. 18, 1409). Raffinose may be extracted from cottonseed cake and Eucalyptus manna by alcohol, and purified by crystallisation. See also Tollens (i.c.); Tenne (Zeit. d. Ver. 31, 795); Schaaf (Z. V. 33, 699); Wolff (Deutsche Zuckerind., 1887, 1413); Berthelot (l.c.); Lindet (C. R. 110, 795); Gunning (C. C. 1891, ii. 798).

Properties .- Rassinose crystallises in cauliflower - likes segregations consisting of thin microscopic rhombic prisms, which contain $C_{18}H_{32}O_{16}.5H_{2}O$. The $H_{2}O$ is in greater part eliminated in a vacuum over sulphuric acid, and the remainder easily at 100° (O'Sullivan). If heated too quickly it melts, and then cannot be dried without decomposition. Berthelot obtained crystals containing 6H₂O (C. R. 109, 548; Scheibler, B. 18, 1779; Rinne in Rischbieth Dissert. über Raffinose, Göttingen, 1885). It is easily soluble in water, very slightly in strong alcohol, and slightly in methyl alcohol, being much more soluble than cane sugar in this solvent. The dry sugar melts at 118°-119° (Scheibler, B. 19, 2868). Its solutions are optically active, the specific rotatory power of crystallised raffinose for the D line being [a]n = The solutions are dextrorotatory, $[a]_0 = 48.6^\circ$; it | 104.5° in 10 p.c. solution; $[a]_1 = 114.7^\circ$ or $[a]_1 = 114.7^\circ$

185.1° for the dry sugar. O'Sullivan observed $[a]_i = 185.8^{\circ}$. No bi-rotation has been observed. It does not reduce Fehling's solution. D = 3.712(Tollens, B. 18, 2616), but this is due to some misunderstanding; D = 3.956 (O'Sullivan, C. J.

1886, 70).

Action of acids. Hot dilute acids hydrolyse raffinose; galactose, lævulose, and probably dextrose are formed (Hädicke a. Tollens, Z. V. 37, 17; A. 238, 308; Beythien a. Tollens, A. 255, 214; Maquenne, C. R. 112, 799). By very careful hydrolysis, Scheibler a. Mittelmeier (B. 22, 1678) have obtained a saccharose and lævulose as the products of the reaction; the saccharose is a new body, which they have called melibiose (q. v.). The mixture of saccharose and lævulose has a specific rotatory power $[a]_D = 50^\circ$. Complete inversion of raffinose takes some hours. Invertase also hydrolyses raffinose (O'Sullivan). The products of hydrolysis are at first lævulose and melibiose (Scheibler a. Mittelmeier, B. 22, 3118), and melibiose is slowly acted on. When heated for some time with sulphuric acid, lævulinic acid is a product (Rischbieth a. Tollens, A. 232, 195).

Action of alkalis. By boiling aqueous solutions of strontia and raffinose, di-strontia raffintions of strontia and raffinose, di-strontia raffinose C₁₆H₂₂O₁₆(SrO)₂·H₂O is produced. Other compounds with baryta C₁₈H₂₂O₁₆·BaO, lime C₁₈H₂₂O₁₆·3CaO.2H₂O, lead oxide C₁₈H₂₂O₁₆·3PbO, and soda, C₁₈H₃₁NaO₁₆ and C₁₈H₃₁NaO₁₆·NaOH, have been prepared (Beythien a. Tollens, B. 22, 1047; A. 255, 195; Rischbieth a. Tollens, A. 232, 172)

232, 172).

Oxidation .- Nitric acid oxidises raffinose, producing 30 p.c. mucic acid, also saccharic and oxalic acids.

Fermentation .- Rassinose is slowly fermented by beer yeast (Rischbieth a. Tollens, A. 232, 242; Tollens, A. 232, 169; O'Sullivan, C. J. 1886. 73). Weak yeast only partially ferments it (Tollens, I.c.; Berthelot, C. R. 109, 548); the melibiose being with difficulty hydrolysed and fermented.

With phenylhydrazine a compound is formed, m.p. 187°–189° (Rischbieth a. Tollens, l.c.).

Melezitose C₁₈H₃₂O₁₈.2H₂O is obtained from Persian manna, a product of Alhagi maurorum (DC.), it crystallises in rhombic prisms, m.p. 147 -148° (when anhydrous); the specific rotatory power of the anhydrous body is $[a]_D = 87.7^{\circ}$. On inversion it yields turanose and dex-87.7°. On inversion it yields turanose and dextrose. Turanose C₁₂H₂O₁₁ [a]_D = 65°-68°, yields dextrose by the further action of acid (Alekhin, J. R. 21, 407).

(d) Hexahexoses.
Gentianose C₂₄H₂₂O₂₁. Obtained by A. Meyer
(H. 6, 185), from the root of Gentiana lutea, by extraction with alcohol, precipitation with ether and re-crystallisation from alcohol. It has a sweet taste, dissolves easily in water, m.p. 210°, does not reduce Fehling's solution, and ferments with yeast. It is hydrolysed by dilute acids; before inversion the optical activity is [a]_D = 83·6°; after, it is 20·2°, and has a reducing power equal to that of dextrose. Strong sulphuric acid chars it, like cane sugar.

Stachyse is obtained from the root of Stachys tuberifera. It has a sweet taste, is destrorotatory, having $[a]_b = 148 \cdot 1^o$ in 9 p.c. solution. It forms triclinic crystals. When in-

verted it yields galactose, dextrose, and imvulose. Its formula appears to be $C_{sc}H_{s}O_{32}+6H_{3}O$ (Planta a. Schulze, B. 23, 1692; 24, 2705), the products of the hydrolysis being the same as those of raffinose.

QUALITATIVE AND QUANTITATIVE DETERMINATION . OF SUGARS.

If the material to be examined is a solution, it must be made neutral, clear, and colourless if it is not already so.

If the material is a dry substance, it must be ground fine. If not sufficiently dry to admit of grinding, it must, if possible, be dried in vacuum over sulphuric acid, or, where this is not possible. in the open, at a low, gradually increasing temperature.

The finely-ground substance is extracted with alcohol sp. gr. 860-880. The solution is neutralised and the alcohol distilled off. The residue is taken up with water. The examination then comes under the head of a solution, and the treatment is the same.

The solution is turbid and coloured after neutralisation. The turbidity may be removed by simple filtration; if not, a little aluminium hydroxide (prepared by precipitating a solution of alum with excess of ammonia and washing free from ammonia and sulphuric acid) may be employed. A little (well washed) Swedish filter paper-pulp is at times found useful. The turbidity and colour may be removed together by animal charcoal, lead sulphide, barium sulphate, &c. Animal charcoal, either prepared from blood or bones, the former by preference, thoroughly extracted with hydrochloric acid and washed free therefrom, is best employed in all cases of investigation. The crude substances are employed to remove the colour, &c., from sugar syrups in the manufacture of refined cane sugar. These decolouring agents must always be used in the least possible quantity, and with the understanding that the charcoal especially is capable of taking up some sugar as well as Dried, freshly-made bone celouring matter. charcoal does not take up more than .006 p.c. of its own weight from pure cane-sugar solution (Casamajor, C. N. 41, 66). In quantitative work, when the decolourising agents have to be used it is well to have a knowledge of the influence of the agent on the sugar or sugars under examination. Charcoal retains sugar, other substances influence the optical activity. Part of the sugar is again given up on washing the agent with water, or the agent is placed on a filter and a portion of the solution to be examined passed through it and rejected before the por-tion intended for examination is collected. This is done on the supposition that the charcoal is sooner saturated with sugar than with colouring matter.

Having thus the sugars in clear solution, the means at our disposal for identification are:-

1. Taste of solution.

- 2. Form of crystals and melting-point thereof. Depression of the freezing-point (Raoult's method of determining molecular weights).
- 4. Specific rotatory power.

5. Reducing power.

- 6. Action of unorganised ferments: enzymes.
- 7. Action of organised ferments.

- 8. Action of acids.
- 9. Action of alkalis.
- Action of phenylhydrazine, and melting-points of the resulting osazones and hydrazides.
- 1. The solution tastes sweet if a sugar is present. It must not be forgotten, however, that some other bodies are also more or less
- 2. On evaporating this solution (best in a vacuum) to a syrup, if there is no preventive material present, crystallisation takes place. The microscopic appearance of the crystals will often be sufficient to identify the sugar; indeed, the habit of crystallisation will often suffice. substance or substances may be present which altogether prevent the crystallisation of the syrup, although it may contain a crystallisable sugar. This substance may be an inorganic or organic salt, or another body, or, indeed, another sugar. Treatment with strong or absolute ethylic or methylic alcohols may at times eliminate some or the whole of the substances preventing the crystallisation, and dissolve the sugar in so clean a state as to admit of the formation of crystals on concentration.

3. Depression of the freezing-point (Raoult's method). For references to Raoult's work see Victor Meyer, B. 21, 536; Auwers, id. 701; Tollens a. Meyer, id. 1566; and Brown a. Morris, C. J. 1888, 610. When crystals are obtainable from the solution as described above, a determination of the molecular weight by this method will decide to which group it belongs: a hexose or a pentose, a dihexose or dipentose, a trihexose. In the recorded observations water of crystallisation appears not to have received proper attention. Tollens a. Meyer record observations for dextrose C₈H₁₂O₆, so do Brown a. Morris. Water of crystallisation is not taken into account; the former treat of $C_{12}H_{22}O_{11}.H_1O$ for lactose, the latter omit the H_2O , while both employ crystallised raffinose $C_{13}H_{22}O_{12}.5H_2O$, mol. = 594, with the result that T. a. M. find the observed molecular weight between 544 and 644, and B. a. M. between 518 and 533. In these experiments with raffinose and lactose, it is not possible to say whether it is intended that the crystallisation water functions with the solid sugar or with the water; the calculations make it function with the sugar, but the results, as might have been expected, are unsatisfactory-it does not function with the sugar. It is perfectly clear that water of crystallisation of a sugar must be looked upon as water in observations with this method-that the quantity of dry sugar should be the factor dealt with. If the crystals contain water of crystallisation it should be determined and allowed for. A determination of the D will give some information as to whether a dry sugar or one containing water of crystallisation is being dealt with. The D of the different sugars in the dry state is given under each sugar. Between 8 and 15 g. dry substance is dissolved in water and the solution made up to 100 c.c. at 15.5°. A determina-tion of the specific gravity of this will give a means of calculating the D, and the number of g. of water to substance employed in the solution. About 60 c.c. of this solution are introduced into a thin glass (120 c.c.) beaker. The

mouth of the beaker is loosely closed with an indiarubber plug, in which three holes are bored. One of these, in the middle, admits of the introduction of a thermometer; the second, at the side, carries a stirrer, of very thin glass rod or platinum, best in the form of a flat coil, so that when the stirrer is moved up and down in the liquid the thermometer will be in the middle of the coil; and the third, also at the side, to admit of the introduction of a small solid particle of the frozen solution or of ice. The thermometer must be graduated for 2° or 3° above and below 0° to the 20th of a degree. By means of a telescope, if the divisions are open, and they should be so, readings to '005° can be made with a fair amount of accuracy. The beaker thus charged and fitted is placed in a freezing mixture of ice and salt—which should not be at too low a temperature, -4° to -5°, not more than 2°-3° below the freezing-point of the solution—contained in a strong beaker of 500-600 c.c. capacity. In a short time the temperature in the inner beaker will be observed to sink below 0°, and, on rapidly moving the stirring rod up and down, to go gradually lower and lower until a point is reached when the solution begins to freeze. This may be accelerated by adding a particle of the solution previously frozen; when freezing begins the mercury of the thermometer rapidly rises and soon becomes stationary. This is the freezing-point of the solution c, and is the observation upon which the molecular weight of the substance employed is calculated.

$$\mathbf{M} = \frac{19}{\mathbf{A}}, \qquad \mathbf{A} = \frac{\mathbf{c} \times \mathbf{y}}{\mathbf{x} \times 100},$$

x = g. substance; y = g. water, and 19 is a number calculated by Raoult for water as a solvent from observations with well-defined compounds. examples, Brown a. Morris (l.c.) with a solution containing 8.258 g. sucrose and 94.93 g. water observed a freezing-point $c = 0.490^{\circ}$, thence

$$M = \frac{.49 \times 94.93}{8.258 \times 100} = 337.5$$
. $C_{12}H_{22}O_{11} = 342$.

Hence, if an unknown sugar were under observation there would be no doubt left as to the molecular weight. O'Sullivan (C. J. 1890, 59) observed for arabinon: sp.gr. sol. 1.02554, y = 96.088 g., x = 6.466 g., $c = 0.535^{\circ}$; thence $96.088 \times .535$ $19 + \frac{96.088 \times .535}{6.466 \times 100} = 239.2$,

$$19 + \frac{96.088 \times .535}{6.466 \times 100} = 239.2$$

the molecular weight of the new sugar. A dipentose requires 282. The indications agreed with further confirmatory observations. the solution contains more than 12 g. per 100 c.c. the results are low; with most sugars a solution containing from 5 to 8 g. substance per 100 c.c. gives the best results, and with more dilute solutions the results are again low. Raoult's latest observations (C. R. 114, 264) for sucrose, made with apparatus constructed to meet the exact requirements of the case, the concentration of the solution being 5.839 g. sucrose in 100 g. water, work out M = 323, against 342, the true molecular weight. The results are, even under the best conditions, low; but the indication is sufficiently good to enable us to decide to which group the sugar we are dealing with belongs. If, instead of the factor 19, 19.8 were substituted, the results would agree with the accepted molecular

SUGAR.

weight of sucrose, and it is probable that this number or 20 will be finally decided upon as the constant.

4. Specific rotatory cower. If the form of the crystals or their habitat does not indicate the sugar present, a determination of the specific rotatory power may give the desired informa-tion. This is the quantitative expression of a property possessed by the sugars in common with many other substances. When light from any source is examined through a Nicol prism-i.e. polarised—no change is evident; but if the light, after passing through one prism (the polariser) is examined by another, it is found that in certain positions of the examining prism or analyser, as it is called -no light passes. If the analyser is made to carry an index, and is so mounted as to rotate with its axis at right angles to a disc graduated to degrees, it will be found that, if the position of the two prisms is so arranged that the index is at 0° on the graduated circle when no light passes, light will pass on the least rotation of the analyser to the right or left, and if the movement is continued another position is found on the disc in which the light is again cut off. This is at 180°, so that the circle should be graduated to 180° right and 180° left. Now, if a cell or tube with flat glass caps be filled with a solution of, say, sucrose and introduced between the two Nicols, and the source of light be a Bunsen burner flame coloured yellow with sodium chloride, when the index of the analyser is at 0° it will be observed that the light passes, and that on rotating the analyser a certain number of degrees to the right a point is found (which is not 180°) at which the light is cut off; and if note be taken of the exact number of degrees, and the analyser rotated further, it is found that the light is not again cut off at 180°, but the same number of degrees beyond 180° as the first extinction was beyond 0°. This is the optical activity of the sugar or. This is the optical activity of the sugar solution. It is the power of rotating the plane of polarisation of the ray passing through the polariser so as to admit of its passing through the analyser when it would not pass had the sugar solution not been introduced. The amount of rotation of the analyser to again find the direction of the plane of polarisation, as indicated by the index on the graduated disc, is the measure of the activity of the sugar solution, and the direction of the movement of the index is the direction in which the rotation has taken place; in the present case (i.e. when the index is moved on the disc in the direction of the hands of a watch) right or +. If the sugar solution be now hydrolysed by dilute acids or invertase, and again introduced between the Nicols, it is found that the analyser must be rotated to the left in order to find the position of extinction—i.e. the direction of the plane of polarisation of the rotated ray. This is left rotation, and is indicated by the sign -. On further rotation of the analyser light again passes, and finally there is a second extinction as far beyond 180° as the first extinction was beyond 0°. From this it is clear that the second reading may indicate right-handed rotation as well as left. Say the first extinction was 10° left of 0° (-10°), the second would be +170°, 10° less than 180°; then the activity might be

-10° or +170°. On diluting the solution say one-half, if the activity is — the readings will be -5° and $+175^{\circ}$, if + they will be $+85^{\circ}$ and -95°. The exact measurement of this activity has been the subject of much investigation, and many plans have been devised to facilitate the operation. It is, however, beyond the scope of this article to deal more fully with the subject (for details see Das optische Drehungsvermögen organischer Substanzen, Landolt, Braunschweig. 1879, Engl. Trans.; Handbook of the Polariscope, Macmillan & Co., 1882; Watts' Dictionary, Suppl. 3, art. Light. In the experiments above described the light of a sodium flame was employed; it was observed early in the investigation of the phenomena that readings sufficiently accurate, especially if the amount of activity was small, could not be obtained. Hence other devices were introduced. In the literature we find the activity expressed [a]_R, [a_j], or [a]_D and [a]_B, [a]_O, [a]_{Li}, &c.
[a]_R values are not now used. They were

[a]_R values are not now used. They were obtained by employing white light, and interposing between the polariser and the source of light a plate of red glass. They are of no value for our purpose, and may be neglected.

value for our purpose, and may be neglected.
[a], values are frequently used, but unless they are referred to a definite standard they, too, are of no value. If any ordinary source of white light be substituted for the sodium flame in the experiments above described, it will be observed that on rotating the analyser to find the effect produced by the sucrose solution no position of the analyser can be found in which all the light is cut off, but at one stage marked blue light passes, and, on further rotation of the analyser, red. This is due to the fact that the sugar solution acts unequally on the different rays of which the beam of white light is composed, the red rays being rotated least and the violet most, so that when the analyser is rotated the ray the plane of polarisation of which is rotated least is first cut off. The first cut off rays are the red, the complement of those cut off passing, the dominant being blue; on further rotation the carefully it is found that the transition from the blue to the red is well marked; this is the a, value; it is the, so-called, transition tint, the ray complementary to the median yellow, jaune moyen; hence a_j. For the same strength of sugar solution the position of the analyser is not the same for every source of white light. The stage at which the transition appears with candle-light is different from that at which it appears with gas-light; the stage in this case differs again from that obtained with the electric light, and even the position for direct sunlight differs from that of the light reflected from a cloud. Hence, when a pair of Nicols are employed as described above, even when the source of light is given, a cannot be looked upon as a standard value. This value has, however, been given to it by the French instrument makers.

Soleil invented an instrument with which lamp- or gas-light is employed (afterwards improved by Duboscq, and known as the Soleil-Duboscq (see Watts' Dictionary, 1st ed. 3, 674, a. Suppl. 8, 1199), by which the activity of a solution is measured by divisions of a sole instead of degrees; 100 of these divisions were

made equal to the amount of rotation promade equal to the amount of research pro-duced by 1 mm. quartz for the a; this was considered to be 24°. Of course, if this is taken as a standard it is of full value; it may not be truly α_1 even for the quartz, but it is α_1 referred to a definite measure, the 100 divisions of the instrument being 24°. This was complicated by the fact, since pointed out by Scheibler, that quartz from different sources has not the same optical activity; hence we have various observers giving different values for the amount of sucrose in 100 c.c. solution, which when observed with the Soleil-Duboscq instrument, in a tube 200 mm. long, equals the activity of 1 mm. quartz. If, however, we look upon the 100 divisions of the instrument as = 24° a_j, we have a standard value for the expression. I believe this is the value given to it by the French observers. The writer employed it in the same way. Another instrument of much the same construction is the Soleil-Ventzke-Scheibler (v. Watts, l.c.). In this the 100 divisions of the scale are made to represent the activity of 26.048 g. saccharon in 100 c.c. solution; we have only to inquire as to the [a] and [a] of cane sugar to arrive at a value in degrees of the 100 divisions for these two expressions. From these two factors we get 100 divisions, Soleil-Duboseq = 24° a, and $21.67^{\circ}a_{\rm p}$, and 100 divs. S.V.S. = 38.34° a, and $34.55^{\circ}a_{\rm p}$. The angular value or any other instrument in use in which the scale is given in divisions can be calculated for a or a by ascertaining the number of divisions required to compensate a solution of sucross containing 10 g. in 100 c.c. at 15.5°, and taking the apparent specific rotatory power of the sugar for the concentration to be $[a]_1 = +73.8^{\circ}$ and $[a]_p = 66.6^{\circ}$, the value of the divisions in degrees for both rays can be calculated. The direction of the rotation is indicated in these struments by the direction of the movement of the 0 point to find the compensation necessary; if from left to right it is right or +, if in a contrary direction left or -. With the other instruments in use sodium flame is the source of light employed; the readings are therefore ap. The scale is a circle graduated to degrees on a disc, beginning with 0 at the top and graduated in half degrees and degrees to 180° to the right, and in the same way to the left. The analyser rotates in the axis of this disc, and carries an index with vernier, which admits of readings being made to minutes. The arrangement is such that the polarised ray before en-tering the active solution has the appearance of a circular disc divided into halves by a perpendicular diameter. The position of the plane of polarisation is not the same in both semidiscs so that when the light is completely out off at one side it passes at the other, and vice versa. To find these positions the analyser has to be rotated several degrees, but between the two positions of complete cut off there is a position of the analyser in which the two semi-discs are equally illuminated; this is a wellmarked position distinctly ascertainable. The 0 point of the index and of the graduated scale are made to correspond exactly with it. It can always be found to within less than a minute. When the active substance is introduced the equality of the illumination of the semi-discs is Vol. IV.

destroyed; the analyser is rotated until it is again restored. The amount of rotation as shown by the graduations gives the activity in degrees and minutes, of degrees and decimals, according to the make of the vernier. These are the half-shadow instruments, of which the Jellet-Cornu and Lourent are examples (see Watts, l.c.). Other devices have been employed to facilitate an accurate determination of the position of the plane of polarisation of the ray before and after rotation; a description will be found in Landolt and in Watts (l.c.). Recently an instrument has been introduced in which the half-shadow contrivance is adopted, white light (a strong gas-flame) being employed. The scale is the same as that of the Soleil-Ventzke-Scheibler instrument; readings with it can be made with great accuracy. It is manufactured by Schmidt & Haensch, Berlin.

When it is necessary to determine the activity for rays of other refrangibility, say for the lithium or the thallium flame, it is only necessary to colour the Bunsen flame with these metals in the same way as in the case of sodium above. The readings are then c₁₁ and α_{Th}. The α_B, α_O, α_D, &c. for any active substance can be found by employing a pair of ordinary Nicols as described above—white light, best a ray of sunlight, being employed—and examining the light after passing the analyser, with a spectroscope. If the positions of the lines of the solar spectrum are marked, the amount of rotation for the active substance introduced between the polariser and the analyser is found, when on rotating the analyser the thickest part of the black band is on the marked position of the line of the spectrum. This is read off on the scale connected with the analyser.

With any of these instruments we can determine the optical activity of a sugar and thus identify it. The sugar is crystallised; it is dried, and 10 g. or thereabouts carefully weighed out. This is dissolved in water, and the solution made up to 100 c.o.' at 15.5°. A portion of this is introduced into a tube of definite length, and an observation made with any of the instruments mentioned above. The formula $[a] = \frac{a_1 \cdot 100}{1.0^{\circ}}$ gives the apparent specific rotatory power for the concentration. a = the angular disturbance observed, l = length in decimetres of tube employed, and c = grams substances in 100 c.c. Let us take an example, 10 g. sucrose, dissolved and made up to 100 c.c. Disturbance observed in a 200 mm. tube with a Soleil-Duboseq instrument, = 61.5 divs.; now for a_1 100 div. = 24°. Then, substituting the values in the above formula we have

$$\frac{61.5 \times .24 \times 100}{2 \times 10} = [a]_{i} = +73.8^{\circ}$$

100 divs. = 21.67° a_D; then

$$\frac{61.5 \times .2167 \times 100}{2 \times 10} = [a]_{p} = +66.6^{\circ}.$$

The scale of the Soleil-Ventzke-Scheibler instrument is so graduated that 100 divisions - the activity of a solution of sucrose containing

This is practically the usual 100 c.o. of a volumetric analysis. For more accurate manipulation see Landola This is, however, unnecessary for the kientification of the sugar—our purpose.

26 048 g. in 100 c.c. in a 200 mm. tube. The apparent specific rotatory power of sucrose in a solution of this concentration is $[a]_D = 66^\circ 33^\circ$ and $[a]_1 = 73^\circ 61^\circ$. Substituting these values in the tormula we get

$$\frac{x.100}{2 \times 26.048} = 66.83;$$

x =the value of 100 divisions in degrees a_D $= 34.55^{\circ}$, and

$$\frac{x' \cdot 100}{2 \times 26.048} = 73.61;$$

 α' = the value of 100 divisions $\alpha_1 = 38.34^{\circ}$.

It is of importance that the values in degrees of the scales of these two instruments should be clearly understood. We find it stated that a quantity of sugar varying from 16:49 to 16:35 g. in 100 c.c. require, in a 200 mm. tube, a compensation with a Soleil-Duboscq instrument = 100 divisions: 16.35 g. is the best-recognised factor; from my observations it is still too high.

y observations it is still too light.

$$\frac{100 \times 24 \times 100}{2 \times 16 \cdot 35} = [a]i = 73 \cdot 39^{\circ}, \text{ and}$$

$$\frac{100 \times 2167 \times 100}{2 \times 16 \cdot 35} = [a]_{D} = 66 \cdot 27^{\circ},$$

figures slightly too low for the apparent specific rotatory power of sucrose for the c, hence 16:35 g. is too high. The number, no doubt, should be 16:28, and this gives factors agreeing well with the observed [a]D and [a], for the c.

A solution containing 10 g. sucrose in 100 c.c. requires a compensation in a 200 mm. tube of 38.5 divisions f a Soleil-Ventzke-Scheibler instrument.

$$\frac{38.5 \times 3834 \times 100}{2 \times 10} = [a]_1 = 73.8^{\circ} \text{ and}$$

$$\frac{88.5 \times 3455 \times 100}{2 \times 10} = [a]_0 = 66.5^{\circ},$$

numbers agreeing accurately with the specific rotatory power for the c. The optical arrangements of these instruments admit of the employment of white light.

If either of the sodium-flame instruments is employed the angular disturbance is introduced directly into the formula. With the 10 g. in 100 c.c. solution of sucrose, the reading in a 200 mm. tube is

 $\mathbf{s_D} = +13.3^\circ$, then $\frac{13.3 \times 100}{2 \times 10} = [a]_D = 66.5^\circ$. The use of this factor is obvious. We have a solution of a known sugar of unknown strength, and want to find the c (g. in 100 c.c.). An observation is made in a tube of known length,

 $a_D \text{ or } a_j$; then $\frac{a.100}{l.c}$ = the determined value of [a]D or [a], a the ray for which the observation is made, and [a] the specific rotatory power for that ray, according to the light employed and

concentration, $c = \frac{a \cdot 100}{[a] l}$

It has been shown that if a solution contains two or more active substances, the observed activity is the algebraic sum of the activities of the constituents. The specific rotatory power of each individual sugar is given in the description of it.

5. The reducing power. As has been stated, most of the sugars possess the power of redu-

cing the oxides of the higher metals and some organic colouring matters. Various propositions have been made to employ this property as a means of qualitatively and quantitatively determining the sugars, and various solutions have been proposed for that purpose; but speaking with many years' experience I may say that they may all be discarded in favour of alkaline copper solution, Fehling's solution; and even with regard to the value of this a great diversity of opinion exists. But there is a general agreement that if the conditions under which it is used are constant the results are constant. For literature see Becquerel, A. Ch. [2] 47, 15; Trömmer, A. 38, 360; Müller a. Hagen, Pf. 23, 221; Neubauer, Fr. 1, 378; Maly, Fr. 10, 383; Seegen, C. C. 1875, 223; Fehling, A. 72, 106; Seegen, C. D. 1818, 225; Feshing, A. I., 100; Claus, J. pr. [2] 4, 63; Neubauer, Ar. Ph. [2] 71, 278; Patterson, C. N. 25, 149; Loisoau, C. R. 1873. 26; Soxhlet, J. pr. [2] 21, 227; Krause a. Städeler, C. C. 1854. 936; Gräger, Fr. 7, 490; Buswitz, B. 11, 1445; O'Sullivan, C. J. 1876, 2, 125; Märcker, C. 7, 699; Brunner, Fr. 11, 32; Bayley, C. N. 37, 211; Allihn, J. pr. [2] 22, 55; Salomon, B. 14, 2711; Digener, Z.V. 31, 349; Salomon, B. 14, 2711; Digener, Z. V. 31, 349; Schwarz, A. 84, 84; Mohr, Fr. 12, 296; Perrot, B. 9, 19; Ulbricht, B. 10, 128; Jean, C.R. 73, 1397; Scheibler, Z. 9, 820; Weil, Fr. 11, 284; Arnold, Fr. 20, 331; Volhard, A. 190, 1; Soldaini, B. 9, 1126; Possoz, C. R. 1874, 721; Pellet, J. Fabra 19, 22; Pavy, C. N. 39, 1004; Löwe, Fr. 9, 20; Vogel, J. Ph. [2] 1, 245; and others of less value. As a result of a study of all this literature, I may say that I have come to the conclusion that if the Fehling's solution is carefully made with pure materials. and em is carefully made with pure materials, and employed as described below, the reducing power of any sugar can be determined with constancy and accuracy, and when the conditions are fulfilled the reduction is molecular—i.e. a definite number of copper oxide molecules are reduced

by a definite number of molecules of the sugar.

Fehling's solution is made as follows:
34.61 g. pure recrystallised copper sulphate are dissolved in 400 c.c. H₂O or thoreabouts, 173 g. sodium potassium tartrate (Rochelle salt), and 74 grams freshly-prepared sodium hydroxide (commercial stick soda) are dissolved to 450 H₂O; when the solution is cold it is gradually added to the copper solution in small portions at a time, so that the pp. at first formed is re-dissolved. When both solutions are mixed the volume is made up to 1 litre. It is very generally stated that this solution does not keep very well. I found it constant in its properties for more than twelve months when kept in carefully-stoppered bottles, sealed with paraffin in a cool, dark place. Some recommend that both the solutions be made up to 500 c.c., kep separately and mixed in equal volumes when re quired for use. This is probably the better plan but unless the solutions are kept in well-stop pered bottles sealed they will deteriorate a badly as if mixed. This solution is used as (a a qualitative test for the reducing sugars.

O. = Organ des Centralvereins für Rübensuckerfabrication in der ötterreichtsch-ungarischen Monarchie.

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Redewald a. Tollens (B. 11, 2072) employ 60 g and they say the increase of alkali to 70 g. diminishe the reducing power of lactose about 1 p.o.

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is also used (b) quantitatively, to determine the reducing power and the quantity of a sugar.

(a) Qualitatively. A portion of the solution supposed to contain sugar, prepared as described, is heated to boiling in a small beaker or test-tube, and is added to 5 c.c. of the alkaline copper solution previously diluted with its own bulk of water, and heated to boiling. The production of a red pp. of Cu₂O indicates the presence of a reducing sugar. There are substances besides the sugars capable of reducing Fehling's solution. The absence of these must be established before it can be inferred that the reduction is due to sugar.

(b) Quantitatively. The reducing power of a sugars, or of a solution containing reducing sugars, can be determined volumetrically or gravimetrically, with Fehling's solution. It is now very generally admitted that the gravimetric method gives the only reliable resulfs.

method gives the only reliable results.

Volumetrically. The sugar solution, prepared as described, should be diluted (0.5 to 1.0 g. reducing sugar in 100 c.c.). This is introduced into a burette, and the Fehling's solution into a second one. Of the latter a definite quantity, say 10 c.c., is measured into a porcelain dish of about 60 to 100 c.c. capacity, and diluted with four times its own bulk of water. The dish is then placed over a small Bunsen, and the contents heated to boiling. The sugar solution is then run in a c.c. at a time until the blue colour of the copper solution has nearly all disappeared, then drop by drop until it has quite gone. The first experiment may only give approximate results; in a second a quantity of sugar slightly less than was found necessary in the first experiment is measured into a small beaker, heated to boiling, and mixed rapidly with the boiling dilute copper solution. If the whole of the copper is reduced, a few drops more of the Fehling's solution are added from the burette. A few experiments of this kind will give fairly approximately the amount of copper solution a certain quantity of the sugar solution is capable of reducing. That the Fehling's solution is not in excess is seen by the absence of blue on subsidence of the Cu.O, and may be confirmed by filtering a little and testing for copper with a dilute solution of potassium ferrocyanide in acetic acid. The absence of a brown colouration indicates the absence of CuO. If the sugar is in excess, more CuO solution is decolourised, but after boiling the sugar in the alkaline solution the amount reduced is not a measure of the quantity of sugar. The final experiment must be performed after two or more observations, when the relative value of the two solutions has been approximately ascertained, as described above, by adding the whole, or nearly the whole, of the sugar at a boiling temperature to the copper solution at once. If only a few drops of the sugar solution are required to remove the last traces of CnO, the error is not great; 10 c.c. of the Fehling's solution, made as directed, contain ·1100 g. CuO; 396 CuO = 180 dextrose, i.e. 5 mols. CuO (79.2 + 5 = 396) are reduced by 1 mol. dex-180, then 396:110 = 180:050 grams dextrose = 10 c.c. Fehling's solution. Soxhlet (l.c.) states that the value of the CuO solution in dextrose varies with the way in which the experiment is performed; that 10 c.c. undiluted Fehling's solution are reduced by

0-04753 g. dextrose, while it takes 0-0494 to reduce the same bulk diluted with four measures of water. The same applies to the other reducing sugars, only in the case of lattose dilution has no effect, while in that of maltose dilution diminishes the amount of sugar required. This is, no doubt, correct under the conditions stated, but it is not necessary in dealing with a reaction of this kind to deviate from recognised conditions such as those laid down above. When these are adhered to it is found that the reducing power of the sugar very closely approaches molecular interaction; in fact, so much so that the molecular relation most closely approximated to by the experimental data may be taken as the normal reducing power of a sugar. These normals for the better-known sugars are:—

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10 c.o. Fehling's solution = 0.0500 g. dextrose.*

" 0.0500 g. lectrose.

" 0.0500 g. lectrose.

" 0.06334 g. lactose.†

" 0.07196 g. maltose.†

" 0.04630 g. arabinose.

" 0.08701 g. arabinose.

Saxhlet says the reducing power of lawrolose is different from that of dextrose. This is not supported; his error is due to his mode of preparing invert sugar.

† Sugar free from water of crystallisation.

Gravimetrically. The Fehling's solution is prepared as described; 25-30 c.c. of it are measured into a beaker of 130-140 c.c. capacity, and about 50 c.c. well boiled water added. The beaker is then placed in a boiling-water bath, consisting of a larger beaker in which water is kept boiling. At the end of five or six minutes, when the dilute copper solution has acquired the temperature of the bath, a known weight or measure of the sugar solution is heated to boiling, and added. If at the end of a few minutes the blue colour is completely destroyed, it can be restored by adding more Fehling's solution, but it is much better to so arrange matters by a few experiments that the amount of sugar solution employed will reduce the Fehling's as nearly as possible, leaving only sufficient blue, on subsidence of the Cu₂O, to make it evident that the copper solution is in slight excess.

After twelve fourteen minutes' boiling the clear supernatant liquid is decanted on to a filter, the Cu₂O is washed by decantation, and finally on the filter. If the Febling's solution is in large excess it is difficult to wash the filter free from unreduced copper oxide (blue colouration), but if the excess is only slight there is no indication that the filter retains copper compounds other than Cu2O. Ignition for four or five minutes in , an open porcelain crucible converts the red precipitate into black copper oxide CuO, in which form it is weighed. From this the sugar is calculated by multiplying by the constants (see next page). It may be again pointed out that the factors given by various authorities differ more or less from these (see the K of individual sugars), but I believe these are the constants, the differences amongst the authors being due to manipulation, to the state of dilution and alkalinity of the solutions, and to the temperature of the mixed sugar and CuO solution. An imperfect knowledge of the composition of the material is a source of error. In dealing with some solutions, other

1	mol.	sugar	to 5 mols.	CuO	: 1 g.	CuC) = 0·4545 g. dextrose	: K = 100
	33	"	5,,	**	1 g.	59	= 0.4545 g. galactose	: K = 100
	,,	,,	5,,	**	1 g.	,,	= 0.4545 g. lævulose	: K = 100
	**	**	7.5 ,,	99	1 g.			: K = 77·67
	,,	"	6 "	,,	1 g.	>2	= 0.7196 g. maltose	: K = 68·16
	**	**	4.5 "		1 g.	•	= 0.4209 g. arabinose	: K = 108·8
	**	,,,	4.5 ,,		1 g.		= 0.7910 g. arabinon	: K = 57·5
					•		• -	

These should be ascertained, determined, and allowed for. In dealing with solutions in which ammonia is found, or liberated by the alkali, Cu₂O is retained in solution. Sundry propositions have been made to avoid the disturbing influence of the alkali in Fehling's solution, but they seem to have met with no favour. Sold ini (B. 9, 1126) proposed copper carbonate in potassium bicarbonate; Possoz (G. R. 1874, 721) and Pellet (J. fb. 19, 22) other solutions of copper in alkaline carbonates. Löwe (Fr. 9, 20) re-commends the use of a solution of CuO in glycerol, but so far little can be said of the value of the solution. In cases where the sugar solution contains other substances than reducing sugars capable of giving a precipitate with Fehling's solution without reduction, the whole precipitate may be dissolved in hydrochloric acid, made strongly alkaline, and added to an excess of ammoniacal solution of silver nitrate. The copper suboxide reduces an equivalent quantity of silver oxide. The silver in the precipitate may be estimated as chloride (Jean, C. R. 73, 1397). As has been stated above, many other solutions and modifications of Fehling's solution, have been proposed for employment in determining the sugars, but they appear to be of no value.

Pavy (i.e.) recommends the addition of sufficient ammonia to the Fehling's solution to hold the Ou,O in solution; the disappearance of the blue is then the indicator of the reaction. The reducing powers for sugars other than dextrose for this solution have not been ascertained; even for dextrose it is doubtful (v. Hehner, An. 6, 218).

Three solutions of mercury salts have been proposed as agents by which sugars can be determined by their reducing power—the one known as Knapp's solution, the other as Sachsse's solution, and the third as Hager's solution. Neither of them are of high value, except in certain circumstances, but Hager's least of all.

Knapp's solution is made by dissolving 10 g. HgCy, in about 600 c.c. water, then adding gradually 100 c.c. sodium hydroxide solution, specific gravity 1·145, and diluting the clear solution to 1 litre; 10 c.c. of this solution equal 0·025 g. dextrose; but according to Soxhlet (l.c.) this is not true, and the quantity varies with the conditions under which the reducing solution and reducible one are brought in determining the absence of mercury. The solution is used as follows:—40 c.c. of it are heated to boiling in a flask, and the sugar solution, which should not contain more than 0·5 p.c. reducing sugar calculated as dextrose, run in as quickly as possible until the whole of the mercury is ppd. as such, the mixed liquids being kept continually boiling. The complete presipitation of the Hg is ascertained by testing for

schekances may be precipitated with the Cu₂O. It with ammonium sulphide, or alkaline tin solutions about for. In dealing with solutions in which ammonia is found, or liberated by the alkali, cu₂O is retained in solution. Sundry propositions have been made to avoid the disturbing influence of the alkali in Fehling's solution, but they seem to have met with no favour. Sold and (B. 9, 126). According to the solution, 2020-202 g. dextrose. 126) proposed corporate in postssium.

reduce 100 c.c. of Knapp's solution. Sachse's solution is made to contain in 1 litre 18 g. mercuric iodide, 25 g. potassium iodide, and 80 g. potassium hydroxide. The mercury salt is dissolved in a solution of the potassium iodide, the solution of the potassium hydroxide added, and the mixture made up to the litre. A measured quantity, 40 c.c., of the solution is boiled in a porcelain dish, and the sugar solution, containing not more than 0.5 g. per 100 c.c., run in until a drop of the supernatant liquid ceases to give a brown colour with an alkaline solution of tin chloride. It is said that in using this reagent more mercury is reduced by adding the sugar slowly than by adding it all at one time, the reverse being the case with Knapp's solution. Soxhlet (l.c.) compares-the value of these solutions for the reducing sugars as follows:-

Taking the reducing power of dextrose = 100, the reducing powers (K) of the other sugars are:

•	Fehling (undiluted)	Knapp	Sachsse
Dextrose	100	100	100
Invert sugar .	96.2	99	124.5
Lævulose .	92.4	102·2	148.6
Galactose	. 93.2	. 83.0	74.8
Lactose (hydrated	?) 70·3	64.9	70·9
Maltose (dry?).	. 61.0	63.8	. 65.0

These relations for the K of the sugars for Fehling's solution do not agree at all with the generally recorded numbers (v. K of individual sugars); there are no data to enable one to form an opinion on the value of the K for the other solutions.

Potassium ferricyanide has been proposed as an agent for determining the reducing power of the sugars by Gentele (Er. 9, 453), but although Stahlschmidt (B. 1, 141), Stammer (D. P. J. 158, 40), and Sostmann (V. Z. 22, 170) have worked with it, we know nothing very definite about its value. It should yield definite results, as the complete reduction is definitely recognisable.

6. The action of unorganised ferments. Ensymes. Sucrose is converted by invertase into levulose and dextrose; the only other sugar acted upon by this enzyme is raffinose (Kjeldahl, Fr. 22, 588; O'Sullivan, C. J. 1896. 70; and O'Sullivan a. Tompson, C. J. 1890. 834), and, as it has been shown, the invertive action is most active at a temperature at which yeast, from which the invertase is prepared, has no fermentative action on the products of the inversion; yeast can be employed instead of prepared invertase. The products of the action of invertase

on rainness are sevulose and meliblose, the latter yielding finally dextrose and galactose. Raffinose is but very sparely distributed. It may be considered that sucrose is present if the optical activity of a solution is materially altered by treatment with invertase and the copper oxide reducing power at the same time increased. The absence of raffinose can be determined by the non-production of mucic acid on treatment with nitric acid. Before applying the invertase test the solution to be tested must be boiled. If this is not done, and active diastase and any of the high-starch transformation products are present, the latter would be acted upon by the diastase, the opticity lowered, and the cupric reducing power increased. "Diastase does not appear to act on any of the sugars, except isomaltose (?)

Other organisms, such as the moulds which grow on steamed rice, contain an enzyme capable of acting on maltose, but this substance has not been employed in the detection or estimation of maltose. There is no doubt, however,

mation of maltose. There is no it is available for the purpose.

7. Organised Ferments (see Fermentation). The hyphomycetes, saccharomycetes, and schizomycetenact on the sugars and yield various products, and, no doubt, can be made available for the detection and estimation of them; but we have only to concern ourselves here with the action of ordinary beer yeast (saccharomyces cerevisiæ); the changes effected by the other organisms come under art. Fermentation. On adding pressed yeast to a very slightly acid solution, and keeping the mixture at a temperature of 20° or thereabouts, if a fermentable sugar be present, a frothy head will form on the surface of the liquid, carbon dioxide will be evolved, and alcohol formed. The specific gravity and optical activity of the solution diminishes. Certain substances known as antiseptics prevent this reaction—they must be proved to be absent. The fermentable sugars, in this sense, are described as such under the respective heads.

The quantitative value of this phenomenon has been studied by many workers, but it is still unsatisfactory. It has been made available with approximate accuracy in determining the total fermentable sugars in presence of other substances from which they cannot otherwise be conveniently separated. The solution should be conveniently separated. The solution should be of about sp.gr. 1.050-1.060, slightly acid, and should not contain much foreign matter. A measured quantity of this is taken, best 100 c.c. if available, introduced into a 150 c.c. flask, and 0.5 to 1 g. freshly-pressed yeast added. If necessary, a little yeast ash dissolved in the least possible quantity of hydrochloric acid, together with a little ammonium tartrate, should be added. A temperature of from 20° to 22° is best suited for the process. The gas evolved is washed by being made to pass through a few c.c. water in two successive wash-bottles. In some cases the fermentation is very slow and takes many days to complete itself, in others it is rapid and is finished in a few days; but in all cases it should be continued as long as gas bubbles through the wash-bottles on shaking the flask in which the fermentation is going on. As soon as this point is arrived at, the contents of the flask are washed with the water of the wash-bottles into a distilling flask, and submitted to distillation. Dilute alco-

hol distils over and is collected in a 100 c.c. flask. If only 20-25 c.c. washerater were used, the distillate, when it amounts to 80-85 c.c., will contain all the alcohol produced. This is then made up to 100 c.c. and its specific gravity taken. On referring to the alcohol tables, the weight of alcohol in the 100 c.c. is ascertained. From this a knowledge of the amount of fermentable sugars is arrived at. Sucrose yields 51 p.c. alcohol, dextrose 48-49 p.c. (Pasteur, A. Ch. [3] 58, 330), maltose 50.4-51.8 p.c. (O'Sullivan, C. J 1876, 479). Hofmann, Graham, and Redwood (C. J. 5, 229) gave expression to the value of the specific gravity of distillate, in points or degrees of specific gravity lost by the saccharine solution fermented for various sugars. These factors are still employed in determining the original specific gravity of beer, from the alcohol it contains and the specific gravity of the residue after distillation. The residue left in the distilling flask mentioned above is with the washings made up to 100 c.c., the specific gravity of this solution subtracted from that of the solution before the yeast was added + 1-or 1000 if water be taken at 1000 instead of 1—will give approximately the specific gravity of a solution containing the amount of sugars or sugar fermented in 100 c.c. The average D of the sugars being known, the quantity fermented within 2 or 3 p.c. can be calculated from this. Inasmuch, however, as the value in specific gravity of the non-volatile products of the fermentation of the sugars has not been accurately determined, this mode of estimation can only be approximate.

It has been proposed to estimate the amount of sugar or sugars by determining the amount of carbon dioxide evolved during fermentation. Pasteur (L.) 'gives 0.4665 g. CO, as the product of 1 g. demose. Jodlbauer (Z. V. 25, 308) states that dry maltose yields 49.54 p.c. CO, and dextrose 46.54 p.c. These figures are, no doubt, true also for all the fermentable '-on' and '-ose'

sugars.

Some of the sugars when in the pure state are not fermented by yeast, but the presence of as small quantity of an easily fermentable sugar sets up the action. Pure galactose is not fer-mented by yeast; the presence of a little dex-trose, layulose, or maltose sets up the process (Bourquelot, C. R. 106, 283; Tollensa, Stone, B. 21, 1572; Stone a. Tollens, A. 249, 257), the fermentation of galactose being as complete as that of dextrose if the suitable nourishment is present. Under the same condition sorbose ferments more slowly and less completely, arabinose and lactose very slowly and incompletely.

Pure arabinose behaves like pure galactose. Sucrose is inverted by yeast, dextrose ferments easily, lævulose less so, maltose still less, and raffinose less still. The other sugars ferment only when these are present; hence it should be possible to detect the presence of individual sugars from the specific rotatory power and K by fractional fermentation. With some varieties of yeast lavulose ferments before dextrose (Dubourg, yeast tevening the 'ose' sugars and to be incapable of fermenting the 'on' ones. A study A study of the action of these organisms will yield results. valuable in the identification and estimation of the sugars.

8. Action of acids. All the di- and tri- sugars are converted in mono- sugars by the action of dilute mineral acids; this is accompanied by an alteration in the K and [a] of the solution. If this took place only with the high sugars, the reaction would be applicable in distinguishing the '-on ' and '-ose -on' sugars from the '-ose; but the K and [a] of these sugars are also affected by digestion with mineral acids, but much more slowly, so that the reaction is only available when carefully performed. If the sugar solution increase in K, and there is a material alteration in [a] on ten or twelve minutes' boiling with 2-3 p.c. sulphuric acid or hydrochloric acid. it may safely be inferred that a high sugar di- or tri-) is present. Some organic acids act differently on the high sugars. Dilute citric acid inverts sucrose; it is without action, at least material action, in a short time on lactose (Jones, l.c.). .

The invertive action of acids—except under well-defined conditions, such as the employment of hydrochloric acid by Clerget in hydrolysing sucrose—cannot, for the reason mentioned above, be employed in estimating these sugars.

Dextrose and substances capable of yielding it can be detected by acting on the material with nitric acid (1 pt. mat. 1 pt. H.O and 5 pts. nitric acid, sp.gr. 1·15). Saccharic acid, recognisable by the microscopic appearance of its acid potassium salt, is produced (Sohst a. Tollens, A. 245,1). Lævulose, galactose, sorbose, and arabinose do not yield this acid (Gans, Stone, a. Tollens, B. 21, 2148). Galactose, lactose, and raffinose, on treatment with nitric gold in the same way, yield mucic acid. This reaction has some quantitative value. Pasteur (C. R. 42, 349) obtained 75 to 78 p.c. mucic acid from galactose. The yield, however, varies very considerably with the quantity and strength of the acid employed. Kent a. Tollens (A. 227, 221) find on employing 1 pt. sugar, 12 pts. nitric acid, sp.gr. 1·15, allowing to crystallise in 1·5 to 2·0 pts. solution, and washing with 5 pts. water that galactose gives 77.4 p.c. mucic acid. Lactose treated in the same way gives 40 p.c., and raffinose (Rischbieth a. Tollens, A. 232, 172) 22-23 p.c. By using 1 g. dry sugar, or a quantity equal thereto, in a concentrated syrup, 4 g. nitric acid sp.gr. 1.25-1.24, heating gently until red fumes began to be evolved, then allowing the reaction to proceed until the violence was over, heating on a water-bath until red fumes ceased to be evolved. allowing to stand for 24 hours to crystallise, I obtained 73 p.c. mucic acid from galactose, 36.9 p.c. from dry lactose, and 28-30 p.c. from dry raffinose (O'Sullivan, C. J. 1886, 73). The mucie acid was collected on a tared filter, washed carefully with 50 c.c. water, dried in a vacuum over sulphuric acid, then at 100°, and weighed. By treating 0.5 g. mucic acid in the same way, the loss was 0.04-0.05 g. Corrected for this the above numbers become 80-81 p.c. for galactose and 40.5-41.5 p.c. for lactose. The number for raffinose was corrected.

The pentoses, and bodies from which they can be obtained, yield on digestion with strong hydrochloric acid, furfural, the detection of which is simple and definite. This reaction has been employed in the estimation of these sugars. It must not, however, be forgotten that the hexoses also yield furfural, although, no doubt, in very small

quantities (Günther a. Tollens, B. 23, 1751; de Chalmot a. Tollens, B. 24, 694; Stone, B. 24, 3019). The first difficulty to overcome was to determine the conditions under which the greatest yield of furfural was obtainable, the next to accurately determine the furfural. 2 to 5 g. of the material are digested with 100 c.c. hydrochloric acid, sp.gr. 1.06, and then distilling, returning the distillate until the reaction is complete; or the mixture of material and acid is submitted to distillation in a flask over a small flame, so that not more than 10 c.c. distillate pass over in five minutes, fresh acid being regularly added until a sample of the distillate ceases to give the reaction for furfural. The distillate is then neutralised with soda, acidified with a few drops of acetic acid, and made up to a definite volume. In this the furfural is estimated by a standard solution of phenylhydrazine, made by dissolving 2 g. phenylhydrazine chloride with 6 g. sodium acetate in 1 litre water. This is standardised with a solution of furfural of known strength (1 g. pure furfuramide in a little acetic acid to 1 ltr. water). Standardisation must be made before each set of determinations, as the phenylhydrazine solution loses its valm in a short time. The titration is performed as follows: 25 c.c. of the distillate are mixed with a measured quantity of the phenylhydrazine solution, the mixture rapidly boiled and cooled; a little of the solution is filtered and boiled with twice its volume of Fehling's solution; if the phonylhydrazine is in excess reduction takes place, but if furfural is in excess there is no reduction. Trials are made until the equivalent amount of phonylhydrazine solution is found (Stone, *l.c.*). The dilute acidified solution is precipitated with phenylhydrazine acetate, the hydrazide collected on an asbestos filter and dried in a vacuum in a specially-constructed apparatus at 50°-60° until the weight becomes constant. The precipitation is always effected in the same volume of solution, so that allow-ance can be made for the solubility of the hydrazide. Arabinose yields on an average 48.72 p.c. and zylose 56.25 p.c. furfural (de Chalmot-a. Tollens).

9. The action of alkalis. This can only be applied as a rough qualitative test. All the hexoses yield a brown colouration when boiled for a few minutes with a 3-4 p.c. solution sodium hydroxide. The '-on' sugars are not affected.

10. The action of phenylhydrazine. The melting-point of the osazones and hydrazides and composition thereof give good indication of the nature of the sugar whence they are prepared. For preparation and melting-point see individual sugars. Maquenne (C. R. 112, 799) finds that different sugars yield, with excess of phenylhydrazine, very different quantities of osazones. By heating 1 g, each sugar for one hour at 100° with 100 c.c. water, and 5 c.c. of a solution of phenylhydrazine acetate, containing in 1 litre 400 g. phenylhydrazine and 400 g. glacial acetic acid, cooling, collecting the precipitate, washing with 100 c.c. water and drying at 110°, he found sorbose gave 0.82 g., lævulose 0.70, xylose 0.40, dry dextrose 0.32, arabinose 0.27, galactose 0.23, rhamnose 0.15, lactose 0.11, maltose 0.11. There must, however, be some error or misunderstanding here, as there is nowifficulty in getting 120 o. o. osazone from arabinose and more than 180 p.c. from lavulose. C. O'S.

SULPHACETIC ACID v. SULPHOAGETIC ACID. SULPHAMIC ACID and SULPHAMATES SULPHAMIC ACID and SULPHAMATES SO. NH. OH and SO. NH. OM! (Amidosulphonic acid and Amidosulphonates.) By passing dry NH, over SO., Rose (P. 33, 81; 47, 471; 49, 189) obtained a compound SO. 2NH. This compound, called by Rose 'sulphatammon,' is generally described as ammonium sulphamate SO. NH. ONH, but Divers a. Haga (C. J. 61, 948) have shown, fairly conclusively, that the compound is tri-ammonium imidosulphonate (N(NH.)(SO. ONH.), [2 = SSO. 4NH.]; this salt is described under Imidosulphonic acid and its salts (v. Sulphonic acid and its salts (v. Sulphonic acids and Derivatives, p. 600).

Barium sulphamate SO_xNH_xO Sa seems to have been obtained by Berglund (B. 9, 1896) by boiling an aqueous solution of barium imidosulphonate HN SO_xO Ba (v. Imidosulphonic acid under SULPHONIC ACIDS AND DERIVATIVES, p. 600) till the solution reacted strongly acid, adding excess BaOAq, boiling so long as NH_x came off, filtering, removing excess of Ba by passing in CO_x, filtering, evaporating the filtrate to a small bulk, and allowing to stand. The salt crystallises in long, lustrous needles; it is not changed by heating to 200°, nor by boiling in solution, even in presence of HClAq.

Berglund (i.c.) says that a solution of potassium sulphamate is obtained by the reaction of nascent hydrogen with potassium oxyamidosulphonic acid under Sulphonic acid under NHOH.SO.OKAq + 2H = NH...SO.OKAq + H.O. B. was unable to isolate the salt. Raschig (A. 241, 176) obtained the potassium imidosulphonate NH(SO.OK), with a little water for some time, removing the H₂SO, that was produced by CaCO, filtering from CaSO,, evaporating, pouring off from K₂SO, that separated, and allowing the syrupy mother-liquor to crystallise. The salt separated in large colourless, rhombic crystals. In 1878 Berglund prepared several sulphamates, viz. the salts of NH, Cd, Ca, Co, Cu, Pb, Li, Mn, Ni, Ag, Na, Sr, Tl, and Zn (Lunds Universitets Arsskrift, 13; abstract in Bl. [2] 29, 422).

SULPHAMO ACD SO, NH, OH. This acid was obtained by Berglund (Lc.) by passing H,S into a solution of the silver salt, filtering from Ag,S, and evaporating over H,SO,. It forms large, transluceat, rhombic crystals; the ratio a:b:c = '9945:1:1056 (Raschig, A. 241, 178). Easily sol. water, less sol. alcohol; aqueous solution only slowly decomposed to NH, H.SO, on boiling; more rapidly decomposed if HClAq is added; not decomposed by heating to 190° (B., Lc.). A solution of the acid gives no pp. with BaOAq; on boiling with HClAq and BaCl,Aq a pp. of BaSO, gradually forms. Raschig (Lc. p. 209) obtained sulphamic acid by saturating a solution of hydroxylamine hydrochloride with SO, allowing to stand for a little, and then evaporating on a water-bath (NH,OH,HClAq + H.SO,OHAq = NH.SO,OHAq + HClAq + H.SO,OHAq

= NH, SO, OHAq + HOlAq + H₂O).

SULPHAMIDE SO (NH₂); (Sulphonamide.

Sulphurylamide.) The neutral amide of sul-

phuric acid is obtained by passing dry NH, into cooled SO, Cl., diluted with 15 to 20 vols. CHCl., to complete saturation, dissolving the pp. so produced in water, making strongly acid by HNO, Aq, ppg. Cl as AgCl by addition of AgNO, Aq, filtering, neutralising by KOHAq, and again ppg. by AgNO, Aq, filtering from SO, NAg (v. Sulphimos, p. 587), adding more AgNO, Aq and then KOHAq, warming and then cooling quickly, and collecting the pp. that forms. This pp. consists chiefly of SO, (NHAg), but there is a small quantity of another Ag salt which must be removed. This is done by washing well, adding exactly enough HClAq to convert all Ag into AgCl, neutralising by NH, Aq, adding AgNO, Aq, filtering from the pp. of the foreign Ag salt, adding more AgNO, Aq and then excess of NH, Aq, when pure SO, (NHAg), is ppd. The salt is decomposed by exactly the proper quantity of HClAq, AgCl is filtered off, the filtrate is evaporated in vacuo at a temperature not above 40°, and the liquid is allowed to remain invacuo over H, SO, when SO, (NHA,), separates in large, colourless crystals (W. Traube, B. 26, 607). Sulphamide is very sol. water, less sol. dilute alcohol, insol. alcohol, ether, and other ordinary organic solvents; it softens at 75° and melts at 81°, begins to give off NH, below 100°, no further decomposition occurring to 250°; above 250° gives off acid vapours, and is completely decomposed. An aqueous solution of sulphamide is neutral; boiled with acids it gives H, SO, Aq and NH₃. Solutions of alkalis split off NH₃ and form alkali salts of SO, OHNH₂. Small quantities of H, SO, Aq are formed after prolonged boiling. By adding AgNO, Aq to solutions of sulphamide, and then NH₃Aq, a pp. of SO₂(NHAg), is formed; other metallic derivativos of SO₂(NHA₂), exist, but have not yet been isolated gatisfactorily.

IMIDO-SULPHAMIDE NH(SO₂.NH₂)₂ v. SULPRIMIDO-AMIDE (p. 587). M. M. P. M. SULPHAMINE-BENZOIC ACID v. Amide of

O-SULPHO-BENZOIC AGED.
SULPHAMMONIC ACIDS AND SALTS v.

SULPHAMMONIC ACIDS AND SALTS v. Sulphur oxyacids, nitrogen derivatives of, p. 619.

SULPHANILIC ACID v. vol. i. p. 154. SULPHANITMONATES, &c. For such salts as sulphantimonates, sulpharsenates, sulphophosphates v. Thio-antimonates &c., under Antimonates &c.

SULPHATAMMON and PARASULPHATAM-MON v. Tri-ammonium imidosulphonate and Di-ammonium imidosulphonate under Imidosulphonic acid and salts, a section of Sulphonic acids and derwatters, p. 600.

SULPHONIC ACIDS AND DERRANTES, P. 800.

SULPHATES and allied salts. Salts of sulphuric acid H₂SO₂. The compositions of the normal sulphates are expressed by the general formules M₂SO₂, M¹¹SO₂, M¹¹SO₃, and M¹¹(SO₄)₂; the greater number of the acid sulphates come under such formules as M¹HSO₄. M¹¹H(SO₄)₂, M¹¹H(SO₄)₃. All sulphates, whether normal, acid, or basic, may be represented by the formula nMO.mSO₃. LHO, where MO stands for a basic oxide. The sulphates are prepared (1) by the interaction of H₂SO₄Aq with metals, metallic oxides, or hydroxides; some metals react with dilute H₂SO₄Aq, giving sulphates and H₂ others react only with

SO, and H.S., and sometimes H also; (2) by the interaction of H.SO, Aq with salts of volatilisable or decomposable scids, e.g. with chlorides, nitrates, or carbonates; (3) by the direct combina-tion of SO₃ with metallic oxides; (4) by oxidising sulphides, by boiling with HNO, Aq, or by reacting with Cl in presence of water, or sometimes by with UI in presence of water, or sometimes by heating in air, e.g. FeSO, CuSO, and ZnSO,; (5) by double decomposition from other sulphates, e.g. BaSO, PbSO. Most of the metallic normal sulphates are soluble in water; BaSO, is insol. water, PbSO, and SrSO, nearly insol., and CaSO, very slightly soluble. The basic sulphates are generally insoluble in water. Sulphates of metals whose oxides are strong bases-the alkali and alkaline earth metals -are not decomposed by heat alone; the sulphates of metals whose oxides are weak bases are decomposed by heating, giving off SO,, or SO, and O, and leaving oxides, or metals if the oxides are reducible by heat. Sulphates are reduced by heating with charcoal, either to sulphides or oxides, with evolution of CO and CO, and also SO, from the sulphates of weak bases. Many sulphates are decomposed completely by heating with HCl gas, giving chlorides (v. Hensgen, B. 9, 1671; 10, 259). Fusion with excess of alkali carbonate produces alkali sulphate and carbonate of the metal of the original sulphate. Many sulphates are reduced by strongly heating in a stream of NH₂, yielding sulphides, oxides, metal, or mixtures of these (v. Hodgkinson a. Trench, C. N. 66, 223). Several sulphates occur as minerals; e.g. BaSO, (heavy spar), CaSO, (gyp-

sum), SrSO, (celestine), MgSO, (Epsom salts), &c. Aluminium sulphates. The normal salt Al₄(SO₄), 18aq occurs native as feather alum; it is prepared by heating clay with conc. H₂SO, Aq and boiling down the solution; also, ascording to Persoz (A. Ch. [8] 56, 102), by adding solution of alum or AlCl, to a large excess of conc. boiling H₂SO₄, when anhydrous Al₄(SO₄), separates as a white powder. Gawalovski (C. C. 1885, 721) says that perfect octahedral crystals of Al₄(SO₄), 17aq are obtained by saturating H₂SO₄Aq with freshly ppd. AlO, H₂ and allowing to stand for some months. Crystallises with difficulty from water; crystallisation hastened by adding alcohol in which the salt is insol. (P., Le.). Concerning ppn. of Al₄(SO₄), xH₄O from aqueous solutions by H₂SO₄ v. Eremin, J. R. 20, 468 (abstract in C. J. 56, 347). When heated gives off all water; heated to redness gives off SO₄ and leaves AlO₂. Various basic salts are known; they are obtained by heating rolution of Al₂(SO₄), with AlO₂H₄, or by partially ppg. solution of the normal salt, by NH₄Aq, or by partial reduction of the normal salt, by NH₄Aq, or by partial reduction of the normal salt, by NH₄Aq, or by Partially condition of the normal salt, by NH₄Aq, or by Partially condition of the normal salt, by NH₄Aq, or by Partially ppg. solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solution of the normal salt, by NH₄Aq, or by Partially ppg. Solutio

89, 9).
The double salts Al₂(SO₁), M₂SO₁, 24aq, where
M=NH, Na, K, Rb, Ca, Ag, or Tl, are alums.
For expansions of alums v. Spring, B. 15, 1254,
1739; 17, 408.

Ammonia alum Al.(SO,), (NH,) SO, 24aq, prepared by adding (NH,) SO, or NH,Cl to Al.(SO,), Aq, so that the salts are in equivalent quantities, crystallises in octahedra; S.G. 1.56;

sone. H.SU., giving sulphates and SO. on S. 5-22 a. p., wary at 100°. Heated to 190°. SO, and H.S. and sometimes H also; (2) by the 2H.O is given off and Al.(SO.). (NH.). SO, and interaction of H.SO.Aq with salts of volatilisable or decomposable acids, e.g. with chlorides, ni- (Lupton, C. J. [2] 13, 201).

Potash alum Al₂(SO₄), K.SO₄. 24aq, prepared by mixing solutions of the two sulphates and evaporating, crystallises in regular cotahedra; S.G. 1.7; S. 3.29 at 0°, 9.52 at 10°, 22 at 30°, 31 at 60°, 90 at 70°, 357 at 100°. The crystals effloresce in air. At 190°, 23H₂O is given off (L., *l.c.*). Also obtained in cubical crystals (v. Polis, B. 18, 360). Solution in water has an acid reaction, and dissolves Zn and Fe, giving off H.

Cæsium and rubidium alums v. Bunsen, P. 119, 1; Godeffroy, B. 181, 176; Redtenbacher, J. pr. 95, 148. Setterberg (A. 211, 100) gives S. in water from 0° to 80° (cf. Cæsium,

vol. i. p. 658).
Silver alum v. Church a. Northcote, C. N.
9, 155.

Sodium alum v. Pouisin, Polytech. Centralbl. 1852, 774; Zellner, S. 36, 183; and especially Augé, C. R. 110, 1139 (abstract in C. J. 58, 1059).

cially Augé, C. R. 110, 1105 (austral) 258, 1059).

The allium alum v. Lamy, Bl: [2] 11, 210.

The double salts of $Al_2(SO_4)$, with FeSO, MgSO, MnSO, and ZnSO, also crystallise with 24H,0.

For double salts with $Fe_1(SO_4)$, $Mn_2(SO_4)$, and $Cr_2(SO_4)$, v. Etard (Bl. [2] 31, 200). For a double salt with PbSO, v. Bailey (C. S. L. 6, 415).

Salt with PbSO, v. Bailey (C. S. I. 6, 415).

Ammonium sulphates. The normal salt (NH₄)₂SO₄ is found in certain volcanic districts; it is prepared by neutralising H₂SO₄Aq by NH₂Aq or (NH₄)₂OO₄Aq and evaporating. Crystallies in clear rhombic forms, is isomorphous with K₂SO₄ (Mitscherlich, P. 18, 168). S.G. 1761 (Playfair a. Joule, C. S. Mem. 2, 401); for S.G. from 10° to 100° v. Spring (B. 15, 1940). Melts at c. 140° (Marchand, P. 42); decomposes above 280°; according to Johnson a. Chittenden (Am. S. [3] 15, 131), gives NH₄HSO₄ and (NH₄)₂S₂O₅, and at incipient redness gives SO₅, H₂O, and NH₄. Absorbs dry HCl, forming some NH₄Cl (v. Thomas, C. J. 33, 372). S. 71 at 0°, 73·65 at 10°, 76·3 at 20°, 78·95 at 30°, 81·6 at 40°, 84·25 at 50°, 86·9 at 60°, 89·55 at 70°, 92·2 at 80°, 94·85 at 90°, 97·5 at 100° (Alluard, C. R. 59, 500). Insol. absolute alcohol. For S.G. of (NH₄)₂SO₄Aq from 1 to 50 p.c. (NH₂)₃SO₄ v. Schiff (A. 108, 338; 110, 74). H.F. (N'₄H*₂S,O'₁ = 284,800 (Thomsen, J. pr. 21, 477). The acid salt NH₄HSO₄ crystallises from solution of (NH₄)₂SO₄ in hot conc. H₅O₄ (NH₂)₄C(So₄H₄O) by adding the proper quantity of H₂SO₄ (NH₄)₂SO₄Aq (Marignac, Ann. M. [5] 12, 89; (2) (NH₄)₂SO₄Q₄ (Marignac, Ann. M. 6) the color of the

Antimony sulphates. The normal salt Sb₂(SO₄), is obtained by dissolving Sb₂O₂ in boiling conc. H₂SO₄ (c. 98 p.c. H₂SO₄), resulting from conc. H₂SO₄, and drying on a porous tile over H₂SO₄. (Adie, C. J. 57, 540; where an account of the action of H₂SO₄ of different concentrations, and of SO₄, on Sb₂O₃, will be found, with references to older papers).

Barium sulphates. The normal salt BaSO, ! occurs native as heavy spar. Prepared by adding dilute H.SO.Aq or dilute solution of a suling dilute H.SO.Aq or dilute solution of a sulphate to solution of a salt of Ba, washing, and drying. A white solid; S.G. 4:525 (G. Rose, P. 75, 409; v. also Schröder, P. 106, 226; a. Wiedemann; P. M. [5] 15, 371). Obtained as a crystalline powder by fusing 1 part K.SO, with 4½ parts dry BaCl, in a closed crucible, and washing with water (Manross, A. 82, 348); also by heating dilute BaCl, Aq with slight excess of H.SO.Aq to 245° (Scheerer a. Drechsel, J. pr. [2] 7, 63). H.F. [Ba,O',S] = c. 338,000 (Th. 3, 516). Insol. water; 1 part dissolves in c. 23,000 parts cold, and in c. 4,900 parts hOt, HClAq S.G. 1-33, and in c. 9,200 parts hNO.Aq S.G. S.G. 1.03, and in c. 9,200 parts HNO, Aq S.G. 102. Struve (Fr. 9, 34) gives S. of BaSO, in conc. H₂SO, as 5·69, and 15·89 in Nordhausen acid. BaSO, is partly decomposed by boiling with conc. solution of an alkali carbonate, or by fusion with alkali carbonate; Spring (Bl. [2]44, 166) found that some BaCO, was formed by compressing BaSO, and Na₂CO, at a pressure of c. 6,000 atmospheres.

An acid salt BaSO₄.H₂SO₄ is formed by dissolving BaSO₄ in hot cone. H₂SO₄ S.G. 1.843, and heating to 100° (v. Garside, C. N. 31, 245).

Beryllium sulphates. The normal salt Deso taq is formed by dissolving BeCO, in dilute 1.SO, Aq and concentrating the slightly For crystalline form v. Topsöe acid liquid. W. A. B. 66 [2nd part], 5). According to Klatzo (J. pr. 106, 233) the salt crystallises with 7H,O. Various basic salts are obtained by the action of BeCO_s or Zn on solution of the normal salt.

Bismuth sulphates. The normal salt

Bi₂(SO₄)₃ is best prepared by dissolving Bi₂S₂ in conc. H₂SO₄ heated to commencing vaporisation; on cooling the salt separates in lustrous, very deliquescent, needles (Hensgen, R. T. C. 4, 401; tendrescent, needes (Hensgen, H. 1. C. 2, 61, cf. Schultz-Sellack, B. 4, 13). For the action of heat on Bi₂(SO₄), v. Bailey (C. J. 51, 680). An acid salt BiH(SO₄), 3aq was obtained by Leist (A. 160, 29) by dissolving Bi₂O₄ in dil. H₂SO₄Aq under definite conditions. Basic salts are also formed by the reaction of dilute H2SO, Aq with Bi₂O₂ (v. Heintz, P. 63, 55, 567), and by the action of H₂O on the normal salt (cf. Hensgen,

According to R. H. Adie (priv. comm.), acid salts BiH(SO₄)₂, xaq (x = probably 1 and 3) crystallise from solutions of Bi₂O₅ or Bi₂(SO₄)₃ in H.SO, Aq of concentrations varying from H.SO, H.O to c. H.SO, 5H.O; from soid of the concentration H.SO, 6H.O, a basic salt crystallises, probably Bi.OH.SO, H.O.

Cadmium sulphates. The normal salt

camnum suppates. The normal salt CdSO₄, aq is obtained by dissolving Cd in dilute H₂SO₄Aq, and concentrating, by boiling, the acid solution (von Hauer, J. pr. 72, 372). Various other hydrates have been isolated. H.F. [Cd,S,O'] = 221,550 (Th. 8, 516). CdSO₄ combines with NH, to form various compounds (v. H. Rose, P. 20, 152; Malagutia. Sarzeau, A.Oh. 181 0, 481; Isambert. C. R. 70. 456: Müller. A. [8] 0, 481; Isambert, C. R. 70, 456; Müller, A. 149, 70). Forms double salts with (NH.), SO, MgSO, and Na,SO,; these salts crystallise with Gaq (von H., l.c.) The double salt with Al₂(SO₂), is an alum.

Cosium sulphates. Normal valt Cs₂SO₄; by neutralising H₂SO₄Aq by Cs₂CO₂ and evapo-

rating. Short needles, not hygroscopic; insol. alsohol 38. 158.7 at -2°. The acra sum constant formed by reacting on Cs,80, with excess of small rhombic prisms

(Bunsen a. Kirchoff, P. 113, 342).
Calcium sulphates. The normal salt CaSO. occurs native as anhydrite, and the dihydrate CaSO, 2aq as gypsum, alabaster, and selenite. CaSO, is obtained in crystals by fusing KaSO. with excess of CaCl, and washing (Manross, A. 82, 348; cf. Mitscherlich, P. 21, 321). CaSO, 2aq is formed by ppg. fairly conc. CaCl,Aq by dil. H2SO, Aq or solution of a sulphate, evaporating, and washing the solid that separates. CaSO, 2aq is said to be formed by the interaction of CaCO, and S moistened with water (Polacci, G. 1874. and S moistened with water (Polacci, G. 1874. 177, 245). CaSO, has S.G. 2·964, and CaSO, 2aq has S.G. 2·31 (v. also McCaleb, Am. 11, 35). S. for CaSO, '19 at 0°, '206 10°, '214 at 40°, '208 at 60°, '195 at 80°, '174 at 100° (Marignac, A. Ch. [5] 1, 274); S. for CaSO, 2aq '2119 at 16·5°, '2352 at 22° (Cossa, G. 1873. 135); S. for CaSO, 2aq in glycerin, '957 at ordinary temperature, S. increases at temperature rises (Asselin G. R. 76 creases as temperature rises (Asselin, C. R. 76, 884). According to Raupenstauch (C. C. 1888. 821) the solubility in water of gypoum increases to 32°, is constant from 32° to 38°, and decreases above 38°. Gypsum loses 2H,O when heated to 80° in a stream of dry air; when the CaSO. thus produced is moistened it takes up 2H.O. becomes crystalline, and expands. The dehydrated CaSO, obtained by heating gypsum to 160° takes up water very slowly; if the gyps is heated to c. 300° the CaSO, formed combines with water with extreme slowness (v. Schott, D. P. J. 202, 52, 355, 513; cf. Plaster of Paris, under CEMENTS, in DICTIONARY OF APPLIED CHEMISTRY, vol. i. p. 468).

According to Potilitzin (J. R. 1893 [1] 201, 207) CaSO₄. 2aq slowly gives off water at 62°-65° till the hydrate 2CaSO₄. aq is formed; CaSO₄ prepared by heating CaSO₄. 2aq to 180°-170° absorbs H₂O from ordinary air until 2CaSO₄. aq is formed when absorption of water ceases. The hydrate 2CaSO, aq absorbs water from air saturated with moisture, forming CaSO. 2aq. The water d crystallisation of gypsum is not equally firmly retained; P. writes the formula

equally firmly retained; P. writes the torindus 2CaSO₄. 4aq; three-quarters of the H₂O is much more readily given off than the other fough. The hydrate 2CaSO₂. aq is more soluble in water than the dihydrate CaSO₄. 2aq.

An acid salt CaH₂(SO₄), is said by Berzelius to be formed by digesting CaSO₄ with H₂SO₄Aq at 80°-100° † it is decomposed by moist air to the premal selt and HSO. For double salts with alkali and alkaline earth sulphates v. Fass-bender (B. 9, 1356; 11, 1968); Struve (Bl. [2] 12, 348); Ditte (C. R. 84, 86); Popp (A. Suppl. 8, 1); Hannay (C. J. 32, 399).

Cerium sulphates, The normal cerous sulphate, Ce₂(SO₄), xH₂O (x being probably 6, 8, 9, and 12) is obtained in colourless crystals by and 12) is obtained in colourless crystals by evaporating a solution of Ce₂(CO₂), in dilute H₂SO₄Aq, or a solution of CeO₂ in H₂SO₄Aq saturated with SO₂. The normal ceric salt Ce(SO₂), 4aq forms, in yellow crystals, from a solution of CeO₂ in dilute H₂SO₄Aq. Cerosceric sulphates, xCe₂(SO₂), yCe(SO₂), 2aq, are obtained by dissolving CeO₂ in cone. H₂SO₄ and exponenting Resis salts as formed by the evaporating. Basic salts are fermed by the

interaction of water with the normal salts. Double salts of $Ce_s(SO_s)$, with $(NH_s)_2SO_s$, K_sSO_s , and Na_sSO_s are known (v. Marignac, A. Ch. [4] 80, 57; Czudnowicz, J. pr. 30, 19; Hermann, J. pr. 92, 126; Zschiesche, J. pr. 107, 65; Rammelsberg, B. 6, 85; Jolin, BL. [2] 21, 523; Wyrouboff, BL. [3] 2, 745; Wing, Am. S. [2] 40, a_sch

Chromium sulphates. The normal chromous salt CrSO. 7aq was obtained by Moissan (BL. [2] 37, 296) by dissolving the acetate in warm dilute H.SO.Aq. crystallising, and drying between paper, all operations being conducted in an atmosphere of CO₂ (for directions for making Cr(C.H.O.), v. NITROGEN, Preparation, vol. iii. p. 557). Blue crystals; isomorphous with FeSO, 7aq. S. 12:35 at 0°; sl. sol. alcohol. Abreducer. A monohydra rSO, aq was obtained as a white crystalline powder by adding the acetate to excess of conc. H.SO, (M., l.c.). Forms a double salt, CrSO, K, SO, 6aq (Péligot, A. Ch.

[8] 12, 539).

The normal chromic salt Cr₂(SO₂), xH₂O exists in two forms. (1) Violet, x=15 (Schrötter, P. 53, 5.6),=18 (Siewert, A. 126, 97); by digesting 1 pt. CrO₂H₂ dried at 100° with 1 to 11 pts. conc. H₂SO₂, in a closed vessel, till a mass of greenish-blue crystals is formed, dissolving these crystals in water, ppg. by absolute alcohol, dissolving again in water, adding alcohol till ppn. just begins, covering the vessel with moist parchment paper, and allowing to crystallise parchment paper, and allowing to crystallise slowly. Regular octahedra; red-violet in reflected light, garnet-red in transmitted light; S. 120 in cold water (Schrötter, P. 53, 516; Löwel, A. Ch. [3] 40, 42). (2) Green, x=5. By heating the violet salt to 100°; the salt melts, gives off water, and then solidifies to a green amorphous mass. Also formed by dissolving CrO₂H, in cone. H₂SO₄ at 50°260°, and evaporating quickly. Easily sol. alcohol; whereas porating quickly. Easily sol. alcohol; whereas the violet salt is insol. alcohol.

Addition of a cold solution of a Ba salt ppts. all SO, from a solution of the violet form, but boiling is needed to complete the ppn. from the green variety. According to Et d (C. R. 84, 1089), the difference between the two forms is one of hydration only (but v. Chromium salts, vol.

ii.p. 167; and v. also Recoura, C. R. 113, 857). Basic salts are obtained by adding a little NH,Aq to solution of the normal salt, also by digesting the normal salt with CrO,H,, or excess olgesting the normal salt with Cru₂H₃, or excess of Cr₂C₄, with H₂S₂S₄ (v. Schrötter, P. 53, 516; Siewert, A. 126, 97; Schiff, A. 1£4, 167, 172; Recoura, C. R. 112, 1439). According to Traube (A. 66, 87), an acid salt, Cr₂(S₂O₃)₂H₂S₂O₄, is formed by heating either variety of the normal salt with excess of H₂S₂O₄ till vaporisation of the said heating and allowing to cool (Schrötter). acid begins, and allowing to cool (Schrötter [l.c.] regarded this as an insoluble variety of the normal salt); insol. water, not acted on by cold

KOHAq, heated strongly gives Cr₂O₃, SO₂, and O. Cr₄(SO₄), forms many double salts; those with the alkali sulphates have the composition

 $Cr_2(SO_4)_3$. M_2SO_4 . 24aq, and are alums.

Ammonia chrome-alum is ppd. by adding $(NH_d)_2SO_4Aq$ and $Cr_2(SO_4)_2$; also formed by mixing $(NH_d)_2SO_4Aq$ and $Cr_2(SO_4)_2Aq$, and evaporating; also by mixing $Cr_2(SO_4)_2Aq$ (violet) with $(NH_d)_2CrO_4Aq$,

adding a little _______ constant anomals at craporate. Crystallises in ruby-red octahedra; S.G. 1-738. Effloresces slowly in air. Solution in water is violet; at 75° it becomes green, but slowly returns to violet on standing for some weeks (regarding this change v. CHROMIUM SALTS, vol. ii. p. 167).

Potass o'hrome alum is produced similarly to the ammonia salt; also by heating K₂Cr₂O₇ with cono. H₂SO₄, more quickl² in presence of a reducer, e.g. SO₂. Crystallises in large dark-purple octahedra; S. 14.5 in cold water. Solution in water is grey-blue with tinge of red; heated to 70°-80° it becomes green and non-crystallisable, but returns to violet after standcrystallisable, but returns to violet after standing for some weeks. For Soda chrome-alum v. Schrötter (P. 53, 513). For double salts of Cr₂(SO₄)₃ with Al₂(SO₄)₃, Fe₂(SO₄)₃, and Mn₂(SO₄)₃ v. Étard (Bi. [2] 31, 200); for double salts of the form Cr₂(SO₄)₃, 3M₂SO₄, where M = Li₁. K, or Na, v. Warnicke (P. 159, 572). For description of other double salts of Cr₂(SO₄)₃ with alkali sulphates, v. Klobb, C. R. 117, 311 (Abstract in C. J. 64 [ii], 573). Chalt sulphates, —The recoval columns and the salts of Craft sulphates.

Cobalt sulphates.—The normal cobaltous salt CoSO, 7aq occurs native as biberite; prepared by dissolving Co. CoO, or CoCO₃ in dilute H₂SO₄Aq, and evaporating. Forms carmine-red crystals, isomorphous with FeSO, 7aq; S.G. 1918 at 15° (Thorpe a. Watts, C. J. 37, 102). Unchanged in air; loses all water by seating, and gives CoSO₄ as a red powder, not decomposed easily by heat; S.G. 3.472 at 15° (T. a. W., *l.c.*). Klobb (C. R. 114, 836) obtained the anhydrous salt in crystals by mixing CoSO₄. 7aq with excess of (NH₄)₂SO₄ and heating in a partly-closed crucible, out of contact with the gases of the flame, till (NH₄)₂SO₄ was all volatilised. The hexahydrate CoSO₅ caq separates from solutions of Co or CoCO₅ in H₂SO₄Aq at 40°-50°; it is isomorphous with the corresponding salts of Mg Ni and Zn (Maximea). Except the helpstone Mg, Ni, and Zn (Marignac). For other hydrates, with 4aq and aq, v. Fröhde (J. 1866, 244); Vortmann (B. 15, 1888). CoSO, 7aq is insol. alcohol; S. water 30.5 at 10°, 36.4 at 20°, 40 at 29°, 46.3 at 35°, 55.2 at 50°, 60.4 at 60°, 65.7 29°, 46°3 at 35°, 55°2 at 50°, 60°4 at 60°, 65°7 at 70° (stated as parts CoSO, dissolved by 100 parts water; Tobler, A. 95, 193). Thomsen (Th. 3, 516) gives H.F. [Co,S,O,7,H $_{\rm c}$ O] = 234,000. By electrolysing CoSO,4 α q in presence of K $_{\rm c}$ SO, and H $_{\rm c}$ SO, $_{\rm c}$, under special conditions, Marshall obtained Co $_{\rm c}$ (SO, $_{\rm c}$), along with K $_{\rm c}$ So,0 $_{\rm c}$ (C. J. 59, 760) 760).

Basic salts are formed by addition of a little NH₄Aq to hot CoSO₄Aq, also by digesting CoSO₄Aq with CoCO₂ (v. Habermann, M. 5, 442; Athanascoo, C. R. 103, 271).

Aumanascsco, C. R. 103, 271).

For double salts with FeSO₄, MgSO₄, MnSO₄, and ZnSO₄ v. Vohl (4. 94, 57).

Normal cobaltic sulplate Co₂(SO₂), was obtained by Marshall (C. J. 59, 767) by electrolysing CoSO₂Aq in presence of H₂SO₄, under special conditions. A blue crystalline powder, unchanged in a stoppered bottle in ordinary air. but decomposes rapidly in dry air set. air, but decomposes rapidly in dry air; soi. water, with evolution of O; sol. conc. H2SO4; in HClAq forms CoCl, and gives off Cl.

Copper sulphates. Only salts corresponding with the oxide CuO have been isolated. The normal salt CuSO, is obtained by dissolving Cu in hot cone. H2SO4, decenting the hot solution, and allowing to cool; also by adding cone. crystals of CuSO, 5aq to c. 230° as long as they lose weight. Klobb (C. R. 114, 836) obtained CuSO, in crystals by heating a mixture of the Ouso, in crystals by heating a mixture of the hydrated salt and excess of $(NH_1)_2SO_4$ in a partly closed crucible till all $(NH_1)_2SO_4$ had volatilised. A white crystalline powder; S.G. 8-606 at 15° (Thorpe a. Watts, C. J. 37, 102). Partly decomposed at red heat, wholly at white heat, to SO2, O, and CuO. Reduced by heating to redness with charcoal, giving Cu, SO, and CO. At a higher temperature some CuS is said to be formed; also reduced to Cu by heating in H; heated in PH, gives off H,O, and leaves a mixture of sulphide and phosphide of Cu. HCl gas ture of suiphide and phosphide of Cu. HCl gas forms CuCl₂ and H₂SO₄. CuSO₄ acts as a powerful dehydrating agent; it rapidly absorbs water, forming CuSO₄.5aq. H.F.[Cu,S,O'] = 182 500 (Th. 3, 516).

The pentalydrate CuSO₄.5aq (blue vitriol) is prepared by dissolving Cu in hot conc. H₂SO₄, evaporating, and recrystallising from water the colid that convertes. At a 200 there is a very

solid that separates. At. c. 20° there is a very slight reaction, with formation of Cu₂S and CuSO₄; at c. 270° the reaction is Cu+2H₂SO₄ = CuSO₄ + SO₂ + 2H₂O (Pickering, C. J. 33, 112). According to Anthion (R. P. 81, 344), CuSO₄.5aq free from nitrate, is obtained by dissolving Cu in a warm mixture of dilute H₂SO₄Aq and HNO, Acr and crystallising. (For preparation of commercial blue vitriol v. DICTIONARY OF APPLIED CHEMISTRY, vol. i. p. 608.) Large blue, triclinic crystals; S.G. 2.284 at 15° (Thorpe a. Watts, C. J. 37, 102). Solubility in water is given by Poggiale (A. Ch. [3] 8, 463) as follows:-

	8. 		s.	
0° 31 10 36 20 42 30 48 40 56	0.5nq Cus :61 18: :95 20: :31 23: :81 26: :90. 30: :83 34:	20 60° 92 70 55 80 63 90 29 100		CuSO. 38·83 45·06 53·15 64·23 75·25

Gerlach (D. P. J. 181, 129) gives the following

Percentage	S.G.	Percentage	S.G.
CuSO. 5aq	of solution	CuSO. 5aq	of solution
2.	1.0126	14 .	1.0933
4.	1.0254	16 .	1.1063
6.	1.0384	18 .	1.1208
8 .	1.0516	20 .	1.1354
10 .	1.0649	22 .	1.1501
12	1.0785	24	1.1659

Insol. absolute alcohol; S. in 40 p.c. alcohol at 15°=25 (Schiff). Fairly sol. glycerin. Effloresces in dry air, giving off 2H₂O; heated for some time to 100° loses 4H₂O, the last H₂O is removed at c. 230°. For dissociation-pressures of water given off at various temperatures v. Lescœur (C. R. 102, 1466). Solution in HClAq gives CuCl, 2H,O on evaporation. The dry salt in powder, absorbs HCl, the water of crystallisation being set free (Kane, A. 19, 1); several compounds of CuSO, HCl, and H₂O are formed according to Latschinoff (J. R. 1888 [1] 586, 657, 707; abstract in B. 22 Ref. 192). Combines with NH, forming CuSO, 5NH, all water of crystallisation being removed (L., l.c.).

Other hydrated copper sulphates are (1)

CuSO, 6aq and (2) CuSO, 7aq, obtained by Lecoq de Boisbaudran (C. R. 65, 1240), the former by placing a crystal of NiSO, 4aq in a warm supersaturated solution of CuSO₄.5aq, to which a few drops of H₂SO₄Aq had been added, and the latter by placing a crystal of FeSO₄.7aq in the mother-liquor from the first-named hydrate; (3) CuSO, 3aq, by keeping CuSO, 5aq in dry air at 25°-30° (Magnier de la Source, C. R. into H₂SO₄Aq, S.G. 1.7, and washing the pp. with small quantities of absolute alcohol (Thorpe a. Watts, C. J. 37, 104); (4) CuSO, 2aq by keeping the pentahydrate in vacuo at 20° for some days, the pentanydrate in vacuo at 20° for some days, or by pouring conc. CuSO, Aq into cold conc. H_SO, and washing the pp. with absolute alcohol (T. a. W., l.c.); (5) CuSO, aq by heating powdered pentahydrate at 110° till it ceases to lose weight (T. a. W., l.c.). T. a. W. (l.c.) give the S.G. of these hydrates, at 15°, as: monohydrate, 3·289; dihydrate, 2·953; trihydrate, 2·663. Lescœur (C. R. 102, 1466) obtained only the power trie and respectively. the penta-, tri-, and monohydrates.

Double salts with the alkali sulphates, of the

form CuSO4.M2SO4.6aq, are obtained by crystallising mixtures of the constituents in the proper proportions (v. Graham, P. M. 1835. 327, 417; Brunner, P. 15, 476; 32, 221; Pickering, C. J. 49, 1). Vohl (A. 94, 57) has described several Zn, are described (v. Rammelsberg, P. 91, 321; also Lefort, A. Ch. [3] 23, 95; von Hauer, P. 125, 633). Several basic salts of the form 120, 038). Several vasic states of the holm $CuSO_{+}xCuO$, aq are known: -x=1, v. Roucher $(J \cdot P)t$. [3] 37, 249); x=2, v. Reindel $(J \cdot pr. 100, 1; 102, 204)$, Persoz (A. Ch. [3] 25, 257), Shenstone $(U \cdot J \cdot 47, 375)$; x=3, v. Smith $(J \cdot 25, 257)$, $(J \cdot 47, 275)$; $(J \cdot 47,$ snenstone (U. J. 41, 375); x = 3, v. Smith (J. 25, 280), Pickering (C. J. 43, 336; 49, 1), Grimbert a. Barré (J. Ph. [5] 21, 414), Kühn (Ph. C. 1847. 595), Kane (A. 19, 1); x = 4, v. Smith (l.c.); x = 7, v. Pickering (l.c.). For other basic sulphates v. Steinmann (B. 15, 1411), Brunner (P. 15, 476; 32, 221), Becquerel (C. R. 67, 1081), Carcelmann (F. 4. 24) Casselmann (Fr. 4, 24).

Didymium sulphates (v. Marignac, A. Ch.

[3] 58, 148; Cleve, Bl. [2] 21, 246; 39, 151;
Hermann, J. pr. 82, 385; Frerichs a. Smith, A.

191, 348). The normal salt Di₂(SO₄), 8ag crystallises in red, lustrous, monoclinic crystals from a solution of Di₂O₂ or Di₂(O₃), in excess of H₂SO₄Aq; S.G. 2·878; S.H. 1948 (Nilson a. Pettersson, B. 13, 1459). Heated to 300° loses all water of crystallisation, leaving Di_a(SO₄), as a red powder; S.G. 3.735; S.H. 1187 (N. P., l.c.); S. 43.1 at 12°, 11 at 50°, 2 at 100° (Marignac). For effect of heat at various temperatures v. Bailey (C. J. 51, 682). Hydrates with 6aq and aq crystallise from cold saturated solutions of Di₂(SO₄)₃; Marignac (*l.c.*) also obtained a hydrate with 9aq. *Double salts* of the form Di₄(SO₄)₃, M₂SO₄, Saq, where M is an alkali metal, are known. *Basic salts* are formed by heating the normal salt, also by adding a little NH₂Aq to solutions of the normal salt.

The normal auro-auric Gold sulphates. sulphate AuSO, was obtained by Schottländes (A. 217, 312) by evaporating solution of

AuO.H.Du, (v. vajrp) nearly to argness at 250°, and drying in a desiccator over lime. Lustrous, and drying in a desiccator over lime. Lustrous, scarlet prisms, that rapidly absorb moisture from the air, with partial decomposition. A basic salt AuO.H.SO, (auryl sulphate) was obtained (S., l.c.), as a yellow crystalline powder, by heating AuO.NO, with conc. H.SO, at c. 200° (AuO.NO, was formed by dissolving AuO,H, in HNO,Aq S.G. 1.4, filtering through asbestos, and evaporating under reduced pressure over lime and soda). A double salt AuK(SO,), was formed by dissolving KHSO, in solution of AuO.H.SO,, and evaporating at 200° (v. also Allen, C. N. 25, 85).

Indium sulphates (v. Winkler, J. pr. 94, 1; 95, 414; 98, 344; 102, 273; B. Meyer, A. 150, 429). The normal salt In₂(SO₄), is obtained by dissolving In or InO,H, in excess of H2SO,Aq, evaporating to dryness, and heating till excess of acid is mg od dylason, status but the removed; a white, very hygroscopic powder; S.H. 129 (Nilson a. Pettersson, B. 13, 1459). S.G. 8-438 (N. a. P., C. R. 91, 232). By dissolving in water and evaporating, a hydrate with 9ac is obtained as a gummy solid. The solution of In or InO.H. in excess of H.SO.Aq yields a syrupy liquid on evaporation which probably contains an acid salt (? In₂(SO₄), H₂SO₄). By adding (NH₄), SO₄Aq to solution of In₂(SO₄),, and evaporating, the double salt with the composition In (SO,)...(NH,).SO, 24aq is obtained; this salt is an alum; it is sol. in 1 part water at 16°, and in 1 part water at 30°. On evaporating the mother-liquor, the salt In (SO,)...(NH,).2SO,. Saq in btained (Rössler, J. pr. [2] 7, 13). Double salts with K.SO, and Na,SO, crystallising with 8aq, have also been obtained. Iridium sulphates. By treating IrS, with

conc. HNO, Aq, Birnbaum (A. 136, 179) obtained an amorphous, brownish-yellow solid, easily sol. water, probably a sulphate of Ir. The double salt Ir. (SO), 3K, SO, was obtained by Lecoq de Boisbaudran (C. R. 96, 1406, 1551) by fusing KHSO, with Ir compounds, treating with water containing KHSO, dissolving the residue in hot

water, and crystallising; green, translucent crystals, probably regular octahedra; almost insol. saturated KHSO,Aq.

Iron sulphates. I. Ferrous salts. The commal salt, FeSO, is obtained by heating powdered FeSO, 7aq very carefully to 300° till it ceases to lose weight (the heating is best done in a stream of H); at a slightly higher temperature SO2 and O begin to be given off, and finally Fe₂O₂ remains. Fe₂O₃ is a white powder; S.G. 3·346 (Thorpe a. Watts, C. J. 37, 102). Several hydrates of FeSO, are known, ordinary green vitriol being the most common and best examined of these; this heptahydrate, FeSO. 7aq, is best prepared by adding iron filings to warm dilute H,80,Aq until the acid is saturated and a little iron remains undis-solved, boiling for a little, filtering into a vessel that has been rinsed with a very little conc. H.SO., allowing to crystallise, washing the crystals two or three times with very small quantities of cold water, and then with alcohol till all soid is removed, drying at c. 80°, powdering the dry crystals, and strongly pressing between paper or linen. As thus prepared the salt does not readily oxidise in the air. If alcohol is added to the hot solution, filtered from undissolved

iron, FeSu., 7aq is ppd. in minute crystals; if this pp. is washed with alcohol till acid is re-moved and then spread on filter paper, in dry air, till the alcohol has evaporated, the salt is air, till the alcohol has evaporated, the sait is obtained as a bluish white powder, which does not oxidise except in very moist air. Blue-green, monoclinic crystals; S.G. 1-8889 at 4° (Playfair a. Joule, C. J. 1, 138), 1-9854 at 16° (Pape, P. 120, 872). H.F. [Fe,S,O,*,7H*O] = 240,100 (Th. 3, 516). Heated to 100° gives off 6H_O, and at c. 800° leaves FeSO, (v. supra). S. 60°9 at 10°, 70 at 15°, 114-95 at 25°, 227-27 at 46°, 263-15 at 60°, 270·27 at 84°, 370·37 at 90°, 333·33 at 100°, Gerlach (D. P. J. 181, 129) gives the following data (v. also Schiff, D. P. J. 1858. 38):—

G. FeSO,Aq	Petge. FeSO, 7aq	Petge. FeSO
1.0267	5	2.811
1.0537	10	5.784
1.0823	15	8-924
1.1124	20	12.
1.1430	25	15.834
1.1738	80	19.622
1.2063	35	23.672
1.2391	40	27.995

Insol. glacial acetic acid and absolute alcohol. FeSO, 7aq is fairly easily oxidised; exposure to air produces basic ferric sulphates. FeSO, Aq absorbs NO, forming FeSO, xNO (x probably = 1 or \frac{1}{3}; v. Gay, A. Ch. [6] 5, 145, and cf.

NITRIC OXIDE, vol. iii. p. 563). Other hydrates of ferrous sulphate are (1) FeSO, 4 and formed by of jerrous surplinate and it less of Acq at 80° (Regnault, A. Ch. [3] 1, 201), also by exposing finely-powdered FeSO, 7aq over H.SO, in an atmosphere of Oo, until it ceases to lose weight (Thorpe a. Watts, C. J. 37, 102); S.G. 2.227 (T. a. W.); Watts, C. J. 37, 102); S.G. 2:227 (T. a. W.); (2) FeSO₄. 3aq, by evaporating FeSO₄Aq made strongly acid by H₂SO₄ (Kühn, S. 61, 235), also by dissolving FeSO₄. 7aq in hot HClAq and crystallising (Kane, A. 19, 7); (3) FeSO₄. 2aq by boiling the heptahydrate with successive quantities of alcohol; S.G. 2:773 (T. a. W., Lc.); (4) FeSO₂. aq, by heating powdered FeSO₄. 7aq to 120° in H; S.G. 2:994 (T. a. W.; v. also Mitscherlich, P. 18, 152). Several double salts of ferrous sulphate are known; they are generally prepared by crystallising a mixture of the conprepared by crystallising a mixture of the conprepared by crystallising a mixture of the constituent sulphates in the proper proportions. The salts FeSO, M₂SO, 6aq, where M = NH₄, K, Na, or Tl, form blue-green monoclinic crystals (v. Marignao, Ann. M. [5] 9, 19; Schiff, A. 108, 326; Tobler, A. 95, 193; Wilm, A. Ch. [4] 5, 56). For the salts FeSO, MSO, 14aq, where M = Mg or Zn, v. Schiff (l.c.), and Murmanh (W. A. B. 27, 172). For various triple and quadruple salts containing FeSO, alkali sulphates, and sulphates of Mn, Mg, Zn, &c., v. Bette (A. 14, 278) and Vohl (A. 94, 57).

II. Ferric salts. The normal salt Fe(SO), is obtained by adding 1 part cone.

Fe₂(SO₄), is obtained by adding 1 part conc. H₂SO₄ to 5 parts Fe₂SO₄. 7aq dissolved in water, warming, and adding HNO₄Aq little by little till exidation is complete, evaporating to a syrup, and then heating very cautiously so long as soid fumes are given off; on cooling Fe,(SO₄), remains as a white amorphous solid; S.G. 8.097 at 18° (Pettersson, Upsala, Nova acta, 1874). Fairly large quantities of FeSO. 7aq should be used, as evaporation of a dilute solution containing Fe₂(SO₄), produces ppn. of basic sulphates. The hydrate Fe₂(SO₄), 9aq occurs native as

obtained rhombic leaflets of a hydrate with 10aq (J. 1874. 268). Fe₂(SO₄), is slowly sol. in water; the presence of a very small quantity of FeSO₄ causes Fe₂(SO₄), to dissolve rapidly in water (Barreswil, Ph_{\bullet} C. 1845, 604). Fe₃(SO₄), is insol. in conc. H_2 SO₄; it is reduced to FeSO₄ by most metals, more quickly if a little H₂SO₄ is present. Fe.(SO₄), forms several double salts. The sent. Fe₂(SO₄), forms several double salts. compounds Fe₂(SO₄)₂, M₂SO₄. 24aq, where M = NH₄ or K, are alums. Potash iron alum Fe₂(SO₄)₂.K₂SO₄. 24aq is prepared by dissolving parts FeSO₄. 7aq in water, adding 5 parts conc. H2SO4, oxidising by HNO3Aq, adding 8.75 parts K,SO,, and crystallising; or by mixing 10 parts powdered FeSO, 7aq with 4 parts KNO,, slowly adding 5 parts conc. H₂SO,, warming so long as NO₂ is given off, dissolving the residue in 4 times its weight of water at 80°, and allowing to stand at 0° for some time (Heintz, A. 44, 271). The salt slowly decomposes in the air; heated to 80° it gives Fe₂(SO₂)₂₀, basic ferric sulphate, and H₂SO₄; a similar decomposition occurs when an aqueous solution of the salt is heated (Rose, P. 94, 459). Addition of KOHAqto a conc. solution of the salt till a slight permanent pp. is formed, followed by evapora-tion, produces a double salt of K,SO, with a basic ferric sulphate (v. Richter a. Scheerer, P. 87, 73). Ammonia iron alum is formed similarly to the K salt; loses 23H₂O at 150° (v. Lupton, C. J. 28, 201). For double salts with Al₂(SO₄)₃, Cr₂(SO₄)₃, Mn₂(SO₄)₃ and MnSQ₄, v. Etard (Bl. [2] 31, 200). Some double compounds of Fe₂(SO₂), with (NH₃),SO₄, and with FeSO₄ and (NH₃)₂SO₄, are described by Lachaud a. Lepierre (C. R. 114, 915).

A great many basic salts have been described: generally prepared by the action of air on solu-tions of $FeSO_4$. 7aq, or by heating $Fe_2(SO_4)_3Aq$ in sealed tubes (v. Athanasesco, C. R. 103, 271). Pickering (C. J. 37, 807) gives very full references to all the memoirs on those basic salts, and comes to the conclusion that only one exists, viz. 2Fe₂O₃.SO₃; in a later paper (C. J. 43, 182) he gives reasons for writing the formula rather as 6Fe₂O₃.3SO₃.xH₂O, or Fe₂(SO₄)₃.5Fe₂O₃.xH₂O. Lanthanum sulphates. The normal salt

La₂(SO₄), is obtained by dissolving La₂O₅ in excess of H₂SO₄Aq, evaporating, drying the crystals of La2(SO4)3. 9aq that separate, and heating to dull redness; a white powder, S.G. 8.6 (Nilson a. Pettersson, C. R. 91, 232); S.H. 1182 (N. a. P., B. 13, 1459). Much mere sol. cold than hot water; Mosander (P. 11, 406) gives S. 16.6 at 2°-3°, 2.35 at 25°, 87 at 100°. The hydrate with 9aq, formed by the slow evaluations of the O. according to the contraction of the O. according to the O. accordi The hydrate with 9aq, formed by the slow evaporation of La₂O₂ in excess of H₂SO₄Aq, crystalliese in large, lustrous, hexagonal prisms (Topsos); S.G. 2853 (N. a. P., C. R. 91, 232). A hydrate with 6aq was obtained by Frerichs a. Smith (A. 191, 331). Several double salts with the alkali sulphates have been obtained; the principal are M.(NH₁)₂SO₄, 8aq, M.3K₂SO₄, and M.4K₂SO₄, where M = La₂(SO₄)₂ (v. Cleve, Bl. [2] 39, 151; 43, 56). A basic salt was obtained by F. a. S. (l.c. p. 360).

Lead sulphates? The normal salt PbSO₄ occurs in various lead ores. It is obtained as a white, heavy powder, by heating Pb with conc.

white, heavy powder, by heating Pb with conc. H.SO. by the interaction of warm H2SO,Aq

and PbO, or of PbO, and SO, and by ppg. solutions of lead salts by dilute H₂SO₄Aq or solution of a sulphate. PbSO₄ is prepared in small rhombic crystals by melting PbCl₂ with K₂SO₄. and washing with water. S.G. 6.2 (Schröder, P. Ergünz. Bd. 6, 622); 5.96 at 17° (Pettersson, Upsala, Nova Acta, 1874). H.F. [Pb, S, O'] = 216,200 (Th. 3, 516). Nearly insol. water; Rodwell (C. N. 11, 50) says that \$1,062 parts water at 15° dissolves 1 part PbSO. Struve (Fr. 9, 34) gives S. in conc. H.SO, as 13, and S. in Nordhausen acid as 4·19 (v. also Kolb, D. P. J. 209, 268). For solubility in dilute HClAq and HNO₃Aq v. Rodwell (C. J. 15, 59); for S. in various salt solutions v. Löwe (J. 1859, 668); Staedel (J. 1863, 245); Store (C. N. 21, 17); Dibbits (Fr. 1874, 187). Heated to redness, PbSO₄ melts without decomposition, but at a white heat it gives PbO, SO₂, and O (Boussingault, C. R. 64, 1159). Heated in a stream of H, it is reduced to Pb with evolution of SO, H.S. and steam; heated with charcoal, PbO.
PbS, or Pb is formed according to the proportions of the reacting substances. Reduced by Fe or Zn in contact with water. Rubbed with K2CrO, produces PbCrO,; with KIAq yields K₂CrO₄ produces PbCrO₄; with KIAq yields PbI₂, and with NaCl is partly decomposed to PbCl₂ (v. Matthey, Ar. Ph. [3] 13, 233). For reaction when heated in NH₂ v. Rodwell (C. N. 15, 137). A double salt PbSO₄(NH₂)₂SO₄ is formed by adding excess of H₂SO₄Aq to Pb(C₂H₂O₂)₂Aq, neutralising excess of acid by NH₂Aq, boiling, and allowing to cool. An acid salt PbSO₄H₂SO₄, aq was obtained by Schultz (P. 133, 137) by dissolving PbSO₄ in conc. H₂SO₄ and setting aside. A basic salt Ph.SO, and setting aside. A basic salt PbSO, PbO is formed by digesting PbSO, with NH,Aq (Kühn, Ar. Ph. [2] 50, 281).
Lithium sulphates. The normal salt Li,SO, is obtained by dissolving Li,CO, in H,SO,Aq,

evaporating, drying the crystals of Li₂SO, aq that separate, and heating them to c. 135°. S.G. 2·21 at 15° (Brauner, P. M. [5] 11, 67). Melts at 518° (Carnelley, C. J. 38, 280). S. 35°. at 0°, 34°36 at 20°, 32°8 at 45°, 30°3 at 65°, 29°. 24°. Property of the control of the at 0°, 34·36 at 20°, 32·8 at 45°, 30·3 at 65°, 29·24 at 100° (Kremers, A.99, 47). Easily sol. alcohol; insol. SO, (Weber). H.F.[Li²,S,O¹] = 333,200 (Th. 3, 516). Heated in HCl gas below redness gives LiCl (Hensgen, B. 8, 125). The monohydrate Li₂SO, aq crystallises in monoclinic forms (Rammelsberg, P. 129, 311). S.G. 2·052 at 21° (Pettersson, Upsala, Nova Acta, 1874). Effloresces a little in air, gives up water at a little above 130°. An acid salt LiHSO, is obtained by dissolving Ji.SO. in H.SO An S.G. 1·5 tained by dissolving Li, SO, in H, SO, Aq S.G. 1.6 to 1.7 (Schultz, P. 130, 149); prismatic crystals, melting at c. 120° (Lescour, Bl. [2] 24, 516). Double salts with K.SO, are obtained by evaporating mixed solutions of the constituent salts (b. Rammelsberg, A. 128, 311; Schabus, J. 1854. 323). For double salts with Rb₂SO, and Na₂SO, w. Wyrouboff (Bull. soc. mineral. de France, 1882. part 2). Wernicke (P. 159, 576) describes 1882. part 2). Wernicke (P. 159, 576) describes a salt 3Li₂SO₂,Cr₂(SO₂), formed, in green needles, by adding Cr₂O₃ to molten LiHSO₂. Li₂SO₄ does not form alums, nor does it combine with the magnesian sulphates (Rammelsberg, Lc.; Scheibler, J. pr. 67, 485).

Magnesium sulphates. The normal salt MgSO, is obtained by dissolving MgO or MgCO, in H₂SO, Aq (or by heating dolomite till CO₂ is

removed, treating with HClAq, which dissolves CaO, and dissolving the residual MgO in CaO, and dissolving the residual MgO in H.SO.Aq), evaporating, crystallising out MgSQ₁, 7aq, drying this salt, and heating it gradually to c. 300° till it ceases to lose weight. A white solid; S.G. 2.709 at 15° (Thorpe a. Watts, C. J. 37, 102); 2.77 to 2.795 at 14° (Pettersson, Upsala, Nova Acta, 1876). H.F. [Mg,S,O'] = 302,300 (Th. 3, 516). [MgSO',Aq] = 20,765 (Pickering, C. J. 47, 100). Decomposed to MgO, SO₂, and O at c. 360° (v. Bailey, C. J. 51, 682). Not acted on by HCl gas below incipient red heat (Hensgen, B. 9, 1671; 10, 259). The heptahydrate MgSO, 7aq (Epsom same) occurs in many mineral springs, in sea water, and in some rocks. It crystallises at the water, and in some rocks. It crystallises at the ordinary temperature from solutions of MgO or MgCO₂ in H₂SO₄Aq. Translucent, rhombic prisms; from supersaturated solutions crystallises in hexagonal forms, and from solutions lises in hexagonal forms, and from solutions containing some FeSO₄ in monoclinic forms (v. Marignae, Ann. M. [5] 12, 50). S.G. 1-678 at 15° (Thorpe a. Watts, C. J. 37, 102); 1-683 at 4° (Playfair a. Joule, C. J. 1, 138). H.F. [Mg,S,O',7H°O] = 326,400 (Th. 3, 516). Melts at 70° (Tilder, C. J. 45, 267); gives up 6H_cO by prolonged heating at 150°-160°, and all water of crystallisation at c. 280° (v. Pickering, C. J. 47, 100). The following data for solubility in water are calculated by Multier from observawater are calculated by Mulder from observations by Gay-Lussac, Tobler, and others :-

Temp.	8.	Temp.	s.
00	25.76	600	55.0
5	29.3	65	57.3
10	31.5	70	59.6
15	83.8	75	61.9
20	36.2	80	$64 \cdot 2$
. 25	38.5	85	66.5
30	40.9	90	68.9
35	43.3	95	• 71.4
40	45-6	100	73.8
45	48.0	105	76·2
50	50.3	108.4	77.9
55	52·7	1	

Gerlach (Fr. 8, 287) gives the following:-

** **			
.o. mg50.	S.G. MgSO.Aq	P.c. MgSO	S.G. MgSO.Aq
1	1.01031	14	1.15083
2	1.02062	15	1.16222
8	1.03092	16	1.17720
4	1.04123	17	1.18618
5	1.05154	18	1.19816
6	1.06229	19	1.21014
7	1.07304	20	1.22212
8	1.08379	21	. 1.23465
9	1.09454	22	1.24718
10	1.10529	23	1.25972
11	1.11668	24	1.27225
12	1.12806	25	1.28478
13	1.18945	Į.	

8. at 15° in 10 p.c. alcohol 39.3, 20 p.c. alcohol 21.3, 40 p.c. alcohol 1.62 (Schiff, A. 118, 365). Heated with NaCl gives off HCl, leaving Na SO, MgCl, and some MgSO, (Ramon de Luna, J. pr. 66, 256). Decomposed, almost entirely, by heating in steam, giving off H₂SO, and leaving MgO (Clemm, J. 1864. 764). Strongly heated with charcoal gives off SO₂ and CO₂ (or CO), and leaves MgO. Mixed with NaCl and heated in Steam gives Na₂SO₄, MgO, and HCl.
Other hydrates of magnesium sulphate. (1)

MgSO, aq occurs native as kiescrite, S.G. 2-281 at 16° (Pape, P. 120, 869); dissolves slowly in cold wafer, easily in boiling water, forming MgSO, 7aq; prepared by heating the heptahydrate for a long time at 150°-160° (Pickering, C. J. 47, 100); S.G. 2-445 (Thorpe a. Watts, C. J. 37, 102). (2) MgSO, 6aq, by crystallising a solution of the heptahydrate above 40°; S.G. 1-734 (T. a. W., I.c.). (3) MgSO, 5aq, by drying the heptahydrate over conc. H₂SO₄; S.G. 1-869 (T. a. W., I.c.). (4) MgSO, 2aq, by boiling powdered MgSO, 7aq with absolute alcohol; S.G. 2-373 (T. a. W., I.c.). (5) According to Jacquelaine (A. Ch. [3] 32, 201), the hydrates 4M. 7aq, 4M.9aq, and 2M.5aq exist (M=MgSO).

Asid salts. Schiff (A. 106, 115) obtained deliquescent, hexagonal plates, MgSO, H₂SO₄; from a solution of MgSO, in hot conc. H₂SO₄; according to Schultz (P. 130, 149), the crysfals are MgSO, 3H₂SO₄. MgSO4. aq occurs native as kieserite. S.G. 2.281.

are MgSO, 3H₂SO, With K₂SO, or (NH₁)₂SO, to form compounds MgSO₄, M₂SO₄, 6aq; by crystallising mixtures of the component salts in tallising mixtures of the component salts in proper proportion. For solubility and S.G. of solution of the K.SO. compound, v. Tobler (A. 95, 193), Schiff (A. 113, 183), Gerlach (Fr. 8, 287). The compound of MgSO. and Na.SO. contains 4aq (cf. van't Hoff a. Deventer, B. 19, 2144). The compound MgSO. KCl. 3aq occurs native as kaintie (v. Reichardt, Ar. Ph. 159, 204; Erlenmeyer, B. 2, 289). A double salt MgSO. Al.(SO.). aRL20 occurs as feather alum, and wickeringite. Some triple salts of McSO. and pickeringite. Some triple salts of MgSO₄ with CaSO₄ and K₂SO₄ cocur as minerals (v. Reichardt, Ar. Ph. 159, 204; Precht, B. 14, 2138)

Manganese sulphates. salts. The normal salt MnSO, is obtained by dissolving MnCO₃ or Mn in warm dilute H₂SO₄Aq, crystallising out MnSO, 5aq, drying this salt, and heating to c. 280° until it ceases to lose and heating to c. 280° until it ceases to lose weight. A white salt, with very faint rose tint; S.G. 3-282 (Thorpe a. Watts, C. J. 37, 113). H.F. [Mn,S,O] = 249,900 (Th. 3, 516). S. 56-5 at 6.3°, 60 at 18.7°, 68.7 at 37.5°, 67 at 75° (Brandes, P. 20, 575). Decomposed by heating to full redness, giving off SO₂ and O, and leaving Mn₃O₄; heated in steam is said to give an oxysulphide Mn.OS (Arfvedson, P. 1, 50).

Hydrates of manganous sulphate. (1)
MnSO₄.7aq separates from solutions of Mn or MnCO, in H_2 SO, Aq below 6° (Mitscherlich, P. 25, 287; Classen, Ar. Ph. [3] 25, 310). Very pale se-coloured, monoclinic crystals; isomorphous with FeSO, 7aq. Very sol. water; S. at 18.5° c. 200 (Jahn, A. 28, 110). According to Etard (C. R. 86, 1399), solubility increases from 0°-55°, and decreases from 55°-145°; the from 0°-55°, and decreases from 55°-145°; the changes are probably due to the formation of different hydrates. (2) MnSO, 5aq, obtained by crystallising between 7° and 20°, or by treating a conc. solution of MnSO, with 95 p.c. alcohol and allowing to crystallise slowly (Claassen, Ar. Ph. [3] 25, 340). S.G. 2·103 (Thorpe a. Watts, C. J. 37, 113). H.F. [Mn,S,O.5ETO] = 263,600 (Th. 3, 516). (3) MnSO, 4aq, obtained by crystallising between 20° and 30° (C., Lc.; Mitscherlich, P. 25, 287). *S.G. 2·261 (Topsoë, C. C. 4, 76). This is the main constituent of ordinary manganese subbate. Mulder gives ordinary manganese sulphate. Mulder gives solubilities as follows:—

Temp.	S. MnSO, 4aq	Tem	B. MnSO. 480
0#	55.4	50°	74.8
5	58.2	54	75.3
10	63.8	63.5	61.3
20	66.3	64	61.5
25	68.5	85	61.3
30	70.4	90	60.3
85	71.9	95	57:9
40	73.1	100	52.9
, 4 5	74.0	•	

Insol. absolute alcohol (cf. Schiff, A. 118, 365). (4) MnSO₄. 2aq, obtained by boiling the powdered pentahydrate with absolute alcohol; also by pouring a saturated solution of the pentahydrate into cone. H₂SO₄; S.G. 2·526 (T. a. W., *l.c.*). (5) MnSO₄, aq, obtained by heating the pentahydrate at 100° till it ceases to lose weight; S.G. 2·845 (T. a. W., *l.c.*).

hydrate at 100 till it ceases to lose weight; S.G. 2-845 (T. a. W., l.c.).

Linebarger (Am. 15, 225) has obtained hydrates of MnSO, with 1, 2, 3, 4, 5, 6, and 7 H.O. Below - 10° mixtures of the heptahydrate and ice separate from MnSO, as; above 117° only MnSO, separates. The solubilities of the various hydrates are discussed; the more water in the hydrate, the more soluble it is.

Acid salts MnSO, H,SO, and MnSO, 3H,SO, were obtained by Schultz (P. 130, 149) by dissolving the normal salt in hot cone. H,SO,.

Basic salts are formed by adding a little warm KOHAq to a large excess of boiling MnSO₄Aq (V. Gorgeu, C. R. 94, 1425).

Double salts; (1) with sulphates of Cu, Fe, Mg,

Double salts; (1) with sulphates of Cu, Fe, Mg, and Zn to form salts MnSO, MSO, MSO, MHQO, WHQO (v. Rammelsberg, P. 91, 321; Vohl, A. 94, 73).

(2) With Al₄(SO₄)₃, Fe₂(SO₄)₃, and Cr₂(SO₄)₃ v. Etard (C. R. 86, 1399; 87, 602).

(3) With alkali sulphates to form MnSO, M₂SO, 4aq or 6aq (v. Marignao, Ann. M. [5] 9, 1; Pierre, A. Ch. [3] 16, 239; von Hauer, J. pr. 74, 431). For various triple salts of MnSO₄ with alkali sulphates and CuSO₄, MgSO₄, &c.; v. Vohl (A. 94, 57).

II. Manganic salts.—The normal salt Mn₂(SO₄), is obtained by the action of hot conc. H₂SO₄ on MnO₂. Carius (A. 98, 53) recommends to prepare pure MnO₂ by passing Cl into. NaOHAq containing MnCO₂ in suspension, to wash and dry the MnO₂, to rub up to a paste with conc. H₂SO₄, and heat gradually to 110° till O is given off and the mass becomes greyviolet, then to heat to c. 135°-140° till the whole is liquid, to pour the solid that forms as the liquid partially cools on to warm unglazed porcelain, after H₂SO₄ has become absorbed to mix with a little conc. HNO₂Aq and allow to drain on the porcelain, to repeat this treatment with HNO₂ six or eight times, and finally to heat at 150° till all HNO₂ is removed. Franke (J. pr. [2] 36, 451) detained Mn₂(SO₄), by heating 8 g. KMnO₄ with 100 c.c. conc. H₂SO₄ at 100° for some time. A dark-green powder; Franke describes it as green crystals. Decomposed above 160°, giving MnSO₄. Insol. conc. H₂SO₄ or conc. HNO₂AQ. Sol. conc. HClAq to a brown liquid, which gives off Cl whon warmed. Mn₂(SO₄), is very hygroscopic; quickly decomposed by water, with separation of MnO₂xH₂O (Carius, I.c.).

Forms double salts with Al₂(SO₄)₂, Fe₂(SO₄)₂, and Cr₂(SO₄)₂ (v. Étard, C. R. 86, 1399). The double compounds of Mn₂(SO₄)₂ with alkali sul-

phates—Mn₁(SO₄), M₂SO₄, 24aq—are alums. According to Fremy (C. R. 82, 1231), the salt Mn(SO₄)₂, manganese disulphate, corresponding with MnO₂, is formed by decomposing KMnO₄ by a considerable excess of cold conc. H₂SO₄ (cf. Franke, J. pr. [2] 36, 453).

Franke, J. pr. [2] 36, 453).

Mercury sulphates. I. Mercurous salts.

The normal salt Hg₂SO₄ is obtained by gently warming equal weights of Hg and conc. H₂SO₄. removing the white solid so produced before the whole of the Hg is changed, washing with cold water, and drying at a low temperature. Divers a. Shimidzu (C. J. 47, 639) recommend to mix Hg with fuming sulphuric acid rich in SO, in a covered dish, in a cool place, adding a little more Hg from time to time till there is sufficient to saturate the SO, in the acid, but avoiding excess, and when the Hg is all converted into Hg₂SO₄ to set the dish in a warm place to expel SO₂. Hg₂SO₄ is also obtained by adding 6 pts. water to 18 pts. HgSO, and rubbing with 11 pts. Hg (Planche, A. 66, 168). Also by ppg. HgNO, Aq by dilute H₂SO Aq or solution of a sulphate; or by rubbing together HgNO, and Na₂SO, and washing with cold water (H. Rose; Stoedeler, A. 87, 129). A white powder, consisting of mono-clinic prisms (S., l.c.); S. G. 7-56 (Playfair a. Joule, C. S. Mem. 2, 401). Sl. sol. water; S. in cold water '2, in boiling water '33; more sol. dilute HNO₃Aq; sol. conc. hot H₂SO₄, crystallising out on cooling. Hg₂SO₄ becomes grey on exposure to light (v. Buchner, Chem. Zeitung, 10, 759): hence the salt should be kept in the dark. Hg₂SO₄ melts to a reddish liquid, and decomposes at a higher temperature, giving off SO₂ and O, and also partially subliming. Slowly changed by boiling water to an acid salt, and a yellow powder which is probably a basic salt (v. Kane, P. 42, 367). An acid salt Hg.SO.,H.SO. is said to be formed by the prolonged reaction of conc. H₂SO₄ containing a drop of HNO₄Aq on Hg (Braham, C. N. 42, 163). A double salt Hg₂SO₄.2HgSO₄ was obtained by Brooks (P. 66,

Hg_BO_.211gSO, was obtained by House (r. ob. 63) by gently warming mercuro-mercuric nitrate (formed by warming 2 pts. Hg with 3 pts. HNO₃Aq S.G. 1.2) with Na₂SO, 4a. II. Mercuric salts. The normal salt HgSO, is obtained by the reaction of 6 pts. boiling conc. H₂SO, with 5 pts. Hg, till SO₂ ecases to be evolved, and a little of the white solid produced gives no pp. of HgCl when dropped into dilute HClAq; the white mass is gontly warmed till acid fumes cease to be given off. A white powder; S.G. 6466 (Playfair a. Joule, C. S., Mem. 2, 401). Becomes yellow, then red when heated; decomposes at red heat to Hg, O, and SO₂, a little HgSO, subliming (Mohr, A. 31, 180). Decomposed by water to a yellow basic salt and H₂SO₄Aq. Hot HgSO, absorbs HCl and HBr gases; according Dittle (A. Ch. 15) 17, 120) the compounds HgSO₂.2HCl and HgSO₂.2HCl is said to be sol. water without formation of basic salts, and HgSO₂.2HCl is said to sublime unchanged when heated. Solution of HgSO₄ in H₂SO₄Aq is said to react the Hg, 10 form the compound (3HgOO₃).Hg, P(H. Rose, P. 40, 75). Monohydrated mercuric sulphate HgSO₄-aq was obtained by Eisfeldt (Ar. Ph. [2] 76, 16) by covering a thin layer of HgSO₄ with the calculated quantity of water. The basic salt HgSO₄.2HgO

(=8HgO.SO.) is obtained by the action of hot water on HgSO, also by adding Na, SO, Aq to bot Hg(NO₃)₂Aq; a citron-yellow powder, J.G. 644; nearly insol. water (v. Cameron, An. 1880-144). Decomposed by Cl at the ordinary emperature. Absorbs HCl and HBr, forming IgSO.2HgO.6HOl(or 6HBr) (Ditte, l.c.). This asic salt was formerly known as minerale urpethum or turbith mineral (from its resemlance to a coloured gum obtained from an lance to a coloured gum obtained from an Uriental creeping plant [Ipomaca turpethum]). Hopkins (Am. S. 18, 364) described another basic salt 3HgSO, HgO = 4HgO.3SO, Double salts. — (1) HgSO, (NH), SO, xHO and HgSO, K,SO, xHO (v. Hirzel, J. 1850. 322). (2) HgSO, HgI, (v. Souville, J. Ph. 26, 474). (3) 2HgSO, HgS (v. Jacobsen, P. 68, 411). Molybdenum sulphates. By evaporating a solution of MoO, in conc. H₂SO, Schultz-Sellack (B. 4, 14) obtained white lustrous crystals of MoO, SO, the compound MoO, 3SO, 2aq, de-

of MoO, SO,; the compound MoO, SSO, 2aq, described by Anderson (B. J. 22, 161), could not be

obtained by S-S.

Nickel sulphates. The normal salt NiSO, is formed, as a clear yellow powder, by heating powdered NiSO, xaq (v. infra) to c. 800°. The salt is obtained in crystals, regular outsted an by heating NiSO., NiO, or NiOO, with five or six times its weight of fused (NH₁)₂SO., separating the yellow crystals of the double salt SNiSO₄.2(NH₁)₂SO, that form, and heating these in presence of some (NH₁)₂SO, in a partly closed crucible out of contact with the gases of the flame till all the ammonium salt is removed; S.G. of crystals 3.67 at 20° (Lepierre a. Lachaud, C. R. 115, 115; Klobb, C. R. 114, 836). Tobler (A. 95, 193) gives solubilities of NiSO, as fol-

Temp.	S.	Temp.	S.
20	80.4	410	49.1
16	87:4	50	52 ·0
20	89.4	53	54· 4
23	41.0	60	57·2
81	45·8	70	61.9

The hexahydrate NiSO, 6aq is obtained by dissolving Ni, NiO, or NiCO, in excess of H.SO,Aq, evaporating, and crystallising. At the ordinary temperature; bluish tetragonal pyramids separate (Brooke a. Phillips, P. 6, 193); greenish monoclinic crystals separate from warm solutions (Pierre, A. Ch. [3] 16, 252). The salt is, therefore, dimorphous (Marignac, A. 97, 294; cf. Mitscherlich, P. 12, 144; also Lecoq de Boisbaudran, A. Ch. [4] 9, 173). By dissolving this hydrate in water, and crystallising at 15°. 20°, emerald-green rhombic prisms of the heptahydrate NiSO. 7aq are obtained, isomorphous with MgSO. 7aq; melts at 98°-100° (Tilden, C. J. 45, 267). When this hydrate is heated to -103° it loses of 100 and leaves the monohydrate Niso, aq. . By passing NH, into Niso, Aq, compounds of the form Niso, xNH, yH, 0 are obtained (x=4, 5, and 6; v. F. Rose, Ammon. Kobaliverbind. [Heidelberg, 1871] 27; also P.

Double salts. (1) With (NH₁)₂SO₄, K₂SO₄, and TL₂SO₄ to form NiSO₄, M₂SO₄, 6aq (v. F. Rose, l.c.; Link, Crell's Ann. 1796 [1] 32; Werther, J. pr. 92, 182). (2) With BeSO₄ to form various compounds [Klatza Them disconnected to the second transfer of them disconnected to the second transfer of them disconnected to the second transfer of the secon sompounds (Klatzo, Über die Constant. der Beritlerie, Lorpat, 1808). (3) With CuSO., CoSO., FeSO., MgSO., MnSO., and with some of these and also alkali sulphates (v. Pierre, A. Ch. [3] 16, 253; Lecoq de Boisbaudran, C. R.

Basic salts are formed by the gradual reaction of NiSO, Aq with NiCO, and by adding a little NH, Aq to boiling NiSO, Aq (Habermann, M. 5, 440

Palladium sulphates. The normal palladous salt PdSO. 2aq is obtained in brown crystals by evaporating a solution of Pd in H₂SO.Aq containing HNO. Addition of a little KOHAq to a cone solution in water of the normal salt ppts. a basic salt PdSO₄.7PdO.6aq (v. Kane, B. J.

24, 236).
Platinum sulphates. By dissolving PtO₂H. in dilute H.SO, Aq, Berzelius (Lehrbuch [5th ed.] in diute H₂SO₄Aq, Berzelius (Lehrbuch [5th ed.] 8, 987) obtained a dark syrup which probably contained platinous sulphate PtSO₄. Platinic sulphate Pt(SO₄)₂ was obtained by Berzelius (L.c., p. 989) by evaporating PtCl₄ with conc. H₂SO₄ (1 part acid for 1 part Pt), as an almost black solid. E. Davy (T. 1820) obtained the salt by oxidising PtS₂ by fuming HNO₃. Prost (Bl. [2] 46, 156) obtained a basic salt by allowing an end of salt that the salt of the acid solution of Pt(SO4)2 to stand for some days; Prost also describes several double salts of Pt(SO4)2 with alkali sulphates.

Potassium sulphates. The normal salt K₂SO₄ is found in the lava from Vesuvius, in small quantities in sea water, and in some mineral springs, in combination with MgSO, and MgCl, as kaintle (K,SO,MgSO,MgSO,MgCl, Saq), in combination with MgSo, and CaSO, as polyhalite (K,SO,MgSO,2CaSO,2aq), and as alum. K,SO, is prepared by decomposing KCl by H,SO, by neutralising H,SO,Aq by KOH or K,OO, and evaporating (for the preparation of K2SO, on the large scale v. DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 279). K,SO, forms in white, hard, four-sided, trimetric prisms, unchanged in air. four-sided, trimetric prisms, unchanged in air, S.G. 2.656 at 4° (Playfair a. Joule, C. J. 1, 132); for S.G. at various temperatures from 0° to 100° v. Spring, B. 15, 1940. Melts above 861° (Carnelley, Melting-and Boiling-Point Tables, 1, 33); melts at 1973° according to V. Meyer a. Riddle (B. 26, 2443). H.F. [K', S, O'] = 344,600 (Th. 3, 516); [K'SO', Aq] = -6167 (Pickering, C. J. 47, 98). Mulder (Scheikund. Verhandg. 1864. 49) gives solubilities in water as follows: gives solubilities in water as follows:-

Temp.	S.	Temp.	8.
5°	9.1	55°	16.8
10	9.7	60	17.8
15	10.3	65	18.8
20	10.9	70	19.8
25	11.6	75	20.8
80	12.3	80	21.8
85	13.1	85	.22.8
40	14.0	90	23.9
45	14.9	● 95	25.0
50	15.8	100	26.2

Gerlach (Fr. 8, 827) gives S.G. of K,SQ,Aq as

Pctge.K,SO.	S.G. K.SO. Aq 1.00829	Petge.K.SO.	S.G. K.SO. Aq 1:04947
2	1.01635	7	1.05790
8	1.02450	8	1.06644
4	1.03277	9	1.07499
5	1.04105	9.92 (satd	.) 1.08805

Insol, absolute alcohol; sol. aqueous alcohol in proportion to amount of water present (v. Schiff, A. 118, 362). Insol. KOHAq 1.32 S.G.; sl. sol. KOHAq 20 p.c. S. in saturated NH₃Aq = 0365 (Giraud, Bl. [2] 43, 552). S. in glycerin (S.G. 1·225) at ordinary temperature = 1·32 (Vogel, N. R. P. 16, 557). More sol. in solution of CuSO, MgSO, or Na SO, than in water. Reacts with strong acids to give KHSO, (for thermal measurements v. Berthelot, Essai de méc. chimique, 1, 389). Dissolves in hot conc. HNO,Aq, KHSO, separates on cooling, then KNO, and then a compound of K,SO, with HNO, ; H, PO, Aq reacts similarly (v. Jacquelain, Biedermann's Techn. Chem. J. 4, 62). Absorbs HCl gas when heated, forming KCl and KHSO. (Thomas, C. J. 33, 372; Hensgen, B. 9, 1671; 10, 259). Decomposed by heating with NH.Cl, giving KCl (H. Rose, P. 64, 568). Heated to redness with iron filings gives KOH mixed with Fe₂O₃ and FeS (d'Heureuse, P. 75, 255). Reduced to sulphide (or KSH) by heating in CO; to KSH and KOH by heating in H (v. Berthelot, C. R. 110, 1106). Sulphur reacts at full red heat, giving SO₂ and polysulphides of K (Berthelot, C. R. 96, 303). SO₂ is without action at a red

Double salts. (1) With $Al_2(SO_4)_3$, $Cr_2(SO_1)_3$, and $Fe_2(SO_4)_3$ to form K_2SO_4 , $M_2(SO_4)_3$, 24aq; v. potash alum, potash chrome-alum and potash iron-alum, under Aluminium sulphates (p. 568), FORMALIM, under ALUMINIUM SULPHATES (p. 568), CHROMIUM SULPHATES (p. 577), and IRON SULPHATES (p. 572). (2) With sulphates of Ce and Di respectively, to form 3K_SO_4M_(SO_4), (v. Cleve, Bl. [2] 43, 359; Czudnowitz, J. pr. 82, 129; Hermann, J. pr. 82, 385); also the salt 2K_SO_4Ce(SO_4)... 2aq (Marignac, Ann. M. [5] 15, 275). (3) With sulphates of Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn to form K_SO_4MSO_4. 6aq (v. Graham, P. M. 1835, 327. 417; Brunner, P. 15, 476; 32. P. M. 1835. 327, 417; Brunner, P. 15, 476; 32, 221; Pickering, C. J. 49, 1; Tobler, A. 95, 193; 221; Pickering, C. J. 49, 1; Tobler, A. 95, 193; Schiff, A. 108, 326; 113, 183; Gerlach, Fr. 8, 287; Marignao, Ann. M. [5] 9, 19; Wilm, A. Ch. [4] 5, 56; Pierre, A. Ch. [3] 16, 239; von Hauer, J. pr. 74, 431; Werther, J. pr. 92, 132). (4) K.SO.,BeSO., 2aq (Awdojeff, P. 56, 101). (5) K.SO.,Na.SO, (Penny, P. M. [4] 10, 401; Mitscherlich, P. 58, 468; von Hauer, J. pr. 83, 256).

Stol.

The acid salt KHSO, occurs in some volcanic districts as miserits; it is formed by heating 13 parts K,SO, with 8 parts conc. H,SO, or by heating KNO, and conc. H.SO, in the ratio KNO, H.SO. Crystallises in white rhombic KNO.:H.SO. Crystallises in white rhombic forms, S.G. 2.273; also in monoclinic forms, S.G. 2245 (v. Wyrouboff; abstract in C. J. 50, 665).

Molts at c. 200°. Easily sol. water; Kremers gives S. 33°9 at 0°, 48 at 20°, 62°9 at 40°, 114 at 100°. An aqueous solution is said to deposit, first K2SO, then KHSO, K2SO, and then KHSO; by evaporating KHSO, Aq at a low temperature until a solid mass formed on removing the flame, arborescent and very deliquescent crystals formed on the surface of the solid, which were 2KHSO₄.11H₂O according to Senderens (Bl. [3]

Other acid salts. (1) KHSO₄,K₂SO₄, obtained by evaporating KHSO₄Aq. (2) 2KHSO₄,K₂SO₄, orystallising from K₂SO₄ in H₂SO₄Aq (Phillips, J. pr. [2] 1, 429; Marignae, Ann. M. [5] 9, 7). (8) KHSO₄,H₂SO₄, formed by heating K₂SO₄ with

less than 5 parts conc. H.SO. (Schultz, P. 133.

137).

Rhodium sulphates. The normal rhodic sulphate Rh₂(SO₄), is obtained by dissolving Rh₂O₄, xaq in H₂SO₄Aq, evaporating, and heating to 400° till excess of acid is removed; a red powder, decomposed by hot water to the yellow basic salt Rh₂(SO₁)₃.Rh₂O₃ (Leidié, C. R. 107, 234). Claus (Beiträge zur Chemie der Platinmetalle [Dorpat, 1854]) obtained the hydrate Rh₂(SO₄)₃. 12aq, as a pale-yellow crystalline salt, by crystallising a solution of Rh.O. xaq in H.SO, Aq, and washing with alcohol. The double salt Rh (SO4) 3K SO4 was obtained by Claus (l.c.) by evaporating a solution of the constituent salts in the ratio Rh (SO₄)₃:5K₂SO₄. The double salt Rh₂(SO₄)₃:Na₂SO₄ was obtained by Bunsen (A. 146, 265; v. also Seubert a. Kobbé, B. 23, RhSO₂.0Na₂SO₃.9aq (formed by heating RhCl₂Aq for some time with NaHSO₃).

Rubidium sulphates. The normal salt

Rb2SO4 is obtained by neutralising H2SO Aq by Rb₂CO₂ and evaporating; it crystallises in transparent, hexagonal forms, unchanged in air. S. 42.4 at 70°. S.G. 3.6438 at 0°; 3.6256 at 50°; 3-6036 at 100° (Spring, B. 15, 1940). If excess of H₂SO₄Aq is used, the acid salt RbHSO₄ separates in rhombic prisms (Kirchoff a. Bunsen, P. 115, 584).

Double salts. (1) With Li₂SO₄ to form RbLiSO₄ (Wyrouboff, Bl. [2] 48, 184, 630). (2) With CaSO₄ and PbSO₄ to form the compounds (2) With Caso, and Paso, to form the combounds Rb₂SO, 2MSO, xag (Ditte, C. R. 89, 641). (3) With Al₂(SO₄), to form rubidium alum Al₂(SO₄), Rb₂SO₄. 24aq (Bunsen, P. 119, 1; Godefiroy, A. 181, 176; Redtenbacher, J. pr. 95, 143).

Ruthenium sulphate. Normal ruthenic sulphate Ru(SO₄)₂ is obtained by oxidising RuS₄ (formed by prolonged action of H₂S on RuCl₂Aq) by conc. HNO, Aq, and evaporating off excess of acid. An amorphous, brownish-yellow, very hygroscopic solid. Strongly heated gives RuO,

(Claus, J. pr. 42, 364).
Silver sulphates. The normal salt Ag, 80, is obtained by heating finely divided Ag with exobtained by neating inner divided Ag with excess of conc. H₂SO₄, by neutralising H₂SO₄Aq by Ag₂O or Ag₂CO₃ and evaporating, by evaporating AgNO₃ with H₂SO₄Aq, or by ppg. AgNO₃Aq by Na₂SO₄Aq. Small, white, lustrous, rhombic crystals, isomorphous with Na₂SO₄ (Mitsoherlich, 2012) and 1952 (1952) and 1952 (crystals, isomorphous with Na₂SO₄ (altesenericit, P. 12, 138; 25, 301). S. 1-15 cold water, 1-45 at 100° (Wenzel, P. 82, 136). S.G. 5-322 (Playfair a. Joule, C. S. Mem. 2, 401), 5-425 when fused (Schröder, P. 106, 226). Decrepitates when heated to 300°; melts at 645° (Carnelley, C. 1000). when heaved to 500°s; meits at 645° (Carnelley, C. J. 33, 279). Decomposed at very high temperature, giving Ag, SO₂, and O. Reduced to Ag by heating in H, with C, or in CO (Stammer, J. pr. 11, 70). Absorbs 2NH, (H. Rose, P. 20, 153).

20, 153).

Acid salts are obtained by dissolving Ag₂SO₄ in different quantities of H₂SO₄Aq and crystallising; Schultz (P. 133, 187) describes (1) AgHSO₄, (2) 2Ag₂SO₄.3H₂SO₄.2aq, (3) Ag₂SO₄.3H₂SO₄.2aq. (3) Ag₂SO₄.3H₂SO₄.2aq. (3) Ag₂SO₄.3H₂SO₄.2aq. (3) Ag₂SO₄.3H₂SO₄.2aq. (3) Ag₂SO₄.3H₂SO₄.2aq. (3) Ag₂SO₄.3G₄.

Forms a double salt Ag.SO.Al. (SO.) .. 24aq; this salt is an alum (v. Church a. Northcote, C. N. 9, 155). Also combines with Ag₂S and with K₂SO₄ (Berzelius; H. Rose, P. 53, 463)

S dium sulphates. The normal salt Na2SO. occurs native as thenardite, in combination with CaSO, as glauberite, and with MgSO, as loweite; the salt also occurs in sea water and in many mineral springs. It is prepared by adding H2SO to NaCl in the ratio NaCl:H2SO, and strongly the NaHSO, thus produced; also by the reaction between NaCl, SO₂, steam and O at 400° 450°; 2NaCl + SO₂ + O + H₂O - Na,SO, + 2HCl (for the application of these processes on the large scale v. Dictionary of APPLIED CHEMISTRY, vol. iii. p. 439). Na.SO, is also obtained in the decomposition of NH.Cl. or NaNO₂, by H₂SO₄; it is formed by neutralising H₂SO₄Aq by NaOHAq or Na₂CO₃, evaporating, and heating to redness the crystals of Na, SO, xaq that separate. Na, SO, is a white amorphous powder; S.G. 2.597 (Playfair a. Joule, C. S. Mem. 2, 401); 2.631 (Karsten, S. 65, 894). Obtained in rhombic crystals, isomorphous with Ag₂SO₄ (Mitscherlich, P. 12, 138; 25, 301), by heating to 40° a solution saturated at 33° B.G. 2.6618, or 2.6637 crystallised at 110° (Nicol, P. M. [5] 15, 94). Dissolves in water with production of heat; according to Berthelot (C. R. 78, 1722) [Na°SO', Aq] = 780 at 21.2°, but -100 at 8°; Pickering (C. J. 45, 686) thinks that two modifications of Na,SO, exist; the salt dried at 100° or 150° gave [Na°SO', Aq] = 57 at 20.4°, but the half tipe to townsorthing a varying from 250°. after heating to temperatures varying from 250° to the melting-point the heat of solution was $[Na^2SO^4,Aq] = 760$. Thomsen (Th. 3, 516) gives H.F. $[Na^2,S,O^4] = 328,600$. Tilden (Pr. 35, 345)gives solubilities as follows: 5 at 0°, 788 at 34°, 42°7 at 100°, 41°95 at 120°, 42 at 140°, 42°9 at 160°, 44°25 at 180°, 46°4 at 230°. Etard (C. R. 113, 854) says that S. increases from 33° to 80°, remains constant to 230°, and then decreases to 820° (v. also Löwel, A. Ch. [3] 33, 334; 49, 32; Gernez, C. R. 60, 833; de Coppet, Bl. [2] 17, 146). For S.H. and expansion of Na₂SO₄Aq v. Thomsen (P. 142, 837) and Marignae (A. Ch. [4] 22, 415). Na,SO, melts at 861° (Carnelley, C. J. 33, 280); at 843° (V. Meyer a. Riddle, B. 26, 2448). S.G. at melting-point = 2·104 (Braun, B. 7, 958)

Heated with charcoal out of air Na₂S0, is reduced to Na₂S; Gay-Lussac (A. Ch. [2] 11, 312) says polysulphides are also formed; CO₂ is evolved, but no CO (Unger, A. 63, 240; Scheurer-Kestner, A. Ch. [4] 1, 412; Stromeyer, A. 107, 361); heated to bright redness with O in a vessel containing air, Na₂S is formed and CO evolved (Berthelot, C. R. 1.0, 1106). Reduced to sulphide by heating to bright redness in carbon monoxide (B., l.c.); reduction by hydrogen begins at c. 500°, the products are Na₂S, NaSH, NaOH, H.O. and H.S (B., Le.). Heated with hydrogen chloride, NaCl is formed (Bousingault, C. R. 78, 593); boiling HClAq produces NaCl and NaHSO, (Thomas, C. J. 33, 373). A little NaCl is formed by heating with ammonium chloride (Nicholson, C. N. 26, 47). Boiled with barium carbonate some Na₂O₂ and BaSO, are formed; after a time a condition of equilibrium is attained. A very little NaOHAq is produced by boiling for some time with milk of lime; ander increased pressure NaOHAq is formed

(v. Scheure: Kestner, A. Ch. [4] 1, 412). Not decomposed by heating strongly with calcium carbonate (S.-K., l.c.). When a mixture of Na, 30, and alumina is heated in steam, 30, is given off and södium aluminate remains; presence of charcoal hastens the reaction (Wagner). According to Stromeyer (A. 107, 361) fusion with iron produces Fe, 0,, Na, 0, and Na, 3.2 FeS. The final products of heating with silica and carbon in a closed crucible are Na, 0.2 SiO₂, S, CO₂ and CO (S.-K., C. R. 114, 117).

Hydrates of Na.SO. (1) The hepta-hydrate Na.SO. Taq is obtained by melting Glauber's salt Na.SO. 10aq in its water of crystallisation, heating to boiling, at once closing the vessel, and shaking repeatedly as the liquid cools till 18° is reached; Na SO, separates at first but dissolves again, and below 18° Na SO, 7aq separates (Löwel, A. Ch. [3] 33, 334; 49, 32). The following method gives better results (L., l.c.): 22 parts Na,SO, 10aq are dissolved in 10 parts water, the solution is heated to boiling, and the flask is then closed with a cork carrying two narrow tubes bent at right angles; when the liquid is cold the outer end of one of the tubes is dipped into 30 p.c. alcohol at 40°, and the alcohol is caused to run into and fill the flask by sucking at the outer end of the other tube. As the alcohol withdraws water, large, translucent, rhombic or tetragonal crystals of Na2SO. 7aq gradually separate. The crystals must be quickly pressed between filter paper.
They rapidly absorb water from the air, changing to Na₂SO₄, 10aq; exposed to air, even under dilute alcohol, they soon change to the decahydrate. According to Löwel (l.c.) the heptahydrate is much more soluble in water between nydrate is much more solubrate. The temperature of maximum solubility is 27°; the solution then contains 56 p.c. Na₂SO₄, which is the same quantity as is present in solution of Na SO. 10aq saturated at 34°-36°. If a crystal of Na, SO, .7aq is added to the saturated solution of this salt at 27° it does not dissolve, but crystals of Na SO. separate until a concentration is reached corresponding with a saturated solution of Na2SO4 at the temperature. The heptahydrate is able form supersaturated solutions, but less readily than the decahydrate; addition of a crystal of Na₂SO, 7aq causes separation of the heptahydrate. These results were confirmed by de Coppet (Bl. [2] 17, 146).

(2) The decahydrate Na. SO., 10aq crystallises from a hot saturated solution of Na. SO, cooled to at least 32°; a supersaturated solution may be cooled in a closed vessel to 0°. If a crystal of Na. SO., 10aq is dropped in, a mass of crystals of the decahydrate is formed, and the temperature rises to c. 18°. Large, white, striated, monoclinic prisms; isomorphous with Na. CrO., 10aq and Na. SeO., 10aq. S.G. 1.469 (Playfair a. Joule, C. S. Mem. 2, 401); 1.485 at 19°, 1.492 at 20° (Pettersson, Upsala, Nova Acta, 1874). [Na. S.O., 10H°O] = 347,800 (Th. 3, 516). Melts at 34° (Tilden, C. J. 45, 267). Effloresces in air. When melted in the water of crystallisation, boiled, and allowed to cool in a closed vessel, Na. SO, separates, but on shaking, this salt dissolves till 18° is reached, after which crystals of Na. SO, 7aq separate (v. supps). Na. SO, 10aq is insol. absolute alcohol; shooth of S.G. *776 dissinsol. absolute alcohol; alcohol of S.G. *776 d

solves 14:85 p.c., of S.G. 972 dissolves 5:6 p.c. and of S.G. 939 dissolves 1.8 p.c. Solubility in water increases with temperature to 33°-34°. whereat the solution contains 55 parts Na₂SO₄ in 100 of water; a crystal of Na₂SO₄.10aq dropped into the solution dissolves, and Na₂SO₄ separates till 49:53 parts Na,SO, are in solution in 100 parts water, which is the same quantity in 100 parts water, which is the same quantity of Na,SO, as is present in a solution made by saturating water with Na,SO, at 34° (Lowel, A. Ch. [3] 83, 334; 49, 82). As temperature is increased above 34° Na,SO, seems to be formed, and the solubility of this salt decreases as temperature rises to the b.p. of saturated Na.SO.Aq. There appear to be three temperatures of maximum solubility for Na2SO, and its hydrates: (1) at 34°, which is the maximum for Na, SO, 10aq, (2) at 26°-27° for Na, SO, 7aq, (3) at 17°-18° for Na, SO,. The quantity of salt in solution, calculated as Na, SO, is about the same at these temperatures. Löwel (l.c.) gives the following

8.G. 1·1015	P.c. Na.80. 11:025	P.o. Na_80. 10aq 25
1.1057	11.466	26
1.1100	11.907	27
1.1142	12.348	28
1.1184	12.789	29
1.1226	13.230	* 80

Acid salts. (1) NaHSO,; by adding 7 parts H₂SO,Aq S.G. 185, to 10 parts Na₂SO,, and heating gently till the mass melts and watervapour ceases to be given off. By dissolving in water, or by evaporating Na₂SO₄ in H₂SO₄at 50°, crystals of NaHSO₄ aq are obtained (Mitscherlich, P. 12, 138; H. Rose, P. 82, 545). (Mitscherlich, P. 12, 138; H. Rose, P. 82, 545). (2) Na,SO, NaHSO, (= Na,H(SO,)2); by crystallising Na,SO, from half as much H,SO, in water as is required to form NaHSO, (M., Lc.; R., Lc.). (3) NaHSO, H,SO, (NaH,(SO,)2); by crystallising Na,SO, from solution in almost 7 parts H,SO, (Schultz-Sellack, J. pr. [2] 2, 459; Lescœur, C. R. 78, 1044).

Double salts. (1) Na, SO, K, SO, (Penny, P. M.

100 parts water contain, when solution is saturated.

Temp.	Na ₂ 80 ₄ Sol. made	Na.SO. 10aq with Na.SO.	Na ₂ SO ₄ Sol. made w	Na.SO. 10aq Ith Na.SO. 10aq	Na _s SO ₄ Sol.	Na.807aq made with N	Na_80 ₄ . 10aq a_80 ₄ . 7aq
0°		_	5.02	12.16	19.62	44.84	59.28
10	-		9.00	23 04	30.49	. 78.90	112.73
15			13.20	35.96	37.43	105.79	161.57
18	53.25	871.97	16.80	48.41	41.63	124.59	200
20	52.76	361.51	19.40	58 ·3 5	44.78	140.01	234.4
25	51.53	337.16	28	98.48	52.94	188-46	865.28
26	51.31	333.06	30	109.81	54.97	202-61	411.45
. 80	50.37	816.19	40	184.09			
83	49.71	305.06	50.76	323-13			
84	49.53	802.07	55	412-22			
40.15	48.78	290.00					
45.04	47.81	275.84					
50.4	46.82	261.36					
59.79	45.42	242.89					
70.61	44.35	229.87					
84-42	42.96	213.98					
103.17	42.65	210.67					

at 19°:-

8.G.		P.o. Na.SO.	P.o. Na SO. 10
1 ·004 0		1.441	1
1.0079		1.881	2
1.0118		1.323	8
1.0158		1.764	4
1.0198		2.205	5
1.0238		2.646	6
1.0278		8.087	7
			8
		8.969	9
		4.410	10
			ii
			12
			18
			14
			15
			16
			17
	•		18
			19
			20
			21
			• 92
	***		28
1-0978		10-584	. 34
	1-0040 1-0079 1-0118 1-0158 1-0198 1-0228 1-0228 1-0318 1-0358 1-0358 1-0459 1-0459 1-0459 1-0550 1-0601 1-0662 1-0662 1-0725 1-0725 1-0725 1-0849 1-0893 1-0931	1-0040 1-0079 1-0118 1-0158 1-0158 1-0238 1-0278 1-0358 1-0358 1-0398 1-0479 1-0520 1-0560 1-0601 1-0642 1-0663 1-0725 1-0766 1-0890 1-0890 1-0890	1-0040 1-441 1-0079 1-881 1-0118 1-323 1-0158 1-764 1-0198 2-205 1-0238 2-646 1-0278 3-087 1-0318 3-528 1-0358 3-969 1-0358 3-969 1-0398 4-410 1-0439 4-851 1-0479 5-292 1-0520 5-373 1-0560 6-174 1-0601 6-615 1-0642 7-056 1-0642 7-056 1-0643 7-497 1-0725 7-938 1-0725 7-938 1-0766 8-379 1-0766 8-379 1-0769 8-320 1-0849 9-261 1-0890 9-702 1-0890 1-168

The following table gives S.G. of Na,SO,Aq [4] 10, 401; Mitscherlich, P. 58, 468; von 19°:—

S.G. P.O. Na,SO, 10aq 1.0040 1.441 1.0079 1.881 2 with Li,SO, (Raumnelsberg, P. 128, 311; Wyrou-10118 1.323 3 boff, Bi. [2] 9, 35. (4) With sulphates of Cd, Ca, Cu, Di, In, Fe, La, Mn, and Mg; references 1.0108 under Cadmium sulphates, Calcium sulphates, &c. (5) The compounds Na SO, M2 (804) . 24aq, where M = Alor Cr, are alums (references under ALUMINIUM SULPHATES and CHROMIUM SULPHATES). Strontium sulphates. The normal salt SrSO, occurs native as celestine. It is obtained by adding H SO, Aq or solution of an alkali sulphate to solution of a strontium salt; large conc. H₂SO₄, adding dilute HClAq, heating to 150°, allowing to cool, again heating to 150° with HClAq, and repeating this treatment three or four times (Bourgeois, C. R. 105, 1072). SrSO₄ or four times (Bourgeois, C. R. 10s, 1072). SrSO, is also obtained crystalline by fusing K.SO, with excess of SrCl₂ (Manross, A. 82, 350). A white solid; S.G. 3-927 to 3-955 crystalline (M., l.c.; Neumann, P. 23, 1); 3-7 ppd. (Schröder, P. 106, 226; v. also Clarke's Table of Spec. Gravs. [New Ed.] 82). H.F. [Sr,S,O.] = 830,900 (Th. 8, 516). Almost insol. water; S. 0145

ordinary temperature, '0104 at 100° (Fresenius); taking care that Sn is in excess, dissolving the insol. dilute H_SO₄Aq; S. conc. H₂SO₄ at 70° = 14 white solid so formed in water, and allowing to NaCl, KCl, MgCl, and CaCl, v. Virck (C. C. 1862, 402). Melts when strongly heated; is de-(Bousingault, J. 1867, 161). Reduced by heating strongly with C, Fe, or Zn (d'Heureuse, P. 75, 277), or in a steam of H or moist CO (Jac-75, 271), of in a seeam of it of moise to concurrent, C. R. 46, 1164). Loses SO, when heated with As,O₃ (Moretti, S. 9, 169), or when heated continuously to redness in HCl (Bousingault, C. R. 78, 593). Decomposed by heating with solutions of alkali carbonates. Forms double salts, SrSO₄M₂SO₄, with alkali sulphates (H. Rose, P. 93, 604; 110, 296). An acid salt SrH₂(SO₄)₂ (= SrSO₄H₂SO₄) is formed by digesting SrSO₄ in conc. H₂SO₄ with excess of SrSO₄ (Schultz, P. 118, 147).

Thallium sulphates. The normal thallous salt Tl₂SO₄ is obtained by dissolving Tl in hot H₂SO₄ or by neutralising H₂SO₄Aq by TlOH or Tl₂CO₃, and evaporating (Crookes, C. N. 24, 38). Forms white rhombic prisms, isomorphous with K-SO, (von Lang, P. M. [4] 25, 348); S.G. 6:77 (Lamy, Bl. [2] 11, 210; v. also Clarke's Table of Spec. Gravs. [new ed.] 79). H.F. [TI; S.O'] = 221,000 (Th. 3, 516). S. 4:74 at 15°, 18:5 at 1000 (Tany, Ia). 100° (Lamy, l.c.). Not decomposed by heating to full redness in absence of air; heated more strongly in air gives Tl2O8, SO2, and O (Carstanjen, J. 1867. 279). Reduced to Tl₂S by heating with KCN. The acid thallous salt TlHSO, 3aq separates from a solution of the normal salt in H₂SO₄Aq after some months. When strongly heated yields Tl₂SO₄ and H₂SO₄ (Carstanjen, l.c.). Double salts, Tl₂SO₄.MSO₄, 6aq, are formed when M = Cu, Fe, Mg, Ni, or Zn (Willm, A. Ch. [4] 9, 5: Werther, Bl. [2] 2, 272). The salt Tl₂SO₄Al₂(SO₄)₃. 24aq is an alum (v. Lamy, Bl. [2] 11, 210). Normal thallic sulphate Tl₄SO₄O₄, 7aq is obtained as thin, white leaflets by dissolving Tl₂O₃.H₂O in fairly conc. H₂SO₄Aq and evaporating. Loses 6aq when heated to 200°, at higher temperatures SO₂ and O are given off and Tl₂SO₄ remains (Strecker, A. 135, 207: separates from a solution of the normal salt in off and Tl₂SO₄ remains (Strecker, A. 135, 207; Crookes, C. N. 8, 243). The double salts Tl₂(SO₄), M₂SO₄ [= TlM(SO₄)₂], where M = K or Na, are described by Strecker (l.c.).

Thorium sulphates. The hydrated normal sulphate Th(SO4)2. xaq is obtained by dissolving ThO, in slight excess of H2SO, Aq, and crystallising at 10°-15°. The anhydrous salt is obtained by heating the hydrated salt to c. 400° (v. Chydenius, P. 119, 43; Delafontaine, A. 131, 100; Cleve, Bl. [2] 21, 115; Demarçay, C. R. 96, 1860). For a full discussion of the conditions of formation, relations, and solubilities of the of formation, relations, and solubilities of the various hydrates of $Th(SO_4)_2$ v. Roozeboom (Z.P.C.5, 198). $Th(SO_3)_2$ has $S.G.4\cdot058$ at $22\cdot8^\circ$ (Clarke, Am. 2, 175); $4\cdot2252$ at 17° (Krüss a. Nilson, B.20, 1675). The S.G. of $Th(SO_4)_2$, 9aq is $2\cdot767$ according to Topsée (Bl.[2], 21, 120). The hydrate Th(SO₁), 9aq is isomorphous (mono-clinic) with U(SO₄), 9aq (Rammelsberg, B. B. 1886. 603). Double salts Th(SO₄), M.SO₄, xaq are known, where M = an alkali metal (Cleve, l.c.; Chydenius, l.c.).

Tin sulphates. The normal stannous salt SnSO, is obtained, in very small white crystals, by dissolving Sn in warm fairly conc. H.SO.Aq,

white solid so formed in water, and allowing to crystallise out of contact with air (Marignac, Ann. M. [5] 15, 221). SnSO, is very sol. water; the solution soon deposits basic salts. The normal stannic salt Sn(SO4)2. 2aq was obtained by Ditte (C. R. 104, 178) by dissolving SnO₂ xaq (ppd. from SnCl₁Aq by alkali) in dilute H₂SO₄Aq and evaporating (v. also Kraskowitz, P. 35, 518). It forms white rhombic leaflets; very sol. water; decomposed by much water with separation of SnO₂. A basic salt SnO(SO₄), aq is said to be formed (Ditte, l.c.) by dissolving the normal salt in H2SO, Aq, warming, adding excess of Sn, and then ether.

Titanium sulphates. Normal titanous sulphate Ti2(SO4)3. Saq is obtained, as violet crystals, by evaporating a solution of Ti in H2SO, Aq; warmed (Glatzel, B. 9, 1833; Ebelmen, J. pr. 42, 76). Normal tilanic sulphate Ti(SO₄)₂, 3aq was obtained by Glatzel (l.c.) by oxidising the titanous salt by HNO₃, adding a drop or two HEADOS SAIL BY INO., BARRING & GROP OF TWO H.SO., Aq. and evaporating; a white, translucent mass. A double salt Ti(SO.)...K.SO., 3aq was obtained by Warren (P. 102, 449), by fusing TiO. with KHSO., treating with cone. H.SO. evaporating, and washing the residue with cold water (v. also Glatzel, l.c.). By dissolving TiO2 water (v. also Giatzei, i.e.). By dissolving 1102 in hot H_SO,Aq, evaporating, drying the residue on a porous tile at 180°, and then heating to c. 350°, Merz (J. pr. 99, 157) obtained the acid salt TiO.SO, as a hard white solid.

Uranium sulphates. Normal uranic sul-

phate U(SO₄)₂. 9aq is obtained, as green monoclinic crystals isomorphous with Th(SO₄)₂. 9aq (Rammelsberg, B. B. 1886. 603), by evaporating a solution of UO₂ in excess of H₂SO₂Aq (R., l.c.; Ebelmen, J. pr. 27, 385). Unchanged in air; slowly loses water of crystallisation when heated; at higher temperatures gives yellow (UO2)SO4, at higher temperatures gives yenow (UU_)SU, and when strongly heated leaves U_0. Heated in H gives UO₂. Easily sol. dilute H_SO₄Aq or HClAq. Decomposed by water, giving basic satts (v. R., l.c.; Athanasesco, C. R. 103, 271). Forms double satts with alkali sulphates (R., l.c.). The uranyl salt (UO.)SO, xaq is obtained, in citron-yellow crystals, by dissolving U,O, in H,SO,Aq with a little HNO,; or by decomposing UO2(NO3)2 by conc. H2SO4, evaporating nearly to dryness, dissolving in water, evaporating to a syrup, and allowing to crystallise slowly (Ebela syrup, and anowing to crystallise slowly (Enermen, A. 56, 230). By evaporating a solution of the hydrated salt in conc. H₂SO₄, Schultz-Sellack obtained the anhydrous salt (UO₂)SO₄ (B. 4, 13). Forms double salts with alkali sulphates (UO.)SO. M.SO. 2aq (Rammelsberg, B. 5, 1005). Vanadium sulphates. Vanadyl sulphate

(VO)SO4. xaq is obtained by heating a solution of V2O, in conc. H2SO, Gerlach (B. 11, 98) prepared several compounds of V2O, and SO, by dissolving V_2O_3 in H_2SO_4 . For more details and descriptions of various salts v. Vanadium Tetrox-

descriptions of the confidence is obtained by dissolving Zn, ZnO, or ZnCO, in dilute H.SO.Aq, evaporating, drying the crystals of ZnSO. 7aq, and gradually heating to c. 280° till water ceases to be given off; it is difficult to drive off every trace of water without decomposing some of the ZnSO, and forming

basic sulphates. Klobb (C. R. 114, 836) obtained ZnSO, in crystals by heating ZnSO, 7aq mixed with excess of (NH₄)₂SO, in a partlymixed with excess of (NH_{d/2}SO₄ in a party-closed crucible, protected from the gases of the flame, till all (NH_{d/2}SO₄ was volatilised. A white solid; S.G. 3:435 at 16° (Pape, P. 120, 367); 3:6235 at 15° (Thorpe a. Watts, C. J. 37, 108). H.F. [Zn,S,O⁴] = 230,100 (Th. 3, 516). Decom-posed to ZnO, SO₂, and O at c. 400° (Bailey, C. J. 51, 681). Heated with charcoal, SO, and CO2 are evolved and ZnO remains; if the temperature is rapidly raised to a white heat, SO, and CO are given off and ZnS is formed. Heating in H produces an oxysulphide of Zn. For solubility in water v. infra. [ZnSO,,Aq] = 9,950 (Th. 3, 516). For compounds of ZnSO, with NH, v. Schindler (Mag. Pharm. 31, 167; 36, 43), Kane (A. Ch. [2] 72, 290), Müller (Z. [2] 5, 250; 6, 96). Hydrated zinc sulphate. Several hydrates are known. The heptahydrate ZnSO, 7aq crystalknown. The heptahyarate Zhou, 'faq drystallises, at ordinary temperatures, in white, right rhombic, prisms, isomorphous with MgSO, '7aq. S.G. 1'964 (Thorpe a. Watts, C. J. 37, 110), H.F. [Zn,S,O',711'O] = 252,700 (Th. 3, 516). Molts at 50° (Tilden, C. J. 45, 267). At 100° loses 6H,O. Poggiale (A. Ch. [3] 8, 467) gives solubility in water as follows:-

	s.			
Temp.	ZnSO. 7aq	ZnSO.		
00	115.22	43.02		
10	138.21	48.36		
20	161.49	53·13		
30	190.90	58.40		
40	224.05	63.52		
50	263.84	68.75		
60	313.48	74.20		
70	369.36	79.25		
80	$442 \cdot 62$	84.60		
90 -	532.02	89.78		
100	653.59	95.03		

Gerlach (Fr. 8, 260) and Schiff (A. 110, 72) give the following data for ZuSO, Aq:-

•			
Gerlach, at 15°	Schiff, at 20.5°	Petge. ZnSO4. 7ac	
1.0288	1.0289	5	
1.0593	1.0588	10	
1.0905	1.0899	15	
1.1236	1.1222	20	
1.1574	1.1560	25	
1.1933	1.1914	30	
1.2315	1.2285	35	
1.2709	1.2674	40	
1.3100	1.3083	45	
1.3532	1.3511	5 0	
1.3986	1.3964	55	
1.4451	1.4439	60	

Almost insol. absolute alcohol; 100 parts of a saturated solution in alcohol of 40 p.c. contain 3-48 parts ZnSO, 7aq (Schiff, J. 1861. 87).

Hexahydrate, ZnSO, 6aq; obtained by crystallising ZnSO, 4aq at 40°; S.G. 2·07 (T. a. W., l.c.; v. also Marignac, J. 1855. 389). Penta-

W., L.; v. also Marignac, J. 1855, 389). Penta-hydrate, ZnSO, 5aq; obtained by boiling the finely-powdered heptahydrate with alcohol of S.G. 825; S.G. 2-206 (T. a. W., Lc.; v. also Kühn, J. 1830, 300; Schindler, Mag. Pharm. 81, 167; 36, 43; Pierre, A. Ch. [3] 16, 242). Dihydrate, ZnSO, 2aq; formed by pouring cold saturated ZnSO, Aq into conc. H₂SO, and wash-

ing the pp. with absolute alcohol; S.G. 2958 (T. a. W., L.c.). Monohydrate, ZnSO, aq; obtained by heating ZnSO, 7aq to 100°-110° till it ceases to lose weight; S.G. 3·28 (T. a. W., L.c.; v. also Graham, P. M. [3] 6, 327, 417). An acid salt ZnSO, H.SO, 8aq is described by von Kobell (J. pr. 28, 492). Several basic salts are formed by boiling solutions of ZnSO, 7aq with ZnO or ZnO.H. (v. Schindler, L.c.; Kühn, L.c.; Kane, A. Ch. [2] 72, 290; Reindel, Z. [2] 5, 508; Habermann, M. 5, 432; Athanasesco, C. R. 103, 271).

Double salts are numerous: (1) With alkali

Double salts are numerous: (1) With alkali Double saits are numerous: (1) With alkali sulphates, ZnSO, M2SO, aaq (v. Pierre, Ph. C. 1846. 410; Tobler, A. 95, 193; Graham, P. M. [3] 6, 827, 417; Karsten, B. B. 1841). (2) With CoSO, FeSO, MgSO, NiSO, &c., to form ZnSO, MSO, xaq (v. Rammelsberg, P. 91, 321; Pierre, Lc.; Etard, C. R. 86, 1399; 87, 602).

Zirconium sulphates. The normal sait

Zirconium sulphates. The normal salt Zr(SO₄)₂ is obtained by dissolving ZrO₄ in slightly diluted H₂SO₄, evaporating, and driving off excess of acid at a temperature below red on excess of acid at a temperature below red heat. $Zr(SO_1)_2$ is decomposed by heating to redness, giving ZrO_2 . By concentrating a solu-tion of $Zr(SO_4)_2$ containing some free H₂SO₄, Paykull (B. 6, 1467) obtained crystals of the tetrahydrate Zr(SO4)2. 4aq (confirmed by Weibull, B. 20, 1394).

Basic salts are obtained by digesting a solution of a salt of Zr with saturated K₂SO₄Aq

(c). Berzelius, P. 4, 117; Warren, J. pr. 75, 361).

Double salts with K.SO, are formed by fusing KHSO, and ZrO, (B., Lc.; W., Lc.).

DITHIOPERSULPHATES. Under the name

of sodium dithiopersulphate, Villes (C. R. 106, 851, 1354) described a salt Na₂S₄O₈. 5aq. This salt was said to be obtained by adding to sodium thiosulphate insufficient water to dissolve all the salt, saturating with SO., adding a little more water, again saturating with SO2, keeping the yellow solution at the ordinary temperature for two or three days, passing in SO, as long as it was absorbed, and, after standing a day or two, evaporating in vacuo over H₂SO₄. A mixture of Na₂S₄O₈ and Na₂S₃O₆ was thus obtained; on exposure to air the crystals of Na2S3O, effloresced, and the Na S,O, was then picked out. The salt Na S.O. was described as white, lustrous, rhombic prisms; unchanged in air; melting at c. 125°, and giving off SO₂ at c. 140°, leaving Na₂SO₃ mixed with S. In a later paper (C. R. 108, 402) V. announced that the salt supposed by him to be Na₂S₁O₆ was only hydrated sodium tetra-thionate Na₂S₄O₆.H.O. NITROSOSULPHATES. In 1800 Davy (Re-

searches, chiefly concerning Nitrous Oxyde) noticed that NO was absorbed by a mixture of Na₂SO₃Aq and NaOHAq, a compound being formed which, on addition of an acid, gave off N₁O while Na₂SO₄ remained in solution; he supposed that the NO was reduced to N₂O, the Na₂SO₄ being oxidised 'o Na₂SO₄ and that the N₂O combined with the NaOH. Pelouze (A. Ch. [2] 60, 151) found that a salt containing N, S, and O was formed in the reaction examined by Davy; to this salt he gave the composition Na, SO, (NO),

A mixture of 1 vol. SO₂ and 3 vols. NO is gradually absorbed by cono. KOHAq or NaOHAq, forming K₂(NO)₂SO₃ or Na₂(NO)₂SO₃.

Ammonium witroscoulphate (NH₄)₂(NO)₂SO₂ is best prepared by passing NO for some hours into cold conc. (NH₄)₂SO₂Aq mixed with 5 to 6 times its volume of NH₄Aq. White crystals of the self-with the cold self-with the cold self-with the selfthe salt gradually form; they are washed with ice-cold NH,Aq, dried in vacuo, and kept in a well-stoppered bottle (Pelouze, l.c.). Potassium nitrososulphate and sodium nitrososulphate, M2(NO)2SO, are prepared similarly to the ammonium salt. Barium and lead nitrososulphates are obtained by ppg. aqueous solutions of the K salt by conc. BaOAq and solution of basic acetate of lead, respectively (Divers a. Haga, C. J. 47, 364). The nitrososulphates readily decompose; they are stable in solution only in presence of excess of alkali. Heated moist they give off N₂O, leaving pure sulphate; heated dry they give NO and sulphite (v. D. a. H., C. J. 47, 208). With acids, and also with most metallic salts in solution, also in contact with spongy Pt, charcoal, Ag₂O, MnO₂, &c., they give N₂O and sulphates. Solution of an alkali nitrososulphate has no reaction with KMnO, Aq (D. a. H., l.c. p. 205). An alkaline solution of the K or Na salt is slowly reduced by Na amalgam, giving K₂SO₂Aq and K₂N₂O₂Aq, or the corresponding Na salts (D. a. H., *l.c.* p. 203).

PERSULPHATES. Pérsulphuric dride S2O, is formed at the anode during the electrolysis of fairly conc. H.SO, Aq (v. Sulphuric peroxide, under Sulphur oxides, p. 616). The acid corresponding with this oxide would be H₂S₂O₈ or HSO₄; this acid has not been isolated, but some of its salts have been prepared

by Marshall (C. J. 59, 771 [1891]).

Potassium persulphate K₂S₂O₈ is obtained by passing a current of 3 to 31 ampères, for some days, through saturated KHSO Aq contained in a Pt dish, wherein is suspended a porous cell containing dilute H₂SO₄Aq; the Pt dish stands in a vessel of copper, through which runs a stream of cold water, and which is connected with the battery so that the Pt dish becomes the anode; the cathode consists of a stout wire of Pt dipping into the dilute H2SO4Aq in the porous cell (for description, and diagram, of the apparatus v. Marshall, C. J. 59, 765-6). The granular salt that slowly separates during electrolysis is collected by filtering through Pt foil, dried on a porous plate, treated with hot water so as to obtain a nearly saturated solution, which is at once rapidly cooled (the mother-liquor yields more K₂S₂O₈ when again electrolysed). K₂S₂O₈ forms small, white, prismatic crystals; by spontaneous evaporation of a solution, large, flat tables are obtained, probably asymmetric. Slightly sol. cold water; S. at 0°=1.77; insol. absolute alcohol, hot or cold. Measurements of the electrical conductivities of solutions of the salt indicated the formula KSO,, and not K₂S₂O,; but Bredig (Z. P. C. 12, 230) showed that Marshall's results were based on data, given by Ostwald, which were not quite accurate (the data were afterwards corrected in Ostwald's Lehrbuch [2nd ed.] 2, 730). Bredig's measurements established the formula $K_2S_2O_4$; and this was confirmed by Löwenberg's determinations of the freezing-points and conductivities of solutions of the salt (Chem. Zeitung, 1892, 838). K,S₂O₈Aq very slowly decomposes at the ordinary tempera-ture, giving KHSO, Aq and O; in contact with

zinc, decomposition is still very slow: with a Cu-Zn couple the rate of change is hastened; heating also hastens the reaction. After keeping for some time in a closed bottle a peculiar smell is noticed on opening the bottle, perhaps due to H₂S₂O₆ or S₂O₇; coone is sometimes also given off. Heat decomposes K₂S₂O₆; K₂SO₄ remains and SO₅ and O are given off.; decomposition is marked at a little above 100°, but is not complete or H₂SO₄, much ozone is given off; Cl is evolved when conc. HClAq is used. K₂S₂O₂Aq does not yield pps. of persulphates with solutions of meyield pps. of persulphates with solutions of metallic salts; when pps. are formed they are due to reactions with K.SO.Aq formed by the decomposition of the K.S.O.Aq. Solution of a salt of Ba slowly throws down BaSO.4; the reaction is very slow, even when the solution is boiled. Solution of a salt of Pb also slowly forms PSO.4. when heated with K.S.O.Aq; if alkali is added, PbO, is ppd. AgNO, Aq produces no pp. at once, but after a time black AgO, the solution becoming acid; several other metallic salts in presence of alkali yield pps. of peroxides with K₂S₂O₈Aq, e.g. salts of Co, Cu, Mn, and Ni. KIAq is slowly decomposed by K₂S₂O₈Aq, with separation of I; litmus and turmeric solutions are gradually bleached; paper and cloth become rotten when dipped in K₂S₂O₈Aq. K₄FeCy₆Aq is exidised to K₂FeCy₆Aq, and alcohol yields aldehyde, by warming with K2S2O8Aq.

Anmonium persulphate $(NH_4)_2S_2O_8$. Prepared, similarly to $K_2S_2O_8$, by electrolysing dilute H_2SO_4Aq (c. 1 to 6 by volume) with $(NH_4)_2SO_4$; the salt is purified by cooling by ice a solution saturated at a little above the ordinary temperature. Crystallises in transparent lozengeshaped, apparently mono-symmetric tables. Very

sol. water; S. at 0'=58'2. Reacts similarly to K₂S₂O₄ (cf. Elbs, J. pr. [2] 48, 185). Barium persulphate Ba₂(SO₄), 8aq. Prepared by rubbing in a mortar saturated (NH₂)_SO₂Aq with excess of pure BaO₂H₂—Ba₂(SO₄), goes into solution, and BaSO, also forms—passing a rapid stream of air till most of the NH, set free in the reaction is removed, placing in vacuo over H₂SO₄ till no free NH, remains, passing in CO₄ to remove excess of BaO₂H₂, keeping in vacuo for a short time (to decompose Ba bicarbonate to BaCO₃), filtering from BaSO₄, and BaSO₅, evaporating in vacuo till crystallisation begins (with addition from time to time of a little BaOAq to neutralise H₂S₂O₈ that is set free during evaporation), dissolving the crystals that first separate in as little water as possible, filtering, cooling by ice, and drying the small prismatic crystals that form on a porous plate. crystals of Ba₂(SO₄), Saq gradually become milky from formation of BaSO₄, the change soon spreads, and the crystals crumble to a moist, powdery mass of BaSO₄. Ba₂(SO₄)₄.8aq is very sol. cold water; S. at 0°=52.2. Sol. absolute alcohol; on standing white crystals are deposited,

alconoi; on standing white crystals are deposited, probably Ba₂(SO₂)₄. 2aq.

Lead persulphate Pb₂(SO₄)₄. xaq; x = 4 or 6, probably 6. Obtained by adding a slight excess of H₂SO₄Aq to cone. Ba₂(SO₄)₄Aq, neutralising with PbCO₂, filtering after some time, evaporating in vacuo over H₂SO₄ (removing PbSO₄ from time to time by filtration) till a solid mass is obtained, which is at once divided between filter payer and which is at once dried between filter paper and

placed in vacuo. Pb₁(SO₄), was not obtained quite free from PbSO₄; it decomposes very readily, giving off pungent fumes, that separate

I from KIAq on paper.

Zinc persulphate was obtained, but not pure,
by adding ZnSO, Aq to Ba, (SO,), Aq in the proper proportions, filtering, and evaporating in vacuo over H₂SO₄. The copper salt was also obtained, but not free from CuSO₄. For thermal data concerning the formation and solution of the persulphates of NH, Ba, K, and Na v. Berthelot

(C. R. 114, 875; abstract in C. J. 62, 931). PYROSULPHATES. (Disulphates. Anhydrosulphates.) Salts of the acid H₂S₂O₂ (v. Pyrosulphuric acid, under Sulphuric acid, p. 620). These salts bear to the sulphates a relation similar to that of the dichromates to the chromates. The sulphates may be written SO₂(OM)₂, and the pyrosulphates OM.SO₂.O.SO₂.OM. The sulphates and pyrosulphates may also be regarded as compounds of the acidic radicle SO, with basic radicles MO; thus sulphates MO.SO,, pyrosulphates MO.SO,. Inasmuch as H.S.O, may be regarded as a partial anhydride of H.SO.(2H.SO., -H.O. = H.S.O.), the acid H.S.O. is sometimes called anhydrosulphuric (cf. ACIDS, vol. i. p. 50).

Potassium pyrosulphate K₂S₂O, is formed by heating K₂SO, with half its weight of H₂SO, till acid ceases to confe off at an incipient red heat. Prismatic needles; S.G. 2.277 (Jacquelain, A. Ch. [2] 70, 311). Melts at 300°, according to Schultz-Sellack (B.4, 109). Cannot be crystallised Schultz-Sellack (B. 4, 109). Cannot be crystallised from water. Solution in fuming H₂SO₄ gives crystals of the acid salt KHS₂O₃, melting at 168° (S.-S., l.c.). Heated with alcoholic solution of KSH gives K₂SO₄, K₂S₂O₃, and H₂S; boiled with C₂H₃ONa in alcohol gives KNaSO₄ and KEtSO₄ (Drechsel, J. pr. [2] 5, 367). The pyrosulphates of NH₄, Ba, Ag, and Na are prepared similarly to K₂S₂O₃ (v. Schulze, B. 17, 2707; J., Lc.; S. S., l.c.). M. M. P. M. l.c.; S.-S., l.c.). M. SULPHAZIDES X.NH.NH.SO₂.Y. M. M. P. M.

Formation .- 1. By the action of alcoholic SO₂ upon diazo-compounds.-2. By the action, of hydrazines upon sulphonic chlorides Y.SO.Cl. 8. By the action of hydrazine hydrochlorides upon sulphinic acids Y.SO.H.-4. By reduction of the compounds X.N. SO.Y.

Reaction .- By heating with aqueous alkalis salphinic acid, a hydrocarbon, and nitrogen:

X.N.H., SO. Y = XH + Y.SO. H + N.

References: Koening, B. 10, 1531; Wiesinger,

10, 1715. Fischer 4, 100, 130. Freeler P.

B. 10, 1715; Fischer, A. 190, 132; Escales, B. 18, 893; Limpricht, B. 20, 1238.

SULPHAZOTISED ACIDS v. SULPHUB OXY-ACIDS, NITROGEN DERIVATIVES OF (p. 619).

SULPHIDES. Binary compounds of sulphur. The name is generally applied only to binary compounds of S with elements less negative than itself-that is, to compounds with elements other than Br, Cl, F, I, or O; thus SO, and SO, are called oxides of sulphur rather than sulphides of oxygen. Compounds of S with organic radicles, which compounds react similarly to sulphides of metals, must be regarded as binary compounds if the definition of the term sulphide is to be made as wide as possible. In the present article, however, only binary compounds of S with less pegative elements are included. Sulphides of

all the metals, and also of the non-metals H. B.

C, N, Si, P, Se, and Te, are known.

Many sulphides of metals occur native. Sulphides are frequently prepared by the direct union of the elements; sometimes by heating metallic oxides with excess of S, e.g. As, S, -in many cases a mixture of sulphide and oxide is formed in this way; addition of alkali carbonate to the mixture of metallic oxide and S sometimes brings about formation of sulphides, e.g. formation of sulphides of Cr and U; polysulphides mixed with sulphates are produced by heating the hydroxides or carbonates of alkali metals with S. Most heavy metals give sulphides when their oxides are heated in H,S gas, also when H2S is passed into solutions of their salts. Heating metals in H2S gas often produces sulphides. Sulphides are also formed by heating one metal with the sulphide of another, more negative, metal. Reduction of sulphates, generally by heating in H or with C, frequently yields sulphides. Some metallic oxides yield sulphides . when strongly heated in vapour of CS2. Sulphides of many heavy metals are formed by immersing the metals in (NH₄)₂SAq containing excess of S (v. Priwoznik, A. 16A, 46). Many metallic oxides yield sulphides by heating with dry Na₂S₂O₃ (v. Landauer, Fr. 1872, 427). The sulphides of the alkali and alkaline earth

metals are soluble in water; other sulphides are insoluble, or only very slightly soluble, in water.

Very dilute aqueous solutions of several metallic sulphides, in the colloidal form, were obtained by Winssinger (BL [2] 49, 452) by the following methods: (1) ppg. the sulphide by H.S from an extremely dilute solution, and dialysing; (2) washing the ppd. sulphide for a long time with cold water, or with dilute H₂SAq; (3) forming the sulphide in a solution free from all substances capable of causing coagulation. In these ways W. obtained colloidal soluble sulphides of Bi, Co, Au, Fe, In, Pb, Hg, Mo, Ni, Pd, Pt, Ag, Tl, W, and Zn. For preparation of colloidal soluble CdS v. Prost (C. C. 1888. 32), and of colloidal soluble CuS v. Spring a. de Boeck (Bl. [2] 48, 165).

Metallic sulphides are decomposed by strong acids, giving salts and H₂S; secondary reac-tions frequently occur, S almost invariably separating. Several sulphides, e.g. Aa₂S, and H₂S, are sublimable out of contact with air; all sulphides are oxidised by heating to redness in air. The sulphides of the very positive metals yield sulphates, and the sulphides of the heavy metals generally form oxides (the sulphides of Au, Hg. Pt, and Ag form metal) and give off SO.. All sulphides of metals yield metallic chlorides and S.Cl. when heated in a stream of Cl. Many metallic sulphides are decomposed by water, at different temperatures, giving oxides or hydroxides and H₂S (cf. de Clermont a. Frommel, C. R. 87, 330). Sulphides of non-metals are decomposed by water, generally to oxyacids and H₂S; NS gives NH, salts of H₂S₂O₄ and H₂S₂O₆. Many sulphides of heavy metals are H₂S₂O₅. Many surprises of next means and decomposed by heating with water and I, giving iodides, S, and a little sulphate (v. Filhol a. Mellies, A. Ch. [4] 22, 58).

The double sulphides, formed by the union of sulphides of more positive elements with sulphides.

phides of less positive elements, are comparable

with the double oxides or oxysalts; most of these double sulphides are probably best regarded as salts of thio-acids corresponding with salts of oxyacids, but it is customary to apply this conception generally only to those compounds which contain sulphides of non-metals or of Sb, As, or Sn. The double sulphides, or thio- salts, are generally decomposed by water, forming oxides and H2S. Many double sulphides, containing K2S or Na2S as one constituent, are formed by fusing metals or metallic sulphates with K₂CO₃, or Na₂CO₃, and S (v. Schneider, J. pr. [2] 7, 214; 9, 209; 10, 55). The sulphides may be classified, like the oxides, as monosulphides, disulphides, &c. It is better, however, to divide them into basic, acidic, indifferent, and persulphides; but this classification has been less developed and applied than in the case of the oxides. Basic sulphides react with acids to form salts and H.S. just as basic oxides react with acids to form salts and H.O. Acidic sulphides react with the basic sulphides to form thio- salts, as acidic oxides react with basic oxides to form oxy- salts; but few compounds have been isolated of acidic sulphides with H.S. corresponding with the compounds of acidic oxides with water which are oxyacids. The more strongly acidic sulphides -that is, the sulphides of non-metals—are decomposed by water, generally giving H2S and oxyacids. The persulphides have not been much studied; any sulphide of an element containing more S than the basic or acidic sulphide of the same element may be placed provisionally among the persulphides. A sulphide which does not react as basic or acidic, and which from its composition cannot well be called a persulphide, may be classed as an indifferent sulphide. The sulphides of C and P combine with several metallic sulphides to form thio- salts; double sulphides (or thio- salts) have not been isolated containing sulphides of B. N. Si, Se, or Te; the sulphides of Sb, As, and Sn combine with the sulphides of the alkali metals, and with some other sulphides of positive metals, to form thio- salts. The greater number of the double sulphides are formed by the union of two sulphides, both of which are metallic. The sulphide of that metal which, on the whole, is the more positive is regarded as the basic radicle; and the sulphide of the metal which, on the whole, is the less positive is regarded as the acidic radicle of the double sulphide. Some metallic sulphides must be classed both as basic and acidic; Cu.S, for example, combines with As.S., and is therefore basic towards the distinctly acidic sulphide of As, but it also combines with K2S, and is therefore acidic towards the distinctly basic sulphide of K. It is impossible to divide the metallic sulphides into two distinctly-marked classes; the relativity of the terms 'basic' and 'acidic' becomes even more apparent in dealing with sulphides than in dealing with oxides. The sulphides BaS, BaS, CaS, and CaS, may be taken as examples of those which are loosely put together under the name persul-phides. As examples of indifferent sulphides NS and Cr.S. may be mentioned. Many metallic sulphides which have been little studied—and which must, therefore, for a time be called indifferentwe very probably basic in their reactions; such we Al, S, and CdS.

M. M. P. M.

SULPHIDO-DIACETIC ACID C.H.SO. 44. S(CH2.CO2.H)2. Thiodiglycollic acid. [129° 42 at 18°. Formed from chloro-acetic acid and alcoholic ammonium sulphide, aqueous Ca(SH), or Na₂S (Schulze, Z. 1865, 73; 1866, 184; Schreiber, J. pr. [2] 13, 472; Lovén, B. 17, 2818). Formed also by heating bromo-acetic acid with benzyl sulphide, allyl sulphide, or ethylene sulphide (Letts, Tr. E. 28, 612). Trimetric tables, v. sol. alcohol. Oxidised by KMnO₄ to SO₂(CH₂SO₂H)₂. The Na salt is converted by treatment with sodium chloro-acetate into $CO_2H.CH_2SMe < {}^{O}_{CH_2}>CO$ [150°] (Delisle, B. 25, 2450). The analogous compound (CO₂H.CH₂)₂S CO₁CO [158°] is formed from chloro-acetic acid, Na₂CO₃, and Na₂S (Delisle), and yields Na₂A" 3aq.

Salts.—K₂A" aq: deliquescent prisms.—

KHA".—CaA". S. 2 at 21°.—BaA".—BaA" 5aq.

ZnA" 4aq.—PbA".—Pb₂A"O.—CuA" aq.—

Ag2A".

Methyl ether Me.A". (135° at 11 mm.). Ethyl ether Et.A". (268° cor.). Formed from chloroacetic ether and alcoholic KSH (Wislicenus, A. 146, 153).

Amide S(CH, CO.NH,), Formed chloro-acetic acid and alcoholic (NH,).S.

Formed from

Amic acid S(CH2.CO2H).CH2.CO.NH2. [125°]. Prisms, m. sol. cold water. - BaA', aq. CaA'2 aq. - AgA': needles (from hot water).

Imide S CH, CO NH. [128°]. Formed by heating the ammonium salt at 200°. Crystals.

Anhydride S < CH_...CO > 0. [102°]. (158° at 10 mm.). Formed by boiling the acid with AcCl

(Anschütz, A. 273, 68). Needles (from CHCl₂). Chloride S(CH₂COCl)₂. Mono-anilide Š(CH₂CO₂H).CH₂CONHPh.

[103°].

Di-anilide S(CH_CO.NHPh), [168°].

p-Toluide S(CH_CO_H).CH_CO.NHC,H,.

[95°]. Needles.

Di-sulphido-di-acetic acid (di-thio-di-glycollic acid) S₂(CH₂,CO₂H), [100° uncor.]. Formed from thio-glycollic acid CH₂(SH).CO₂H by Fe₂Cl₈ or by atmospheric oxidation of the alkaline solution Glaesson, B. 14, 410; Ginsburg a. Bondzynski, B. 19, 114). White plates or prisms. V. sol. water, alcohol, and ether, sl. sol. benzene. Gives with AgNO, a white pp. AgHA". By tin and HCl it is reduced to thio-glycollic acid.— K,A" 1 aq: easily soluble crystals.—KHA" aq.— BaA" 4aq: amorphous pp. Ethyl ether Et.A".

Ethyl ether Et.A". (c. 280°). Amide [155°]. Crystalline. SULPHIDO DI ACETOACETIC ETHER

C₁H₁SO₂ i.e. S(GHAo.CO₂Et)₂. [90°] (S.); [84°] (D.); [76°] (B.). Formed by the action of S₂O₂ (2 mols.) or of SO₄ on sodium acetoacetter thurs.] (mol.) suspended in benzene (Buohka, B. 18, 2092; 22, 2645, 2555; Delisle, B. 22, 2002). 306). Formed also from cupric acetoacetic ether and S in benzene (Schönbrodt, A. 253, 197). Needles, v. e. sol. benzene. Converted by KOH into sulphido-diacetic acid. Yields a crystalline phenyl-hydrazide C₂₀H₂₂N₂SO₄, converted by warming with an alcoholic solution of phenylhydrazine into oxy-phonyl-methyl-pyrazole-azobenzene NPh.CO C:N.NHPh (Michaelis a.

Phillips, B. 23, 560). Phenyl-hydrazine (2 mols.) added to sulphido-di-acetoacetic ether dissolved in cooled HOAc forms C₂₀H₁₈N₁₈O₂, which yields B'HOAc [161°] and B'HOEt (Michaelis, B. 23, 2476; Sprague, C. J. 59, 332).

SULPHIDO-ANILINE v. DI-AMIDO-DI-PHENYL

BULPHIDE.

DISULPHIDO-DI-BENZOIC ACID

S₂(C₆H₁,CO₂H)₂ [244°]. Formed by oxidation of C₆H₄(SH).CO₂H by moist air or by bromine water (Frerichs, B. 7, 794; Hübner a. Upmann, Z. 1870, 294). Formed also from m-diazo-benzoic acid and H.S (Griess, J. pr. [2] 1, 102) and in actu and 11.3 (Griess, 2. Pr. 12] 1, 102) and, in small quantity, by fusing sodium sulphobenzoate with sodium formate (Ador, B. 4, 622; Meyer, B. 6, 1150). Needles, nearly insol. hot water, st. sol. alcohol. -(NH₃)₂A" 2aq. -CaA" 3aq. -BaA" 3aq. -PbA" aq. -Cu₂(OH)₂A" 5aq. -Aa" 11. Ag₂A" 1 aq: yellowish-white pp.

y-SULPHIDO DIBUTYRIC ACID

S(CH₂.CH₂.CH₂.CO₂H)₂. [99°]. Formed by warming its nitrile with fuming HClAq (Gabriel, B. 23, 2492). Flat crystals.

Nitrile S(CH, CH, CH, CN), (above 300°). Formed by boiling γ-chloro-butyronitrile with alcoholic K₂S. Thick liquid.

a-Sulphido-dibutyric acid S(CHEt.CO.H)... a-supplied odistryine acid SIGHELUO, ILI,... [105°]. Formed by heating a-bromo-butyric ether (2 mols.) with an alcoholic solution of KSH (1 mol.) and KOH (1 mol.), and saponifying the product (Lovén, J. pr. [2] 33, 102). Tufts of needles (from water).—Bah".

-Sulphido-di-isobutyric acid SICMc₂-CO,H).

Formed from a-bromo-isobutyric ether and alcoholic K.S, the product being saponified. Tablets (from water), insol. dilute H.SO. -BaA" 2aq.

Di-γ-sulphido-dibutyric acid S₂(CH₂CH₂CH₂CO₂H)₂. [109°]. Formed by boiling the amide with conc. HClAq (Gabriel). Flat plates, v. sol. alkalis.

Amide S₂(C₃H₆.CO.NH₂)₂. [167°]. Formed by dissolving Cy.C₂H₈.S.Cy in cold conc. H₂SO₄.

sulphilo-dicinnamic acid C₁₈H₁₈SO₄
i.e. (PhCH:C(CO₂H))₂S. Formed by boiling sulphido-diacetic acid with Ac₂O and NaOAc (Loven, B. 18, 3242). Small needles (from alcohol) incl. hol), insol. water. Yields $C_{18}H_{14}Br_2SO_4$.—
Na,A''2\sqrt_aq: silvery plates.
Di-a-sulphido-di-cinnamio acid $C_{22}H_{12}S_2O_4$ Yields C18H14Br2SO4-

t.e. (Ph.CH.C.CO.H),S, [179°]. Formed by the oxidation of sulphydro-cinnamic acid Ph.CH.C(SH).CO₂H by iodine in alcoholic solution. Long yellowish needles, v. sol. alcohol, less in benzene (Ginsburg a. Bondzynski, B. 19, 123).

DI-SULPHIDO-DI-METHENYL-DI-AMIDO-DI-NAPHTHYL MERCAPTAN

 $S_2(C \stackrel{N}{\leqslant}_S) C_{10}H_s)_2$. Formed by oxidation of C₁₀H₆<NSC.SH with alkaline K₂FeCy₆ (Jacobson a. Frankenbacher, B. 24, 1408). The (a)-compound melts at 194°, the (β) - isomeride at 180°.

DISULPHIDO - DI - METHENYL-DI-AMIDO -DI-PHENYL MERCAPTAN $S_2(O \triangleleft_{S}^N > C_uH_4)_2$. [186°]. Formed by oxidising sulphydro-methenylamido phenyl mercaptan with K₂Cr₂O, and HOAc Jacobson a. Frankenbacher, B. 24, 1404; cf. Hofmann, B. 20, 1789). Plates (from benzene).

DI - SULPHIDO - DI . METHENYL . DI . BENZENYL - DI - AMIDOSULPHIM

 $S_2(C \stackrel{N}{\leqslant}_{S.N}) > CPh)_r$ [120°]. Formed by oxidation of $C_{\epsilon}H_{s}.C \leqslant_{N,S}^{N} > C.SH$ (Crayen, B. 24, 389). Stellate groups of needles, insol. water, sl. sol. alcohol. Reduced by sodium amalgam to the parent substance.

DI - SULPHIDO - DI - METHENYL - DI - p -TOLENYL-DI-AMIDOSULPHIM

 $S_2(C \leqslant_{S,N}^N \geqslant C.C_6H_4Me)_2$. [169°]. Formed by oxidation of C,H,.C \$\left(\backslash\) N.S \$\right(C.SH)\$ with HNO. free from nitrous acid (Crayen, B. 24, 392). Needles, insol. alcohol and ether, sol. hot C₈H_e.

DI-SULPHIDO-DI-METHYL-ANILINE v. TETRA-METHYL-DI-AMIDO-DI-PHENYL-DI-SULPHIDE.

DI - SULPHIDO-DI-NAPHTHALENE-DI-(B). SULPHONIC ACID $S_2(C_{10}H_{10}SO_1H)_2$. Formed from the product of the action of potassium xanthate on diazotised (β) -naphthylamine (β) sulphonic acid by treatment with alcoholic potash (Leuckart, J. pr. [2] 41, 223). Colourless plates, v. sol. water and alcohol. Reduced by zinc-dust and dilute H.SO, to C10Ha(SH).SO3H. K2A".-PbA": amorphous pp., sl. sol. water.

SULPHIDO-DI-(B)-NAPHTHYL-CARBAMIC ACID. Phenyl ether

SC_{0,H} N.CO.OPh. [215]. S. (96 p.c. alco-hol) 20 at 16°; S. (benzene) 1.20 at 16°, hol) 20 at 16°; S. (benzene) 1.20 at 16°, Formed from the chloride and alcoholic NaOPh

Portner from the emotion and accounts that in (Paschkowszky, B. 24, 2916). Needles.

Chloride S:(C₁₀H_{all}:N.COCI. [255°].

Formed by heating β-imido-di-naphthyl sulphide with COCl₂ in toluene at 170°. Needles (from the country of the countr benzene-alcohol), v. sl. sol. ether. Converted by aniline into S:(C₁₀H_a)₂:N.CO.NHPh, which is crystalline, S. (96 p.c. alcohol) 04; S. (benzene) 18 at 17.5°, converted by boiling aniline into $S(C_{10}H_8NH_2)_2$ and $CO(NHPh)_2$. The chloride is converted by alcoholic NH, at 145° into $S < C_{10}^{C_{10}H_6} > N.CO.NH_2$, crystallising in needles, S (96 p.c. alcohol) ·06; S. (benzene) ·10 at 17·5°. The chloride $S < {C_{10}H_u} \choose {C_{10}H_u} N$.COCl is converted by β -imido-di-naphthyl sulphide in xylene at 280° into $\left(S < {C_{10}H_u} \choose {C_{10}H_u} N\right)$.CO, crystallising in

yellowish plates and tables [over 350°]. SULPHIDO-DI-PHENYL-AMINE v. IMIDO-DI-PHENYL SULPHIDE

SULPHIDO-DI-PHENYL-CARBAMIC ACID. Ethylether SC.H. N.CO.Et. [110].

Formed from imido-di-phenyl-sulphide and CICO_Et (Fränckel, B. 19, 1845). Silky plates.

Phenyl ether S:(O₄H₄),:N.CO₂Ph. [164°], S. (96 p.c. alcohol) '24 at 16°; S. (benzene) 1.9 at 16°. Formed by heating the chloride with NaOPh in alcohol on the water-bath (Paschkowzky, B. 24, 2908). Needles.

Chloride S:(O₄H₄):N.COCl. [172°]. Formed from S:(O₄H₄):NH and COCl₂ at 100°. Colour-less prigms, sol. objectory and hot HOAs.

less prisms, sol. chloroform, and hot HOAc.

p-SULPHIDO-DI-PHENYL-DI-HYDRAZINE p-SULPHIBU-Da-Fills.

S(O,H,NH.NH₂), [116°]. Formed from S(O,H,NH₂), by diazotisation, treatment with NaHSO, and reduction with zinc-dust (Ruhl, B. 23, 3482; A. 270, 149). Yellowish leaflets, decomposing at 130°, sl. sol. cold water and alcohol. Reduces Fehling's solution in the cold. Benzoic aldehyde yields S(C,H,.N,H:CHPh), — B"2HCl. B"H,SO, [219°].—B"H,C,O,. [209°].

SULPHIDO PHENYL NAPHTHYLAMINE

S C H NH. Imido-phenyl-naphthylamine. Formed by heating phenyl-naphthyl-amine with 8 at 240° (Kym, B. 23, 2464). The (a)-compound melts at 138°, the (B)-isomeride at 178°. Both form yellow crystals, m. sol. hot alcohol, and give a deep blue solution in conc. H2SO1.

SULPHIDO . DI . PHENYL . DI . (B) . NAPH . THYL-UREA N(C₁₀H₁)₂.CO.N C₀H₁ S. [225°]. S. (96 p.c. alcohol) ·12; S. (benzene) ·55 at 16°, at 260° (Paschkowezky, B. 24, 2914). White nodules, al. gol. hot alcohol, sol. hot benzene.

Sulphido - tri - phenyl - (8) - naphthyl - urea NPh(C_{1e}H₁).CO.N:(C₆H₁)₂:S. [170°]. S. (96 p.c. alcohol) 52; S. (benzene) 3·38 at 15°. Formed by heating sulphido-di-phenyl-carbamic chloride with phenyl-(\$\beta\$)-naphthylamine at 250° (P.).

SULPHIDO - DI - PHENYL - DI - TOLYL - DI-GUANIDINE (NHPh.C(NH).NH.O,H_u)₂S. [153°]. Formed from the corresponding thio-urea, HgO, and alcoholic NH, (Truhlar, B. 20, 675). Needles

(from ether ligroin). — $C_{28}H_{28}SN_3H_2PiCl_3$.

Sulphido-tetra-phenyl-di-tolyl-di-guanidine (NHPh.C(NPh).NH.C,H₀)₂S. [106°]. Formed by warming an alcoholic solution of (NHPh.CS.NHC,H₆)₂S with aniline and HgO.

Grey amorphous powder, v. e. sol. alcohol. Disulphido-di-phenyl-tetra-tolyl-di-guani-dine NPh:C NH.C.H.S.C.H., NH C.NPh.

[119°]. Formed by heating the corresponding thio-ures with excess of aniline and HgO. Resinous mass, v. e. sol. alcohol.

SULPHIDO - DI - PHENYL - DI . TOLYL . DI-THIO.DI.UREA (NHPh.CS.NH.C.H.,)2S. [134°].
Formed from S(C,H.,NH.), and phenyl-thio-carbimide (Truhlar, B. 20, 670). Needles.

SULPHIDO-DI-PHENYL-UREA C13H10N2SO i.e. S < N.CO.NH₂. [202°]. S. (96 p.c. alcohol at 17.5°) 3; S. (benzene) 2.7 at 17.5°. Formed from S:(C₆H), N.COCl and alcoholic NH, (Paschkowezky, B. 24, 2908), Plates.

Sulphido-tri-phenyl-urea SCO.H. N.CO.NHPh. [169°]. S. (96 p.c. alcohol) 26 at 17.5°; S. (benzene) 3.74 at 17.5°. Formed from S(C₆H₁)₂NCOCl and aniline. Bluish needles, sol. alcohol.

Sulphido-tetra-phenyl-urea S(C,H,),N.CO.NPh. Formed in like manner, using NPh,H. Hexagonal plates.

Di-sulphido-tetra-phenyl-urea $OO(N < \stackrel{\circ}{O}_{OH} > S)$. [225'] (F.); [231°] (P.). S. (96 p.c. alcohol) 048 at 17°; 4·16 at 78°. by heating NH:(C,H,)2:S with S:(C,H,),:N.COCl (Fränckel, B. 18, 1848). Plates (from HOAc), v. sl. sol, ether and hot alcohol,

DI-SULPHIDO-DI-PROPYL-DI-PHTHAL. AMIC ACID C₂₂H₂₁N₂S₂O₄ i.e. S₁(C₂H₂,NH.CO.C₄H₁,CO₂H)₂. [186°]. Formed by boiling (γ)-phthalimido-propyl sulphocyanide with a 10 p.c. solution of KOH (Gabriel a. Lauer, B. 23, 89). Plates (from HOAc), v. sol. alkalis.—K,A": crystalline pp.

(a) SULPHIDO DIPROPIONIC ACID S(CHMe.CO,H), Thiodilactylic acid. [125]. Formed, together with CH,CH(SH).CO,H, by boiling potassium a-chloro-propionate with KSH (Schacht, A. 129, 4; Böttinger, A. 196, 106). Formed also by passing H_sS into a solution of potassium pyruvate (Böttinger, B. 12, 1425) and by the action of CH₂·CH(SK).CO₂K on CH₂·CHCl.CO₂K (Lovén, *J. pr.* [2] 29, 373). Monoclinic prisms, v. e. sol. water, alcohol, and ether. Not affected by nascent hydrogen. Oxidised by dilute HNO₃ to SO₂(CHMe.CO₂H)₂.

- K.A": deliquescent.—BaA": amorphous, v. sol. water (S.). Its solution on boiling deposits a crystalline salt, S. 1 (L.).—Ag₂A": amorphous

Di-(a)-sulphido-dipropionic acid $S_2(CHMe,CO_2H)_x$ [142°]. Formed by oxidation of CH_3 , CH(SH). CO_2H by I or FeCl. (S.; Böttinger, A. 196, 103; B. 16, 1047; Lovén, J. pr. [2] 29, 372). Needles, sl. sol. cold water, v. sol. alcohol and ether. Reduced by zinc and HClAq to CH₂,OH(SH).CO₂H.—(NH₄)₂A".—K₂A" 2aq.— Ag,A": amorphous pp.

Di-β-sulphido-dipropionic acid S_x(CH_x-CC_x-H_y. Formed by oxidation of CH_x(SH).CH_x-CO_xH (L_x). Thin silvery plates.

Tri-sulphido-di-propionic acid

S₄(CHMe.CO₂H)₂. [95°]. Formed from CH₄.CO.CO₂H and H₂S (Lovén, *J. pr.* [2] 47, 173). Plates, v. sol. hot water. Yields a-sulphopropionic acid on oxidation.

SULPHIDO-TOLUIDINE v. DI-AMIDO-DI-TOLYL SULPHIDE.

SULPHIDO - DI - TOLYL - DI - CARBAMIC ETHER S(C.H.Me.NH.CO.Et). [113°]. Formed from imido-di-tolyl sulphide and ClCO₂Et (Truhlar, B. 20, 668). Needles, v. sol. alcohol.

DI-SULPHIDO TETRA TOLYL-DI-GUANI-DINE C(NH) NH.C,H.,S.C,H.,NH C(NH). [196°]. Formed by botting the corresponding thio-urea with alcoholic NH, and HgO (Truhlar, B. 20, 673). White amorphous powder, v. sol. benzene and hot alcohol. -B'₂H₂PtCl₆: brown

amorphous powder. SULPHIDO-DI-TOLYL-THIO-UREA

 $S<_{C,H,NH}^{C,H,NH}>cs.$ [235°]. Formed from S(C,H₈.NH₂)₂ and alcoholic CS₂. Sulphido-di-tolyl-di-thio-di-urea

S(C,H, NH.CS.NH.). [121°]. Formed by evaporating the hydrochloride of di-amido-di-tolylsulphide with ammonium sulphocyanide (Truhlar, B. 20, 669). Amorphous powder, sl. sol.

Di-sulphido-tetra-tolyl-di-thio-di-urea CS<NH.C,H.,S.C,H.,NH.>CS. [231°]. Formed by boiling an alcoholic solution of di-p-amido-di-tolyl sulphide with CS, (Truhlar, B. 20, 672).

wante amorphous powder, nearly insol, ordinary solvents.

SULPHIDO-DI-TOLYL-DI-UREA

S(C.H.Me.NH.CO.NH.). Formed from amido-di-tolyl sulphide, hydrochloride from and potassium cyanate (Truhlar, B. 20, 669). Crystallises from benzene in needles [1510] contain-

Di-sulphido-tetra-tolyl-di-urea

CO NH.C.H. S.C.H. NH CO. Formed from S(C,H₀,NH₂)₂ and COCl₂ (Truhlar, B. 20, 671). White amorphous powder, sol. hot alcohol. SULPHIDO-DI-ISOVALERIC ACID

S(C₄H₈,CO₂H)₂. Formed from bromo-isovaleric acid and K₂S (Lovén, J. pr. [2] 33, 102). Crystals.

-BaA": in soluble powder.
SULPHIMIDE SO₂.NHAq. Obtained only in aqueous solution, which is prepared by decomposing the Ag derivative, SO₂NAg, with the proper quantity of dilute HClAq, and filtering. The compound SO₂NAg is prepared by saturating well-cooled SO₂Cl₂ in 15-20 vols. CHCl₃, with dry NH₃, dissolving the pp: in water, acidifying with HNQ₃, ppg. all Cl by AgNO₃Aq, filtering, neutralising with KOHAq, and adding more AgNO₃Aq; the pp. thus obtained is purified by recrystallisation from water. The compound SO₂.NAg is also obtained by heating SO₄(NH₂)₂ (p. SULPHAMIDE, p. 567) to 200°-210°, dissolving in water, ppg. by AgNO₃Aq, and recrystallising the pp. from water. The solution in water of SO₂.NH is strongly acid; when dilute it may be helical for a characteristic with the solution of the solution of the solution in water of SO₂.NH is strongly acid; when dilute it may be boiled for a short time without decomposition; NH, HSO, is formed on evaporation, even below 40°; the solution is decomposed by warming with acids, giving H₂SO₄Aq and NH₂Aq; excess of alkali reacts slowly even on boiling (W. Traube, B. 25, 2472; 26, 607). Metallic derivatives of SO₂NH wherein H is replaced by NH., Ba, Ca, Pb, K, Ag, and Na are described by T. (cf. Imido-sulphonic acid and salts, under Sulphonic acids and derivatives, p. 600) M. M. P. M.

SULPHIMIDO-AMIDE SO,NH,NH.NH,SO, Imido-sulphamide. Imido-sulphonamide. Imido-sulphurylamide). Prepared by adding ammonium carbamate very slowly to S.O.Cl. well cooled in a small closed flask, allowing to stand for some time with a CaCl, tube fitted through the cork, then heating to 60° for some hours, washing out NH,Cl by repeated treatment with dry alcohol saturated with NH3, dissolving the residue in a little NH, Aq, and placing the solution in ice. Forms white lustrous crystals; boiling NH, Aq transforms it wholly to ammonium imidosulphonate; with boiting conc. HClAq is completely changed to (NH_d)₂SO₄; when boiled with NaOHAq gives off two-thirds of its Nas NH₃ and forms sodium imidosulphonate (Mente, A. 248, 263). M. M. P. M.

SULPHINDIGOTIC ACID v. INDIGO DI-SUL-

PHONIC ACID.

SULPHINES. Alkyl iodides combine with di-alkyl sulphides forming compounds R2SRI, from which moist Ag₂O produces strong bases R2SR'.OH. In these bases the group (SR2R') may be looked upon as a monovalent basylous radicle derived from the hypothetical sulphine (SH.). Thus Me, SEtI may be called di-methyl-sthyl sulphine iodide, but in this dictionary it

is described as the ethylo-lodide of Di-METHYL SULPHIDE. In the same manner Me, SCI may be called tri-methyl-sulphine chloride, but in this dictionary it is described as the methylo-chloride

of DI-METHYL-SULPHIDE.

SULPHINIC ACIDS. Organic acids containing the group SO(OH) where S is united to carbon. They may be obtained by reducing the chlorides of the sulphonic acids, in alcoholic or ethereal solution, with zinc-dust (Otto, B. 9, 1584). Fatty sulphinic acids are formed by the 1584). Fatty suppliffic acids at communication of SO₂ or of SO₃ on zinc alkyls (Hofmann, A. 102, 72; 106, 287). They are readily oxidised to sulphonic acids. The aromatic sulphinic to sulphonic acids. The aromatic sulphinic ethers are readily oxidised by KMnO, and HOAc to sulphonic ethers (Otto a. Rossing, B. 19, 1224). By zinc and dilute H₂SO, sulphinic acids are reduced to mercaptans. The aromatic sulphinic acids yield K₂SO₃ and hydrocarbons when fused with potash. The alkyl ethers of sulphinic acids X.SO.OR are formed by passing HCl into a solution of the acid in the corresponding alcohol, and also by the action of chlorocarbonic ethers Cl.CO.R upon the sodium sulphinate X.SO.ONa in cold alcohol, CO, being evolved. The ethers are not formed by the action of alkyl halogenides upon sulphinates, for by this reaction the isomeric sulphones X.SO. R are produced instead (Otto a. Rossing, B. 18, 2493). H.S passing through benzene sulphinic ether at 50° forms mercaptan, benzene sulphinio acid, benzene sulphonic acid, and other products. (Otto a. Rossing, B. 20, 2275). COCl, converts sodium benzene sulphinate into the anhydride (Ph.SO)2O, which is v. sol. ether and benzene, and decomposed by water and alcohol into benzene sulphinic acid and ether respectively (Otto, B. 20, 3337).

SULPHITES HYPOSULPHITES. AND SULPHITES are salts of sulphurous acid formed by replacing H in H₂SO₃ by metals. All sulphites may be represented by the formula xMO.ySO2, where MO stands for an equivalent of a metallic oxide; the normal sulphites belong to the forms M₂SO₃, M¹¹SO₃, M¹¹¹₂(SO₃)₃, and M¹¹(SO₃)₂; the greater number of the acidic sulphites are of the forms M'HSO, and M''(HSO,)2, a few which contain more than one equivalent of acidic radicle to one of basic radicle may be represented as M12SO4.xSO2. Double sulphites are fairly numerous.

Many sulphites are prepared by passing SO. into water wherein metallic hydroxides or carbonates are dissolved or suspended; some are formed by double decomposition from the alkali sulphites. Several metallic sulphites that are insoluble in water can be prepared by the reaction between solutions of the sulphates and solution of Na2SO2; two main reactions occur, ap-(1) Muso, Aq + Na, So, Aq = Muso, + Na, So, Aq, (2) Muso, Aq + 2H₂O = MO₂H₂ + H₂SO, Aq, so that normal sulphites are formed in some cases and basic sulphites in other cases. This method of forming sulphites has been examined by Seubert a. Elten (Zeit. f. anorg. Chem. 4, 44): they find that normal sulphites are always formed when M - Ba, Cd, Ca, Fe¹, Pb, Ag, Sr, or Tl (with Hg¹¹ a double sulphite HgSO₂, Na, SO₂, H₂O was formed); that normal sulphites are formed at low temperatures, using the salts in the ratio of equal molecules, when M=Mg, Mn, Sn^n , $U(UO_2)$, or Zn, but that at higher temperatures, or with more dilute solutions, basic sulphites of these metals are produced; and that basic sulphites are always obtained when M = Al, Be,

Bi, Cr, Co, Cu, Fe^{III}, or Ni.

The sulphites of the alkali metals, and the acid sulphites of the alkaline earths, are soluble in water; most other sulphites are insoluble. Sulphites in aqueous solution, and many in moist air, readily oxidise to sulphates; salts of other S oxyacids are sometimes formed, and S is frequently separated (cf. Pierre, C. R. 62, 460; 73, 749). Oxidisers, such as ClAq, HNO, Aq, &c., quickly convert sulphites into sulphates; sulphite solutions are, therefore, energetic reducers. Solutions of sulphites are readily reduced, giving H.S or metallic sulphides, by SnCl.Aq, Zn and HClAq, &c. Heated with C, they are reduced to sulphides, sometimes to oxides. Sulphites decompose at a red heat to sulphides and sulphates, compose at a roa neat to suprinces and sulpnates, or to exides and SO₂. Sulphites are decomposed by almost all acids, not by CO₂Aq of boric acid, giving off SO₂. Solutions of sulphites generally form thiosulphates by reacting with S, H.S or alkali hydrosulphides. Sulphites give sulphates and thiosulphates when heated in SO, (Divers, C. J. 47, 205). Sulphites scarcely react with POCl, according to Divers (l.c.); a little metallic chloride and phosphate are formed, but no SOCl₂. Divers (l.c.; also C. J. 49, 577) contends that the normal sulphites have the constitution SO2OM.M-that is, that they contain the sulphonic group SO₂OM - and that they are not thionyl compounds, SO(OM)2.

Aluminium sulphites. The only salt that has been definitely isolated is the basic sulphite Al₂O₂.SO₂. 4aq; obtained by dissolving freshly ppd. AlO₃H₃ in SO₂Aq, and heating to 74°, when the salt separates as a white powder. Heated in air gives off H.O and SO., and leaves sulphate (Gougginsberg, A. 45, 132; confirmed by Röhrig, J. pr. [2] 37, 217).

Ammonium sulphites. The normal salt (NH₄)₂SO₂, aq was found in the fumes from the residues from gas-works used in the preparation of (NH₄)₂SO₄ (Scheitz, Ar. Ph. [3] 5, 332); it is prepared by adding absolute alcohol to SO, Aq made alkaline by NH, Aq, or by passing moist SO, and moist NH, into absolute alcohol (Muspratt, P. M. [3] 30, 414). White monoclinic leaflets; sol. in 1 part water at 12° with disappearance of heat. Does not deliquesce in air, but oxidises gradually to sulphate (Marignae, Ann. M. [5] 12, 25). The acid salt NH, HSO, is obtained, as very deliquescent rhombic crystals, by saturating a solution of the normal salt with SO₂ and allowing to crystal-lise in vacuo; loses SO₂ at the ordinary temperature; S separates on exposure to light; a saturated solution heated to 150° in a sealed tube decomposes to S, H2SO4Aq, and (NH₁)₂SO₄Aq (Barbaglia a. Gucci, B. 13, 2325). The basic salt 3(NH₄)₂O.2SO₂, 2aq described by Muspratt could not be obtained by Marignac. Double salts are described under the various aulphites.

Barium sulphites. The normal salt BaSO. is prepared by double decomposition from BaCl₂Aq and Na₂SO₃Aq; a white powder, insol. water; may be crystallised in hexagonal forms

from warm saturated SO.Aq; heated in a closed tube decomposes to BaSO, and BaS (Rammels. berg, P. 67, 891). Easily sol. HClAq (Johnson, C. N. 58, 155; cf. Hodges, ibid. 128).

Beryllium sulphites. No salt has been isolated; a solution of a sulphite (? BeSO₂) is obtained by dissolving BeO₂H₂ in SO₂Aq, but crystals do not form on evaporation alone or over H₄SO₄; addition of alcohol causes formation of a thick syrup (Atterberg, Bl. [2] 24, 358; cf. Berthier, A. Ch. [3] 7, 77).

Bismuth sulphites. A basic salt

2Bi₂O₃SO₂. 5aq is formed by the action of conc. SO₂Aq on BiO₃H₄ (Rörrig, J. pr. [2] 37, 217; cf. Muspratt, P. M. [3] 30, 414).

Cadmium sulphites. The normal salt CdSO₃

is obtained by dissolving CdCO, in SO Aq, and crystallising; white, indistinctly crystalline salt; scarcely sol. water; heated gives SO2, CdO, CdS, and CdSO, (Rammelsberg, P. 67, 256). By treating Cd with SO.Aq, filtering from CdS, and concentrating carefully, Fordos a. Gélis obtained the dihydrate CdSO, 2aq; the same salt was obtained by Muspratt (Lc.); confirmed by Röhrig (Lc.). Denigès (BL. [3] 7, 569) failed to obtain this hydrate, but states that a trihydrate is produced by mixing equal vols. of 10 p.o. solutions of CdSO₄ acidified with acetic acid and Na₂SO₃. A double animonium-cadmium sulphite CdSO₃ (NH₄)₂SO₃ was obtained by Rammelsberg (l.c.).

Calcium sulphites. The normal salt CaSO₃.2aq is prepared by ppg. CaCl₂Aq by Na₂SO₃Aq, dissolving in SO₂Aq, and crystalli-The normal salt sing; it forms small lustrous crystals (Muspratt, Lc.). Also obtained by passing SO, into water with CaCO, in suspension (Röhrig, Lc.). Heated to 80° gives 2CaSO, aq and loses all water at 100° (R., Lc.). R. failed to isolate any acid salt.

Chromium sulphites. A basic chromic salt 2Cr.O. 3SO₂. 16aq was obtained by Muspratt (P. M. [3] 30, 414), as a pale-green pp., by adding alcohol to solution of CrO₃H₃ in SO₂Aq; composition confirmed by Röhrig (J. pr. [2] 37, 217). Alkali sulphite solutions do not ppt. solutions of chromic salts even after long boiling (Berthier, A. Ch. [3] 7,77). By adding K₂SO₃Aq to CrCl₂Aq, Moberg (J. 1847-8. 413) obtained a reddish pp. which was perhaps a chromous sul-

Cobalt sulphites. The normal cobaltous salt CoSO₃. 5aq was obtained by Muspratt (l.c.), as a red granular pp., by passing SO2 into water with CoCO, in suspension, boiling out air from the Solution, and letting cool in a closed vessel. By evaporating in H, Rammelsberg (P. 67, 391) obtained the trihydrate; the existence of both hydrates has been confirmed by Röhrig (l.c.). Double salts CoSO₃.K₃SO₃ and 2CoSO₃.Na₂SO₃.CoO were obtained by Schultze (J. 1865. 270) by heating CoSO₃ or CoCl₂ with albeit sulphite solutions. Double salts of alkali sulphite solutions. Double salts of cobaltic sulphite Co. (SO.). M. SO., where M = K or Na, were obtained by Geuther (A. 128, 157) by continued heating of CoO,H, with fresh

quantities of cone. M.SO.Aq.
Copper sulphites. Neither cuprous nor cuprie sulphite has been isolated, but several double salts of cuprous sulphite are known. The green liquid obtained by dissolving CuCO. (Berthier, A. Ch. [3] 7, 86) or CuO.H. (Bettger, A. 89, 178)

in SO.Aq probably contains Cu.SO.; but this solution rapidly decomposes with separation of a red pp. and formation of CuSO Aq. The red solution formed by passing SO, into water with freshly prepared Cu₂SO₂(NH₄)₂SO₂ (v. infra) in solution was supposed to contain Cu.SO, by Bogojski (J. pr. 53, 403); but Péan de Saint-Gilles obtained only Cu.SO₂. CuSO₂. 2aq from this solution (A. Ch. [3] 42, 23), and this was confirmed by Svensson (B. 4, 713).

According to Newbury (Am. 14, 232), a basic cupric sulphite 6CuO.4SO... 3aq is formed by passing SO. into cold water with CuO.H. in suspension, and sending a stream of air into the green solution so formed until a bright-yellow pp. is produced. When this basic salt is boiled with water for a few minutes CuSO, Aq is formed, and a brown pp. is thrown down. The brown pp. is thought by N. to be Cu2SO3; on continued

boiling with water it gives off SO, and Cu,O

remains.

Double cupro-cupric sulphites. The dihydrated salt Cu₂SO₃. CuSO₃. 2aq was obtained by Chevreul (A. Ch. 83, 183) by heating CuO or CuCO₃ with SO₂Aq; it is also prepared by boiling CuSO₄Aq with solution of an alkali sulphite or thiosulphate, by boiling the green double salt Cu2SO3.(NH4)2SO3 (infra) with water (P. de St.-G., I.c.), by passing SO, into conc. Cu(C.H.O.).Aq at 65° till the yellow pp. that forms is dissolved, and then letting stand in air (Étard, C. R. 93, 725), and by passing a slow stream of SO2 into 10 p.c. CuSO, Aq containing a roll of thin sheet Cu till the liquid is almost colourless (the salt deposits on the Cu) (Newbury, Am. 14, 232). Translucent, garnet-red octahedra; S.G. 3.57; gives up 2H₂O, and also SO₂, above 150°, and at a higher temperature leaves Cu2O with some CuSO₄ (Rammelsberg, P. 67, 391). Soluble SO₂Aq, HClAq, and NH₃Aq; KOHAq ppts. hydrates of CuO and Cu₂O; heated with water to 200° gives CuSO, Aq and Cu in crystalline leaflets (Geitner, A. 129, 350). The pentahydrate Cu2SO3. CuSO3. 5aq separates, as a greenish-yellow pp., from conc. Cu(C₂H₃O₂)₂Aq, into which a slow stream of SO₂ has been passed till the liquid has become emerald-green (P. de St.-G., l.c.). Easily sol. SO Aq or acetic acid, also in solutions of cupric salts and in NH, Aq; when boiled with water the red dihydrate is formed.

Double salts of cuprous sulphite with alkali sulphites are readily produced by the reaction of conc. solutions of alkali sulphites with solutions of cupric salts. double salts are colourless and crystalline; their composition is $xCu SO_3 yM_SO_3$, zaq (x generally = 1), where $M = NH_3$, K, or Na (for details of preparation, composition, and properties v. Rogojski, J. pr. 53, 403; Péan de Saint-Gilles, A. Ch. [3] 42, 23; Vohl, J. pr. 95, 218; and A. Ch. [3] 42, 23; Vohl, J. pr. 95, 218; and Svensson, B. 4, 713). Some acid salts of the form Cu₂SO₃,xM₂SO₃,ySO₂, zaq have also been prepared (S. l.c.), and some salts of alkali sulphites with both Cu₂SO₃ and CuSO₃ (P. de St.-G., l.c.; R., l.c.).

Didymium sulphites. The normal salts

Di₂(SO₃), was obtained, as a reddish white powder, by passing SO₂ into water with Di₂O₃ in suspension, and boiling off excess of SO₂ (Marignac, A. Ch. [8] 58, 148; Cleve, Bl. [2] 89, 161).

tes. No gold sulphite has

Double salts of Au,SO,
and Na,SO, of the form Gold sulphites. been isolated. with Am, SO, Au,SO,3M,SO, Saq are known; also a Ba salt Au,SO,3BaSO, aq. The Na salt is obtained by adding Na,SO,Aq to a boiling alkaline solution of NaAuO₂, or by saturating NaAuO₂Aq at 50° with SO₂, then carefully adding BaCl₂Aq to the solution till free H₂SO₃ and H₂SO₄ are ppd., filtering, adding more BaCl₂Aq, quickly filtering off the purple-red Au₂SO₃.3BaSO₃, aq that separates, washing the pp. rapidly out of contact with air, decomposing it by the proper quantity of Na₂CO₃Aq, adding some alcohol to the solution, filtering off any Ba salt that ppts., and adding more alcohol, when the Na salt separates as an orange-red, very easily decomposed, pp. (v. Himly, A. 56, 252; 59, 95). When AuCl₂Aq is added, drop by drop, to a warm solution of (NH_.)₂SO₃ in cone. NH₂Aq, white, lustrous, six-sided plates separate of the salt (NH_.)₂SO₃3(NH₂Au)₂SO₃. 3aq; the inother-liquor from this salt yields the salt Au₂SO₃.3(NH₄)₂SO₃. 3aq, very similar to the corresponding Na salt (Haase, Z. 1869. 535).

Indium sulphites. The only stilt that has been isolated is a basic salt 2In2O3.3SO2. 8aq. Obtained by boiling a solution of a salt of In with excess of NaHSO3Aq; insol. water, sol. in dilute acids; loses 3H,O at 100°, and all water

at 260°; decomposed at 280°, giving off SO₂ and leaving In₂O₃ (Bayer, A. 158, 372).

Iridium sulphites. The normal iridic salt Ir₂(SO₃)₃. 6aq is obtained, in yellow crystals, by passing SO₂ into water with IrO₄H₃ in suspension, filtering and evaporating. The salt loses all water at 160°-180°; at a higher temperature Ir.O, remains; sl. sol. water, easily sol. acids; decomposed by boiling with KOHAq with separation of Ir₂O₃ (Birnbaum, A. 136, 179). The insoluble matter that remains on treating IrO, H, in water with SO₂ is a basic salt Ir.O₂.SO₂. 4aq (Birnbaum, l.c.). Double salts of iridous sulphite were obtained by Seubert (B. 11,1761) in separating Ir from Rh by means of Na2SO (by Bunson's method, A. 146, 274). Seubert gave the formulæ IrSO₃.3Na₄SO₃, 10aq and IrH₂(SO₃)₂.3Na₄SO₃, xaq, x being = 4 and 10,

Iron sulphites. The normal ferrous salt FeSO₃, 3aq is formed, along with FeS₂O₃, by dissolving iron wire in SO2Aq out of contact with air; on evaporating (out of air) the sulphite crystallises out, leaving the thiosulphate in solution (Fordos a. Gélis, J. Ph. [3] 4, 333; cf. Koene, P. 63, 245, 631; also Muspratt, P. M. [3] 30, 414). Sl. sol. water, easily sol. SO Aq; loses H2O, and then (at 250°) SO₂, on heating. Basic ferric salts are formed by reacting on ferric salt solutions with alkali sulphites; on adding alcohol to the red liquids thus formed, Koene (P. 63, 245, 481) obtained the salts Fe,O, SO, 6aq and 2Fe,O, 38O, tained the sins rely, sol, out and arely, sol, (cf. Muspratt, l.c.). By passing SO, into water with FeO,H, in suspension, and adding KOHAA, Muspratt (l.c.) obtained the double sals Fe,O, SO, 2K,SO, 5aq.

Lead sulphites. Only the normal salt PbSO, has been obtained; a white powder, insol. water, formed by adding Na.SO.Aq to solution of a salt of Pb (confirmed by Röhrig, J. pr. [2] 37, 217).

Lithium sulphites. The normal salt Li.SO, aq is prepared by passing SO, into water with Li.CO, in suspension, till CO, ceases to be given off, and evaporating on a water-bath or over H₂SO₄ (Röhrig, J. pr. [2] 37, 217). Danson (C. J. 2, 205) represented the salt as a hexahydrate. By adding other to the solution obtained from Li, CO, as described, R. got the dihydrate Li,SO, 2aq. Easily sol. water, somewhat sol. alcohol, very sl. sol. ether; oxidised in moist air. Röhrig failed to obtain an acid salt. By adding the proper quantity of K2CO, to the acid solution of Li₂CO₂ in SO₂Aq, evaporating to a syrup, and placing in a freezing mixture of snow and salt, R. obtained the double salt 2LiKSO₂ aq; by a similar process he got monoclinic crystals of

6Li,8O, Na,8O, 8aq (J. pr. [2] 37, 217).

Magnesium sulphites. The normal salt MgSO₃. xaq is formed by suspending magnesia alba in water, passing in SO2, and concentrating the solution (Rammelsberg, P. 52, 89); if evaporation is carried on over H₂SO₄ (Röhrig, l.c.), or in vacuo below 100° (Hartog, C. R. 104, 1793), the hexahydrate separates; if evaporation proceeds above 100° the trihydrate is obtained Muspratt, l.c.; R., l.c.; H., l.c.). Slowly oxidises in air to sulphate: loses all water at 200°; when more strongly heated the salt loses SO, and

leaves MgO.

Double salts with (NH,),SO, are formed by mixing the constituents and evaporating; also by dissolving MgO.H₂ in cold (NH₄)₂SO₃Aq (Rammelsberg, P. 94, 507; Hartog, l.c.). **Manganese sulphites.** Several hydrates of

the normal manganous salt MnSO, have been described. By adding alkali sulphite solution to dilute MnCl_Aq so long as the pp. that forms dissolves again, and then letting stand, monoclinic crystals of the trihydrate MnSO₃. 3aq are obtained; this hydrate is also formed by mixing 10 p.c. of MnSO₄Aq, acidified with acetic acid, and Na₈SO₄ (Deniges, Bl. [3] 7, 569); if Na₈SO₄Aq is added to hot dilute MnCl₄Aq the monohydrate is said to be produced. (Rammelsberg (P. 67, 245, 391) gives the formula 2MnSO, 5aq to the salt obtained by reacting on Mn acetate solution with Na, SO, Aq, and this is confirmed by Röhrig (J. pr. [2] 37, 217; cf. also Muspratt, P. M. [3] 30, 414). Double salts MnSO, K, SO, and 2MnSO, K, SO, were prepared by Gorgeu (C. R. 96, 376) by saturating 20 p.c. K₂SO₂Aq with SO₂, adding 4 p.c. MnSO₃. 3aq, and evaporating over an absorbent of SO₂; double Mn-Na salts are also described by G. (l.c.).

Mercury sulphites. According to Péan de Saint-Gilles (C. R. 34, 905) the normal mercuric salt HgSO, is formed by adding dilute Na SO Aq to a very conc. solution of Hg(NO₃)₂ free from excess of acid; it is, however, difficult to obtain the salt free from basic sulphites. basic mercuric sulphite 2HgO.SO, was obtained pure by P. de St.-G. by using solution of basic mercuric nitrate. The normal salt is easily decomposed; boiling water produces Hg, SO, and Hg. Boiling water is said (P. de St. G., l.c.) to convert the basic salt into the isomeric compound Hg,SO, (2HgO.SO₂ = Hg,O.SO₃). Divers a. Shimidzu (C. J. 49, 533) say that formal mercuric sulphite cannot be isolated; the reac-tion of Na,SO,Aq with Hg(NO₃)Aq produces at first the basic salt 2[2HgO.SO₂], aq, and then a

salt which is most simply represented at HgSO₂.Hg₂SO₂. 4aq, and which is called mercurosic (or mercuro-mercuric) sulphite by D. a. S., and represented by them as

 $H_g < SO_2 O > Hg_2$, 4aq. D. a. S. represent the basic salt as Hg SO, OHgO Hg. aq, and call it

mercuric oxysulphite.

For the best conditions of preparation of 2HgO.SO₂ v. D. a. S., l.c., p. 550, and for the reactions of this salt v. ibid. pp. 546-50; for preparation of mercurosic sulphite v. ibid. p. 564. and for the reactions of this salt, pp. 559-63.

By adding dilute Na SO, Aq to moist Hg SO, or to HgNO, Aq, D. a. S. (l.c., p. 572) obtained a greyish-black amorphous solid to which they gave the formula Hg, (SO,)2. aq, the constitution Hg SO 0 Hg3 aq, and the name mercuric hupomercurous sulphite or hypomercurosic sulphite. For the best method of preparing this salt (action of SO,Aq on Hg,SO, or Hg,NO,) v. D. a. S., l.c., p. 571; for the reactions of the salt v. pp. 567 70. It is evident that the formula given to this sait is the same as that of normal mercurous sulphite (Hg,(SO₃)₂=2Hg₂SO₃); the salt is produced from mercurous compounds, and in many of its reactions yields mercurous compounds; D. a. S. insist that the salt belongs to a new class of Hg compounds that contain what they call the 'hypomercurous radicle.'

By treating solid HgCl, with NaHSO, Aq, Wicke (A. 95, 176) obtained a solution that deposited a white crystalline powder to which he gave the composition $Hg(HSO_3)_2$ —i.e. acid mercuric sulphite. According to D. a. S. (l.c., p. 554) the pp. is HgSO₂.Na₂SO₃.aq. By reacting on HgO with SO₂Aq a white solid is formed, together with a solution containing a compound of Hg. Rammelsberg thought that the white solid was a basic mercurous sulphite of varying composition, and that the solution contained Hg₂SO₄ (P. 67, 405; the reaction was also examined by P. de St.-G. and by Vogel). D. a. S. say that the white residue is HgSO, Hg₂SO, 4aq (mercurosic sulphite, according to D. a. S.); by using freshly ppd. HgO suspended in water, and adding a little of this to SO, Aq (nearly free from H2SO4), D. a. S. obtained a clear solution which reacted as a solution of HgSO, in H2SO, and which they regarded as a solution of acid mercuric sulphite, Hg(HSO₃)₂ (v. l.c., pp. 554-8). Several double salts of mercuric sulphite with alkali sulphites have been isolated. The chief are HgSO, M,SO, xaq, where M = NH, K, or Na, and 2HgSO, Na,SO, aq (v. P. de St.-G., C. R. 34, 905; Hirzel, A. 84, 258; D. a. S., Le., pp. 538-46). D. a. S. regard these double salts as alkali derivatives of the hypothetical acid Hg SO OH (they greatly doubt the existence of the salt 2HgSO, Na, SO, described by P. de St.-G.); this view is confirmed by Barth's measurements of the electrolytic conductivities, and the freezing-points, of solutions of these salts (Z. P. C. 9, 176); Barth's results point to the

dissociation in dilute aqueous solution of these salts into three ions, HgS₂O_s, R, and R'. Nickel sulphites. The normal salt NiSO_s, Saq separates, in green tetrahedric erys.

tals, on slowly evaporating a solution formed by passing 80, into water with NiO. zaq in suspension (Rammelsberg, P. 67, 391). By boiling the solution of NiO. zaq in SO,Aq, Muspratt (P. M. [8] 30, 414) obtained a tetrahydrate NiSO. 4aq; this hydrate was also obtained by Röhrig (J. pr. [2] 37, 217) by quickly evaporating the solution at c. 150°. The compound with ammonia, NiSO, 3NH, 3aq, separates, as a blue crystalline

pp., on adding alcohol to an ammoniacal solution of NiSO₄ (Rammelsberg, l.c.).

Osmium sulphites. The normal salt OsSO₃ was obtained by Claus (J. pr. 90, 65) by treating OsO₃Aq with excess of SO₂, and evaporating or deline No. Os. No. No. SO₃ and evaporating or adding Na₂CO₃ or Na₂SO₄; after drying the salt is a blackish-blue powder, insol. water, sol. HClAq without giving off SO₂, reppd. from this solution by KOH or K₂CO₃, decomposed to K₂SO₃ and OsO. xaq by long boiling with conc. KOHAq. When moist the salt oxidises in air to OsSO. The double salt OsSO, 2K,SO, 2KHSO, 4aq was obtained by Claus (A. 63, 355) as a pale rose-red crystalline powder, by heating K,OsCl, with K,SO,Aq.

Palladium sulphites. Only the double pallado-sodium salt PdSO, 3Na, 3O,, 2aq has been isolated; a white pp. obtained by dropping NaOHAqinto PdCl₂Aq, after adding SO₂ (Wöhler,

A. 174, 199).

Platinum sulphites. Neither platinosulphite PtSO₃ nor platinisulphite Pt(SO₃)₂ has been isolated. Several salts which may be regarded as double compounds of PtSO₃, but are better classed as platinosulphonates or platinosulphites, have been obtained; they are shortly described under PLATINO-SULPHONATES (this vol., p. 285). By passing SO, into water with PtO,H, in suspension, and adding alkali sulphites to the dark-red liquid so formed, Birnbaum (A. 139, 172) obtained double salts of the form PtO SO. M. SO. and the form of the form the form PtO.SO₃.xM₂SO₃.yaq, where M = K or Na, x varied from 1 to 2, and y also from 1 to 2. These salts gave no pp. of BaSO, with BaCl2Aq, with HClAq SO, was given off and PtCl, formed; hence they are better classed as double salts of platinyl sulphite, Pto.So, than of platinous sulphate PtSO.

Potassium sulphites. The normal salt K2SO2. 2aq is obtained, in large, deliquescent, monoclinic prisms, by passing SO2 into K2COAq as long as CO₂ is given off, and evaporating over H₂SO₄ at the ordinary temperature (Muspratt, P. M. [3] 30, 414). More soluble cold than hot water; decomposed by heat to K₂S and K₂SO₄ (Rammelsberg, A. 50, 259; results of M. and R. confirmed by Röhrig, J. pr. [2] 37, 217; v. also Hartog, C. R. 109, 179, 221, 436). The acid salt KHSO, separates in white needles on adding alcohol to a solution of the normal salt saturated with SO₂ (M., l.c.; confirmed by Röhrig, l.c.). By passing SO₂ into hot saturated K₂CO₃ till CO₂ ceased to come off and the solution was greenish, and then allowing to cool, Muspratt (l.c.) obtained hard monoclinic crystals of the acid salt K₂SO₂, SO₂ (= K₂S₂O₃), sometimes called pyrosulphite; only sl. sol. water; decomposed by heat to K₂SO₄, SO₂, and S (confirmed by Röhrig, l.c.). Dilute K₂SO₂Aq heated in a closed tube to 100° and then let stand is very slowly decomposed to K,SO, H,S,O, and S (Saint-Pierre, C, R, 62, 460; 73, 749). K,SO,Aq with KNO,Aq

gives K salts of various acids; v. Surruuz oxy-ACIDS, NITROGEN DERIVATIVES OF (p. 619).

Double sulphites of potassium and sodium. Schwicker (B. 22, 1728) obtained two socium. Schwicker (B. 22, 1729) obtained two distinct salts KNaSO, xaq; one by neutralising cone. KHSO, Aq by the proper quantity of Na,CO, and evaporating over H,SO, the other by adding K,CO, to NaHSO,Aq. Röhrig (J. pr. [2] 37, 217) ppts. the salts by adding alcohol, or better ether. The first salt, heated with EtI to 140°, gives 4(SO,Et.OK). NaI, the second gives 4(SO,Et.ONa). KI; hence the first salt seems to be NaSO, OK and the other KSO, ONa. Schwicker assigns different quantities of crystalline water to the salts, viz. NaSO, OK. 2aq and KSO, ONa. aq; Röhrig (l.c.) gives 2aq to both salts. The two Röhrig (l.c.) gives 2aq to both salts. salts seem to be isomeric. Aqueous solutions of these salts have identical electrolytic conductivities, as would be expected (Barth, Z. P. C. 9, 176). Schwicker (*l.c.*) also describes the salts KNa H(SO₃), 4aq and K₂NaH(SO₃), 3aq. Hartog (*R.* 109, 179, 221, 436) describes the salts (*K.* SO₂, 2Na SO₂, 5Qaq (= K₂O.2Na₂O.4SO₂, 9aq) and 2K₂SO₃(NH₂), SO₂SO₂, 9aq $(=2K_2O.(NH_1)_2O.4SO_2.9aq).$

For other double salts of potassium sulphite v. supra, cobalt sulphites, copper sulphites, iron sulphites, lithium sulphites, manganese sulphites, mercury sulphites, osmium sulphites, and platinum sulphites; and infra, ruthenium

sulphites and silver sulphites.

Rhodium sulphites. The normal rhodic salt Rh. (SO₃)₃. 6aq is prepared, as a yellowish crystalline mass, by dissolving RhO₃H₄. aq in SO₄Aq and evaporating; fairly sol. water, insol. alcohol (Bunsen, A. 146, 265). The double rhodous salt 4RhSO, 6Na,SO, 9aq is obtained by treating Na, RhCl, 12aq with excess of NaHSO, Aq (Bunsen, l.c.); it has been examined by Seubert a. Kobbé (B. 23, 2556), who prepared it by heating a solution of RhCl, 4aq with excess of NaHSO, Aq for some time, washing the pp. with cold water, and drying over P.O.. Pale-yellow solid; very sl. sol. hot water; dissolves in dilute HNO₃Aq, giving off SO₂; warmed with conc. H.SO₄ forms Rh₂(SO₄)₃.Na₅SO₄ (B., l.c.; S. a. K., l.c.).

Ruthenium sulphites. Only the double rutheno-potassium salt RuSO, K,SO, has been isolated; prepared by heating K,RuCl,Aq with K,SO,Aq till a dark-red solution is formed, evaporating to dryness, dissolving, again evaporating to dryness, and repeating these processes till a pure white residue is obtained (Claus, J. pr. 42, 351).

Silver sulphites. The normal salt Ag.SO, forms small, white lustrous crystals; obtained by treating AgNO, Aq with alkali sulphite solution or with SO,Aq; if excess of SO,Aq is allowed to remain in contact with the salt for Some time Ag is formed (H. Rose, P. 88, 240). Darkens in air (Muspratt, P. M. [3] 30, 414; Sodeau, C. N. 65, 102); products depend on method of preparation of the salt (v. Stas, Stas, Name P. Heatted close C. 114. Mouv. R.). Heated alone, or with water, to 100° gives Ag₂SO₄, Ag, and SO₂ (Berthier, A. Ch. [3] 7, 82; cf. Geitner, J. 1864. 142, who says that decomposition begins at 200°). Scarcely sol. water or SO₂Aq; sol. NH,Aq (Berthier, Le.), also in alkali sulphite solutions.

Double salts. AgNaSO, 2aq; small lustrous needles, formed by dissolving Ag,SO, in hot saturated Na,SO,Aq, letting cool, and pressing salt that separates (cannot be washed with water (Svensson, B. 4, 714). AgKSO₃, xaq, prepared like the Na salt. Svensson (l.c.) describes three double salts with (NH₄);SO₃, obtained by dissolving Ag₂SO₃, or AgCl, in (NH.), SO, Aq; he gives the formulæ Ag(NH.) SO,, Ag, SO, 6(NH.), SO,, 19aq, and Ag, SO, 3(NH.), SO, 4(NH.) HSO, 18aq.
Sodium sulphites. The normal salt Na, SO,

is prepared by completely saturating Na₂CO₃Aq with SO₂, warming, adding an equal quantity of the same Na₂CO₂Aq, evaporating, and crystallissame Na₂O₃Aq, evaporating, and crystanising above 33° (Rammelsberg, P. 56, 298; Schultz-Sellack, J. pr. [2] 2, 459). Also obtained by heating the hydrate Na₂SO₃. 7aq to 150°. Na SO, also crystallises from solution of NaHSO, that has been made strongly alkaline. Heated above 150° melts to a yellowish-red mass containing sulphide and sulphate in the ratio Na₂S:3Na₂SO₄ (R., P. 67, 246; 94, 507). The heptahydrate Na₂SO₃ 7aq is obtained by crystallising at the ordinary temperature a solution of Na₂CC₃ saturated with SO₂, warmed, and mixed with an equal quantity of the same according to Röhrig (J. pr. [2] 37, 217) only the heptahydrate exists.

The acid salt NaHSO, is formed by saturating Na₂CO₃Aq with SO₂ and cooling; better crystals are obtained by treating Na₂CO₃. 10aq with SO2 and evaporating the liquid so produced in SO₂. Easily sol. water, but less sol. than Na₂SO₂, 7aq. (For heat of solution v. De Forcrand, C. B. 98, 738.) Gives off SO₂ on exposure to air; SO₂ is also removed from Na₂SO₄ by researce of a principle of the solution of NaHSO₂Aq by passage of an indifferent gas (Gernez, O. R. 61, 606). When heated gives off H₂O, SO₂, and S, leaving Na₂SO₄; heated in a closed tube forms Na, SO, H., SO, S, and H.O (Barbaglia a. Gueci, B. 13, 2325). Reacts with I to give NaHSO, and NaI (Spring a. Bourgeois, Ar. Ph. 229, 707, where references are given to other experiments). Another acid salt Na₂SO₃.SO₂ (= Na₂S₂O₃), sometimes called pyrosulphite, is said to separate, in lustrous prisms, from conc. hot NaOHAq saturated with SO2

(v. Röhrig, l.c.).

Double salts with anmonium sulphite. Marignac (Ann. M. [5] 12, 30) described a double salt obtained by passing NH, into conc. NaHSO, Aq; the salt is probably identical with that described by Schwicker (B. numerical with that described by Schwicker (B. 22, 1728), to which he gives the formula Na₂SO₂,(NH₄)HSO₂, 4aq. By partially saturating conc. (NH₄)HSO₂ with Na₂CO₂Aq, Trauber (J. C. T. 1888. 44) obtained the salt 2Na₂SO₂(NH₄)₂O₂. 10aq; Hartog writes the formula of this salt 2Na₂O₂(NH₄)₂O₄. ASO₂, and says it orystallises with 9aq (O. R. 109, 179, 221, 486). For other double salts of Na₂SO₂ v. supra, cobalt sulphites, copper sulphites, gold sulphites, iridium sulphites, lithium sulphites, manganese sulphites, mercury sulphites, palladium sulphites, platinum sulphites, potassium sulphites, rhodium sulphites, and silver sulphites.

Strontium sulphites. The normal salt SrSO₃ is formed by passing SO₂ over SrO at 290° (Birnbaum a. Wittich, B. 13, 651); also by decomposing SrCl₂Aq by alkali sulphite solution. Small white crystals; slowly oxidises in air to sulphate (Muspratt, P. M. [3] 30, 414); gives SrS and SrSO, on heating (Forster, P. 133.

Thallium sulphites. The normal thallous salt Tl₂SO₃ is prepared by adding Na₂SO₃Aq to TLSO, Aq, and crystallising the pp. from warm water. White crystals; S. 3:34 at 15°; insol. alcohol; S.G. 6:427 at 20° (Scubert a. Elten, Zeit. f. anorg. Chem. 2, 434). The same salt was obtained by Röhrig (J. pr. [2] 37, 217) by passing SO, into solution of a thallous salt, evaporating at 100° or over H.SO., or adding alcohol.

Tin sulphites. Basic stannous salts, xSnO.2SO₂. 20aq, x being probably 5, 8, and 11, were obtained by Röhrig (J. pr. [2] 37, 217) by treating freshly ppd. SnO. xaq with SO₂Aq.

Titanium sulphites. Berthier (A. Ch. [3] 7,

77) made some observations, but described no definite salts.

Uranium sulphites. A basic uranous salt UO₂.SO₂. 2aq = U(OH)₂SO₃. aq is obtained, as a greyish-green pp., by adding Na SO Aq to UCl Aq (Rammelsberg, P. 56, 125; confirmed by Röhrig, J. pr. [2] 37,217). The uranyl salt UO, SO, xaq was obtained, in yellow prisms, by Muspratt (P. M. [3] 30, 414), by passing SO₂ into water with UO, in suspension, and allowing the solution so formed to evaporate at the ordinary temperature; Muspratt gave x=3, according to Röhrig (i.c.) x=4 (cf. Girard, C. R. 34, 22; and Reinele, P. 125, 238).

Zine sulphites. The normal salt

Zino sulphites. The normal salt 2ZnSO₃, 5aq is prepared by evaporating, or by adding alcohol to, a solution of ZnCO₃ in SO₂Aq (Rammelsberg, P. 52, 90); also by mixing cold 25 p.c. SnSO₄Aq acidified with acetic acid with cold 25 p.c. Na₃SO₃Aq, and letting stand (Denigès, Bl. [3] 7, 569). Muspratt (l.c.), Fordos a. Gélis (J. Ph. [3] 4, 363), and Koene (P. 63, 245, 431) give the formula ZnSO₃, 2aq; but Röhrig (J. pr. [2] 37, 217) confirms Rammelsherg's formula.

berg's formula.

Zirconium sulphites. Compositions of salts obtained by ppg. Zr salt solutions by alkali sul-

phites are doubtful (v. Berthier, A. Ch. [3] 7, 77; Hermann, J. pr. 31, 77).

HYPOSULPHITES. (Hydrosulphites.) Salts of the acid H.S.O., Hyposulphurous acid is known only in aqueous solution. Schützenberger (A. Ch. [4] 70, 351) obtained the Na salt, and an aqueous solution of the acid, in 1869; he gave the formula H,SO, to the acid; but Bernthsen (A. 208, 142; 209, 285; 211, 285) in 1881 showed that the acid has the composition H.S.O., This acid corresponds with the oxide $S_2O_3(S_2O_4 + H_1O = H_2S_2O_4)$. Schützenberger prepared the Na salt by digesting conc. NaHSO₃Aq with zinc shavings in a closed flask for c. half an hour, pouring the liquid from the crystals of the double Na-Zn sulphite which formed (this is a basic Zn-Na sulphite, according to Bernthsen, A. 211, 297) into a flask about three-fourths filled with conc. alcohol, allowing to stand for

some time in the closed flask, and then pouring off into flasks, each flask being quite filled with the liquid and then sealed; after a time crystals of the hyposulphite were formed, to which S. gave the composition NaHSO. Bernthsen (l.c.) after reducing NaHSO, Aq by Zn, pouring off from the double sulphite formed, &c., removed sulphite and sulphate by adding BaCl, Aq; he then filtered and titrated the solution by ammoniacal CuSO, Aq, which is decolourised by Na.S.O, Aq to a cuprous salt (and eventually to Cu.II, and Cu.S). For details of the method of analysis v. Bernthsen (B. 13, 2277; A. 211, 292 note). B. failed to obtain Na S.O. free from Na SO., Na SO., Na₂S₂O₃ and Zn salts.

B. expresses the first part of the reduction of NaHSO₃ by the equation $4NaHSO_3Aq + Zn = Na_2S_2O_1Aq + ZnSO_3 + Na_2SO_3Aq + 2H_2O$, and the

complete change by the equation 10NaHSO, Aq + 3Zn =

 $3{\rm Na}_2{\rm S}_2{\rm O}_4{\rm Aq} + {\rm Na}_2{\rm SO}_3{\rm Aq} + {\rm Zn}_3{\rm Na}_2{\rm S}_3{\rm O}_{10} + 5{\rm H}_2{\rm O}.$ Moist sodium hyposulphite is rapidly oxidised in air to Na SO,; when dry it is unchanged in O; it is easily sol. water, less sol. dilute alcohol, and insol. cone. alcohol; but according to B. even approximately pure Na S2O, has not been Na2S2O1Aq is oxidised by iodine so-

By heating Na.S₂O₄Aq with an equivalent quantity of II.SO₄Āq or H₂C₂O₄Aq, an aqueous solution of hyposulphurous acid II.S.O.Aq is obtained; this solution is an energetic reducer, decolourising indigo, and reducing salts of Cu, Hg, Ag, &c.; the solution rapidly decomposes in air with separation of S. M. M. P. M.

SULPHO Use of this prefix applied to inorganic compounds: for sulpho- compounds and sulpho-salts v. the compounds or salts to the names of which sulpho- is prefixed; thus sulpho-molybdates are described under MOLYBDATES; but the prefix thio- is used in almost every case in preference to sulpho- to denote the replacement of O by S. Sulphocyanides and similar compounds are described under Cyanides : sulphocyanic anhydride is described as Cyanogen BULPHIDE.

SULPHO-ACETIC ACID C,H,SO, SO₃H.CH₂.CO₂H. [75°].

Formation.-1. By adding SO, to cooled HOAc (Melsens, A. Ch. [3] 5, 392; 10, 370; A. 52, 276) .- 2. By the action of fuming II SO, on acetamide or acetonitrile (Buckton a. Hofmann, C. J. 9, 247).—3. By boiling chloro-acetic acid with aqueous K_2SO_3 (Strecker, Z. [2] 4, 214; Collmann, A. 148, 109).—4. By heating Ag₂SO₄ with AcCl at 120° (Kämmerer a. Carius, A. 131, 165).-5. By boiling chloro-acetic acid with ammonium sulphite solution (Hemilian, A. 168, 145).—6. By heating Ac₂O with H₂SO, at 130° (Franchimont, C. R. 92, 1054; cf. Baumstark, A. 140, 83).—7. By heating ClSO₂H with HOAc the 140° (Baumstark). at 140° (Baumstark).—8. By oxidation of isethionic acid by CrO₃ (Carl, B. 14, 63).

Properties. - Deliquescent crystals (containing 1 aq) giving off water of crystallisation at about 160° and decomposed at 230° into CO, SO, acetic acid, and other products (Franchimont, R. T. C. 7, 25). V. sol. water. Its salts are sol. water, insol. alcohol. PCl, acting on the Nasalt forms CHCl(SO₂Cl).COCl (R. Siemens, B. 6, 659). Vol. IV.

Salts.—K,A" aq: hard crystals.—KHA"; six-sided tables.—BaA" aq. S. 267. at 20°. six-sided tables.—BaA" aq. S. 267 at 20°.—BaA"Et,SO, (Laube, A. 218, 258).—CaA" aq.—

PbA": radiating needles.—Ag,A" ag: flat prisms.

Mono-ethyl ether EtHA". Formed by passing HCl into the Ag salt suspended in alcohol. Syrup, v. sol. water.—AgEtA": plates. Ethyl ether Et.A". Oil. Formed, together with C₆H₁₁Ag₂S₄O₁₈ by the action of Ag₂A" on EtI (F.). May be distilled (Mauzolius, B. 21,

Sulpho-diacetic acid v. DI-METHYL SULPHONE DICARBOXYLIC ACID.

Di-sulpho-acetic aldehyde C.II.S.O. CH(SO,H), CHO. By adding chloral hydrate to conc. KHSO, Aq at 80° there are formed crystals of C.H.K.S.O.K.HSO., and these when boiled with HClAq yields C.H.K.S.O. aq, from which C.H.BaS.O. 2aq may be prepared (Bathke, A. 161, 154). Boiling K.CO., yields C.H.(SO.K.), potassium formate, and K.SO.

SULPHO-AMIDO-BENZOIC ACID v. AMIDO-

RULPHO-BENZOIC ACID.

DI-SULPHO-ANILINE v. DI-AMIDO-DI-PHENYL DISHLPHIDE

(B.) - SULPHO - ANTHRACENE - (A) - CARB. OXYLIC ACID C.H. CCH >C.H. (SO.H).

[above 360°]. Obtained by dissolving anthracene-(A.)-carboxylic acid in cold cone. II.SO, and allowing to stand for 12 hours on ice (Behla, B. 20, 706). Minute yellowish prisms (from alcohol). V. sol. water and alcohol, insol. benzene and ether. The aqueous solutions of the acid and its salts have a strong blue fluorescence .-BaA": very soluble vellowish minute prisms.

Di-sulpho-anthracene-(A.)-carboxylic acid C₁₁H₂(SO₂H)₂.CO₂H. [above 360°]. Formed by disselving anthracene-(A.)-carboxylic acid in cold fuming H.SO₁ (Behla). Yellow prisms (from alcohol). V. sol. water and alcohol, insol. benzene. Its aqueous solution scarcely fluoresces. but the cone. H₂SO₄ solution has a strong yellowish green fluorescence. - A'''₂Ba: very sparingly soluble crystalline powder.

SULPHOBENZIDE v. DI-PHENYL SULPHONE. o-SULPHO-BENZOIC ACID C, HaSO, i.e.

C₈H₁(SO₃H).CO₂H. S. 50 in the cold. Formation.—1. Together with its imide, by oxidation of toluene o-sulphonic amide with KMnO₄ (Remsen a. Fahlberg, Am. 1, 433).—2. By heating the imide with HGlAq at 100 '(Fahlberg a. Remsen, B. 12, 472; Fahlberg a. Barge, B. 22, 754; Brackett a. Hayes, Am. 9, 399). this means the acid ammonium salt is first obtained (F.; Remsen a. Dohme, Am. 11, 332). -3. By boiling o-diazo-benzoic acid with alcoholic SO₂ (Wiesinger, B.•12, 1349). -4. By oxidation of toluene o-sulphonic acid by KMnO₄.

Properties. - Trunctric crystals (containing 3aq or 4aq); a:b:c = .551:1: .812, v. e. sol. water, sol. alcohol, insol. ether. According to Fahlberg (B. 22, 754), it crystallises with 3aq, and is decomposed at 105°. According to Remsen (Am 11, 332), it crystallises with 4aq, melts at 69° ic its water of crystallisation, melts at 130° wheat anhydrous, and gives a sublimate of long needles (containing 2aq). Resorcin (1.2 pts.) at 195° forms 'sulphofluorescein' $C_{19}H_{12}SO_{2}$ 2aq, which fluoresces in aqueous and alkaline solutions (Remsen a. Hayes, Am. 9, 872). By condensation of resorcin (4 mols.) with o-sulpho-benzoic acid there is likewise formed a similar body C₁₁H₂₀SO₈4aq (Fahlberg a. Barge, B. 22, 765).

C₁₁H₂₂SO₄4aq (Fahlberg a. Barge, B. 22, 765). Potash-fusion gives salicylic acid.
Salts.—KHA": transparent plates, sol.
water.—K₂A" 2aq.—Ba(HA")₂ 2½aq: needles, sol.
water. — Ba(HA")₂ 2aq. — BaHA" 2, 4½aq. —
BaA" 2aq. — Ca(HA")₂ 6aq. — ČaA" 5aq. —
CuA" 3½aq. — Ag₂A". — C₆H₄(SO₄NH₄).CO₂H.
Formed by heating the imide with HClAq at

Anhydride
$$C_0H_4 < SO_{SO} > 0$$
. [119°] (F.)

Anhydride C₀H₄<SO₂>0. [119°] (F.). [128°] (Remsen a. Dohme, Am. 11, 332). Formed by heating the K salt with PCl_s at 180° or the acid with P₂O₅ at 130°. Monoclinic tables, insol. cold water. NH₃ passed into its solution in benzene forms $C_0H_1(CONH_2)SO_2ONH_1$ [256°], which crystallises from alcohol in needles.

Chloride C,H,(SO,Cl).COCl. [73°]. Prisms (from ether). When reduced by zinc-dust and H2SO, it yields C. II (SH). CO. H (Delisle, B. 22,

2205).

Amic acid C_uH₁(CO.NH₂)SO₃H. Crystals (containing aq), v. sol. alcohol and water. Got by the action of H₂S on C₂H₁(CONH₂).SO₃Ag aq, which is obtained by adding silver nitrate to C₀H₄(CONH₂).SO₃NH₄ prepared as above (Fahlberg a. Barge, B. 22, 760).

Amic acid C₈H₁(SO₂NH₂).CO₂H. Sulphamine-benzoic acid. Formed by boiling toluene o-sulphonic amide with K₃FeCy₆ and aqueous potash (Noyes, Am. 8, 178; cf. Fahlberg, Am. 1, 170). Slunder needles or prisms, v. sol. water, alcohol, and ether. Melts at 155° when slowly heated, and at 167° when quickly heated. At 180° it is completely converted into imide. Gives rise to the salts MgA', 6\[\]_40, BaA', 2\[\]_40, BaA', 2\[\]_40, BaA', 2\[\]_40, BaA', and Ag,C,H,NSO. By passing HCl into an alcoholic solution of the imide, the ether C,H,(SO,NH,),CO,Et (S3°) is formed. The methyl and propyl ethers have also been obtained and may be converted by aniline into $C_0H_1(SO_1NH_2)$.CONHPh [189°], by o-toluidine into $C_0H_1(SO_1NH_2)$.CONHC.H. [193°], and by means of p-toluidine into the isomeric p-toluide $C_0H_1(SO_2NH_2)$.CONHC.H. [202°].

Imide C.H. SO2>NII. Saccharin. [220°]

(Remsen a. Fahlberg, Am. 1, 432). Formed by oxidising CH₂C₂H₄.SO₂NH₂ with KMnO₄ in neutral solution (Remson a. Fahlberg, B. 12, 469; Remson a. Fahlberg a. List, B. 20, 1597; 21, 242; Remson a. Linn, Am. 11, 73). Elongated triangular plates (by sublimation), sl. sol. cold water, v. sol. alcohol sudimation), st. sol. cold water, v. sol. alcohol and ether. Has a very sweet taste (500 times that of cane sugar). The solubility of commercial saccharin is given by Gravill (Ph. [8] 18, 337) as S. (water) 2 at 15°; 6 at 100°; S. (alcohol) 5·4 at 15°; S. (ether) 1·3 at 15°. According to Stift (B. C. 18, 458) and Aducco and Mosso (C. C. 1887, 1148) it retards digestion, and is autisentic. The imide is converted into and is antiseptic. The imide is converted into and is antisepile. The initial is obtained with $C_0H_1(SO_2NH_2),CO_2H$ on evaporation with $KOHA_0$. Conc. hydrochloric acid at 150° forms $C_0H_1(SO_2NH_1),CO_2H$. The imide gives rise to salts of the form $C_0H_1 < \frac{SO_2}{CO} > NAg$, of which the following have been described.-KA' aq: prisms, v. sol. water .- NaA' 2aq : tables .-

BaA', 1\frac{1}{2}aq.—BaA', 4aq (Noyes, Am. 8, 180).—AgA': needles (from hot water). To detect 'saccharin,' a suspected liquid may be acidified. extracted with ether, the ether evaporated, the residue fused with NaOH, and the product tested for salicylic acid and for sulphate (C. Schmitt. Fr. 27, 396; Allen, An. 13, 105; Börnstein, Fr. 27, 165). 'Saccharin' evaporated to dryness on a water-bath leaves a residue which, when warmed with alcoholic potash, exhibits yellow, blue, and red colours (Lindo, C. N. 58, 51, 155).

Methylimide $C_0H_1 < \frac{SO_2}{CO} > NMe$. [132°].

Formed by heating $C_eH_4 < SO_2 > NAg$ with MeI at 100° (Brackett, Am. 9, 406). Long flat needles, sol. ether, alcohol, and hot water.

 $C_{\alpha}H_{4} <_{\rm CO}^{\rm SO_{2}} > NEt.$ Ethylimide [97°].

Needles (from water). Converted by boiling alcoholic potash into C₀H₁(SO₂NHEt).CO₂H [116°], which yields C₀H₁(SO₂NKEt).CO₂K crystallising in nacreous scales, Na₂C₂H₂NSO₁, CuA'₂ 2aq, and AgA' (Fahlberg a. List, B. 20, 1596).

Propylimide C, H, SO, NPr. [60°-70°]. m-Sulpho-benzoic acid

[1:3]C,H,(SO,H).CO,H.

11:3)_C, R₄(SO₃H). OO₂H.

Formation.—1. By mixing benzoic acid (2 pts.) with SO₃ (1 pt.) (Mitscherlich, P. 31, 287; 32, 227; Barth, A. 148, 33).—2. By heating BzCl with Ag₂SO₄ at 150° (Kämmerer a. Carius, A. 131, 153; B. 4, 219).—3. By heating BzCl with H₂SO₄ (Oppenheim, B. 3, 735).—4. By the action to a character of SO₂ are discovered. action of an alcoholic solution of SO2 on m-diazobenzoic acid (Wiesinger a. Vollbrecht, B. 10, 1715).—5. By oxidation of *m*-sulpho-benzoic aldehyde with air at 95° (Kafka, B. 24, 796).

Properties.—Deliquescent crystalline mass. Yields m-oxy-benzoic acid when fused with

potasb.

potash.

Salts.—NaHA" 2aq: triclinic crystals.—
Na_A"Me_SO_4 (Stengel, A. 218, 260). Crystals.—
Na_A"Et_sO_4: v. sol. water.—KHA" 2\(\frac{1}{2}\)aq.—
KHA" 3aq (Otto, A. 122, 155).—BaA" 3aq: v. sol. water (Fehling, A. 27, 322).—BaH_A" 2aq.
White monoclinic prisms. S. 5 at 20° (M.).—
BaA"Me_SO_4.—BaA"Me_SO_4 3\(\frac{1}{2}\)aq. S. 34 at 21°.
—BaA"Et_sO_3 3\(\frac{1}{2}\)aq. S. 31 at 21°. Formed from the acid NaHSO. -BaA'Et,SQ, 3,3aq. S. 31 at 21°. Formed from the acid, NaHSO,, and alcohol (Stengel). Long needles.—BaA''Tr,SQ, 7aq. S. 11 at 19°.—PbA''2aq: stellate groups of white needles.—PbA''Et,SQ, 2,3aq.—CuA''Me,SQ, 2,3aq. Crystals.—CuA''Et,SQ, 2,3aq.—AgHA'': nodules (Limpricht a. Uslar, A. 106, 50).—Ag,A''aq: small yellowish prisms.

Mono-ethyl ether EtHA". Formed by the action of alcoholic NH, on Et, A" or on the chloride (Limpricht a. Uslar, A. 102, 252). The free acid is unstable.—EtNH,A": four-sided triclinic tables (Keferstein, A. 106, 385).—
NaEtA"xaq. — Ba(EtA")₂xaq: efflorescent tables.

Ethyl ether Et,A". Formed from the chloride and alcohol. Syrup, miscible with water. Saponified by heating with water. Semi-chloride C.H.SO.Ol. Formed by

heating the acid (1 mol.) with PCl_s (1 mol.) (L. a. S.). Formed also by leaving the chloride C.H. (SO, Cl) (COCl) in contact with water for several weeks. Crystalline powder, sol. ether. Converted by hot water into the acid.

Chlorids C.H.(SO.Cl).COCl. Formed by heating the acid (1 mol.) with PCl, (2 mols.) at 100°. Thick oil, slowly decomposed by water. Yields C.H.(Cl.COCl on distillation and on heating with PCl, at 150° (Kämmerer a. Carius, A. 131, 159).

Benzoyl derivative $C_{11}\Pi_{10}SO_{g}$. The first product of the action of BzCl (2 mols.) on Ag SO, (1 mol.) (K. a. C.). Amorphous, sol. ether. Resolved by water into benzoic and sul-

phobenzoic acids.

Amic acid CaH, (SO2NH2).CO2H. nhamine-benzoic acid. [235° uncor.] (R. a. P.); [247°] (N. a. W.). Formed by the action of conc. KOHAq at 100° on the amide (Limpricht a. Uslar, A. 106, 27). Prepared by oxidation of [1:3] C_aH₁Me.SO₂NH₂ with alkaline KMnO₄, with chromic acid mixture (Remsen a. Palmer, Am. 4, 143), or with alkaline K, FeCy, (Noyes a. Walker, Am. 8, 188). Scales (from water), sl. Yanker, Ans. 6, 188). Scales (from water), st. sol. cold water, v. sol. alcohol. Converted by PCl, at 150°-200° into the oily chloride C₆H₄(SO₂NH₂)COCl. — BaA'₂ 4aq. — AgA' aq. — Ag₂C, H₂NSO₄: amorphous pp., sol. hot water.— EtA'. Monoclinic crystals, sl. sol. hot water.

Amide C₈H₄(SO₂NH₂)(CONH₂). Formed from the chloride and conc. NII, Aq. Small anhydrous crystals (from alcohol) or needles (containing aq). V. sol, hot water and alcohol. PCl₂ at 100° forms C₂H₄(SO₂NH₂)CCl:NH, which is decomposed by distillation into mchloro-benzonitrile, SO, and NH, ; and by treatment with NH, Aq into C, H, (SO, NH,).CN [152°] (Wallach a. Huth, B. 9, 428).

Anilide C. H₄(SO₂NHPh).CONHPh.

Formed from the chloride and aniline. Small crystals (from alcohol).

Isomeride of the amic acid

C, H, C(NH2): N.SO, H. Benzamidine v-sulphonic acid. [247°]. Mol. w. 200 (obs.). Formed by passing SO, into cold benzonitrile (Engelhardt, J. pr. 75, 363; Eitner, B. 25, 471). Prisms and rhombohedra. Converted by HClAq into benzamidine sulphate. - CaA'2. - BaA'2 4aq.

Amorphous isomeride of the

acid. A product of the action of PCl₃ on the amic acid (L. a. U.). Insol. water, alcohol, and ether. Forms amorphous salts. Water at 180° reconverts it into the ordinary amic acid.—
BaA'₂4aq: brittle mass.
p.Sulpho-benzoic acid

[1:4] C_aH₄(SO₃H).CO₃H, [c. 200°]. Formed, in small quantity, together with the m- isomeride, by the action of SO₂ on benzoic acid (Remson, A. 178, 275; Z. [2] 7, 81, 199). Formed also by oxidation of toluene p-sulphonic acid with KMnO₄ (Hart, Am. 1, 342), and by the action of an alcoholic solution of SO₂ on diazotised p-amido-large in the contract of Windows P. 100, 2715. benzoic acid (Wiesinger, B. 10, 1715). Needles, not deliquescent, decomposed by heat. Potashfusion converts it into p-oxy-benzoic acid. The K salt heated with potassium formate yields terephthalic acid.

Salts.—NaHA" 21 aq. Stellate groups of prisms, m. sol. cold water.—BaA"2aq: groups of needles, m. sol. cold water.—BaH₂A"₂ 3aq:

flat needles, v. sl. sol. cold water.

Amic acid C.H.(SO.NH.).CO.H. [c. 280°].

Formed by exidation of C.H.Me.SO.NH. and of

p-sulpho-cinnamic amide (Remsen, A. 178, 299; Fahlberg, Am. 1, 170; Palmer, Am. 4, 164; Noyes, Am. 7, 145; 8, 182). Flat prisms (from water), sl. sol. hot water, v. sol. alcohol. composed on fusion.—NH,A': needles or long lamine, v. sol. water.—BaA', 5aq.—AgA': v. sl. sol. hot water.—C₄H₄(SO₂NHAg).CO₂Ag: v. sol. hot water.—EtA'. [111°].

Di-sulpho-benzoic acid $C_1H_0S_2O_8$ i.e. $C_0H_3(SO_3H)_2CO_2H$ [4:2:1]. [above 28501 C_aH_a(SO₄H)₂CO₂H [4:2:1]. [above 285°]. Formed by oxidation of toluene disulphonic acid with chromic acid mixture (Blomstrand a. Hakansson, B. 5, 1088; Brunner, Sitz. W. [2] 78, 665) and by digesting $C_aH_a(SO_aNH_a) < SO_a > NH$ with HClAq at 160° (Fahlberg, Am. 2, 190). Large crystals (from HClAq), sol. cold water,

insol. alcohol and ether. Yields (4,2,1)-di-oxy-

hiso. alcoho and center. Theos (a,z,1)-di-oxybenzoic acid on fusion with potash.

Salts.—K₃A" 2aq: prisms, v. c. sol. water.—

K₁IIA"aq: large crystals, sl. sol. water.—

Ba₃A"₂7aq.—Cu₃A"₂7aq: minute crystals.

Amic acid C₂I₄(SO₄II)(SO₂NI₂).CO₂H

[2:4:1]. [165°]. Formed by boiling the imide of the amic acid with dilute HClAq for five hours. Large crystals, v. e. sol. water, sl. sol. HClAq, insol. ether.—HKA": crystals (from dilute HClAq), v. e. sol. water.

Di-amic acid C_aH₃(SO₂NH₂)₂CO₂H. [183°]. Formed by heating C_aH₃Mc(SO₂NH₂)₂ with aqueous potassium permanganate and by evaporating C₆H₄(SO₂NII₂)<SO₂>NII with KOHAq (Fahlberg, Am. 2, 186; B. 21, 246). Minute sating needles, v. e. sol. water and alcohol, sl. sol, ether. Tastes acid. Decomposes completely at 250°-260°. Its salts are crystalline. Those of alkalis and alkaline earths are v. sol. water. - BaA'25aq: monoclinic prisms. - CuA', 2aq : pale-blue silky needles.—AgA': white needles.—EtA'. [200°]. Silky needles (from water).

Imide of the amic acid

 $C_{\nu}H_{\nu}(SO_{\nu}NH_{\nu})< SO_{\nu}>NH$. by warming CaH,(SO2NH2)2CO2Et with KOHAq (Fahlberg a. List, B. 20, 1603; 21, 242). Tables, sl. sol. cold water, v. e. sol. alcohol and ether .st. sol. cold water, v. sol. alcohol and coner.—
K.C.H.N.S.O.; deliquescent crystalline mass.—
(CaH.(SO,NH.):SCO₂:N):Ha 3 Jaq: crystals.—
Cu(O,H.N.S.O.), 4aq: minute blue needles.—
AgC.H.N.S.O.

S. Di sulpho-benzoic seid CaH.(SO,H), CO,H.

s-Di-sulpho-benzoic acid C.H. (SO₃H)₂.CO₃H. Formed by heating benzoic acid with H₂SO₄, SO₃, and P₂O₄ (Barth a. Senhofor, A. 159, 217). Hygroscopic prisms (containing xaq). Turns brown at 140°. Yields s-di-oxy-benzoic acid on fusion with potagh. The K salt forms isophthalic acid when fused with potassium formate.—K₄A''' 1½aq: needles.—BaHA'' 2aq: minute needles.—Ba₂A''', 7aq: white prisms.—Cu₂A'''₂ 8½aq.—Ag₂A''' 2aq: crystalline pp.
References.—Browo., Nitro-, Oxy-amido, and Oxy-Sulphobenzoic Acob.

Oxy-, Sulphobenzoic ac os. m-sulpho-benzoic aldehyde

C.H. (SO.H.). CHO. Sulphonic acid of bensoic aldehyde. Formed from benzoic aldehyde and fuming H.SO. below 50° (Wallach a. Wüsten, B. 16, 150; cf. Engelhardt, J. 1804, 350). The Na salt reacts with (a)-naphthylamine forming C_eH_{*}(SO₂Na).CH:NC₁₀H_{*}, and forms with sodium naphthionate C_eH_{*}(SO₂Na).CH:NC₁₂H_{*}.SO₂Na.

Yields m-sulpho-benzoic acid on oxidation .--MgA'₂ (dried at 170°).—BaA'₂ (dried at 170'). Nodules.

The salt C6H4(SO3Na).CH:NOH Oxim. crystallises in plates, v. e. sol. water, m. sol. alcohol (Kafka, B. 24, 791).

Phenyl-hydrazide. The salt CoH, (SO, Na). CH: N. NHPh crystallises in needles, sl. sol. cold water, v. sol. alcohol.

Di-phenyl-hydrazide.

The salt C₆H₄(SO₃Na).CH:N.NPh₂ crystallises

from water in plates.
SULPHOBENZOLIC ACID v. BENZENE SUL-

PHONIC ACID. SULPHO - BENZYL - SULPHAMIC C₆H₂.CH(SO₃H).NHSO₃H. The salt Na₂A" 3aq is formed from C₆H₂.CH:NOH and aqueous Na SO, (Pechmann, B. 20, 2541). It crystallises in needles and is decomposed by NaOHAq into

henzoic aldehyde, Na.SO,, and H(NII,)SO,,
(a).SULPHO-BUTYRIC ACID C, II, SO, i.e.
CH₂.CH₂.CH₂.CH(SO₂H).CO₂H. Formed from butyric acid and CISO,H; and also by the action of (NH₄)₂SO, on α-bromo-butyric acid (Hemilian, B. 6, 196, 562; A. 176, 1; Franchimont, R. T. C. 7, 27). Formed also from crotonic acid and KHSO, at 130° (Beilstein a. Wiegand, B. 18, 483). Syrup. The Ba salt is converted by PCl, into CH₃CH₂CHCl.COCl.—CaA" 2aq: PCl₃ into CH₃.CH₂.CHCl.COCl. — UaA 2aq: needles (from ether-alcohol), insol. alcohol. — BaA"2aq. S. 71 at 16°.—PbA"2aq. — CuA"4aq.

-ZnA" 5aq. -Ag,A": prisms, insol. alcohol.

a-Sulpho-isobutyric acid C,II,8O, i.e.
CMe,(SO,II),CO,H. Formed by the action of Cl.SO,OH on isobutyric acid and also by oxidation of C, H, N, SO, which is prepared by heating thio-urea with a-bromo-isobutyric acid (Andreasch, M. 8, 412).—Na₂H" ½aq.—BaA" 4aq.

Ammonium sulphite appears to convert a-bromo-isobutyric acid into an isomeride which yields BaC, H, SO, 2aq, crystallising in needles, v.

sol. water.

β-Sulpho-butyric acid CH, CH(SO,H).CH, CO.H. Formed β-chloro-butyric ether and (NII₁)₂SO₃ (II.). Got also by oxidising barium oxy-butane disul-phonate with chlorine-water (Haubner, M. 12, 547). Amorphous.—BaA" aq (H.).—BaC, H. SO, White amorphous mass, v. sol. water, almost insol. alcohol. Yields acetic acid by potashfusion.

Sulphodibutyric acid v. DI-PROPYL SULPHONE

 $\begin{array}{ccc} \textbf{DICARBOXYLIG ACID.} \\ \textbf{SULPHOBUTYRIC} & \textbf{ALDEHYDE} & \textbf{C}_4\textbf{H}_8\textbf{SO}_4 \end{array}$ 6.6. CH, CH(SO, H).CH, CHO. Got by saturating a solution of crotonic aldehyde with SO. and distilling in vacuo, afterwards distilling with steam. On neutralisation of the residue with baryta the salt BaA'₂ is got (Haubner, M. 12, 546). The barium salt is converted by hydroxylamine into (CH(NOH).CH2.CHMe.SO3)2Ba, droxylamine into (CH(NOH).CH₂CHMe.SU₂)₂15, which is reduced by sodium amalgam to (CH₂(NH₂).CH₂CHMe.SO₂)₂Ba, which on distillation with lime yields butylamine and a little CH₂CH:CH.CH.NH₂. Sodium-amalgam reduces the sulpho-butyric aldehyde to oxy-butane sulphonic acid CH₂CH(SO₂H).CH₂CH₂OH, whence NaA', which when distilled with lime gives a minimum of butil and actual alcohols. mixture of butyl and crotyl alcohols.
SULPHOCAMPHORIC ACID v. CAMPHORIC

SULPHOCAMPHYLIC ACID v. CAMPHORIC ACID.

SULPHO-CHLORO BENZOIC AAID

CHLORO-SULPHO-BENZOIC ACID.

o-SULPHO-GENDAMIC ACID.
o-SULPHO-GENDAMIC ACID.
C₈H₁(SO₃H).CH:CH.CO₂H. Formed, together with the p-isomeride, by the action of SO₃ or fuming H₂SO₄ on cinnamic acid (Marchand, J. pr. 16, 60; Herzog, J. pr. 29, 51; Rudneff, A. 173, 8). Prisms (containing 3aq), v. c. sol. water and obselved Violence acid acid acid. and alcohol. Yields m-oxy-benzoic acid on fusion with potash.—K,A": amorphous, v. sol. water.—KHA": groups of needles.—CaA" 1½aq.

-BaH_A", S. '45 at 20°.—BaA" 1½aq. S. 4.2 at 16°. - Ag.A".

m-Sulpho-cinnamic acid [1:3] C.H.(SO.H).CH:CH.CO.H. Formed from m-sulpho-benzoic aldehyde, NaOAc, and Ac.O (Kafka, B. 24, 791).—BaA": nodules, v. sol. water, sl. sol. alcohol.

p-Sulpho-cinnamic acid p-suppn-cannamic acta [1:4] C₈H₄(SO₃H).CH:CH.CO₂H. Formed as above. Monoclinic prisms (containing 5aq). Yields p-oxy-benzoic acid by potash-fusion.— K₂A" ½ aq. Nodules (from alcohol). Reduces KMnO₄ in the cold (Liebermann, B. 22, 782).— CaA" ½ aq.—BaA" 3aq.—S. (of BaA") ·12 at 20°.—BaA" aq.—S. ·4 at 18°.—CuA" 6aq: greenish-prismus yeel water. prisms, v. sol. water.

C.H.(SO,NH,).CH:CH.CONH, Amide[218°]. Needles, v. sol. hot water (Palmer, Am. 4, 163).

Amic acid C_aH₁(SO₂NH₂).CH:CH.CO₂H.
S. 058 at 21°. Formed by heating the amide with NaOIIAq. Needles (from water), sol. alcohol, sl. sol. ether. Decomposes at 250°. Yields CaA'₂ aq and BaA'₂ 2aq, both crystallising in needles.

needles.

SULPHO-CUMINIC ACID C₁₀H₁₂SO, i.e.

C₆H₄Pr(SO,H).CO₂H [4:3:1]. [160°]. Formed
by sulphonating cuminic acid (Widman, B. 22,
2276). Crystalline.—BaA" aq: sl. sol. water.—
BaH₂A"₂ 4'₃nq. Prisms, m. sol. water.

Chloride C₆H₄Pr(SO,Cl).COCl. [56°].

Amide C₆H₄Pr(SO,NH₂).CONH₂. [225°].

Tables, sol. hot water.

Tables, sol. hot water.

Amic acid C,H,Pr(SO,NH,).CO,H. [246° cor.]. Formed by heating the amide with KOHAq at 100°. Formed also by oxidising (B)-cymene sulphonic amide [148°] with chromic acid mixture, an isomeric change taking place (Remsen a. Day, Am. 5, 158). Needles, sol. hot water. Yields BaA', 3aq, v. e. sol. water.

Sulpho-n-cuminic acid C₆H₃Pr(SO₃H).CO₂H [4:3:1]. Formed by sulphonation of n-cuminic acid (W.). V. sol. alcohol,

Chloride C₆H₃Pr(SO₂t), COOH₂. [203°].

Table (tree set) Tables (from water).

Amic acid C.H.,Pr(SO,NH.).CO.H. [216° cor.]. Formed from the amide (W.), and also boty. Foliation of p-di-n-propyl-benzene sulphonic amide [103°] (Remsen, Am. 5, 158). Long needles (from water).—CaA'₂ 6aq.—CuHA'₁ 2aq. Long -AgA': flocculent pp.

Sulpho-cuminic acid. Amic acid

C₆HMe₂(SO₂NH₂).CO₂H [5:3:2:x:1]. Formed by oxidation of isodurene sulphonic amide by alkaline KMnO, (Jacobsen, B. 15, 1855). The K salt is amorphous.

Sulpho-cuminic acid. Amic acid C.HMe.(SO,NH2).CO,H [6:4:2:x:1]. Formed by oxidation of the corresponding isodurene sulphonic amide (J.). The K salt is crystalline.

Reference.—Oxy-sulpho-cuminic acid.

SULPHO-CYANIC ACLD v. vol. ii. p. 303.

SULPHOCYANO-ACETIC ACID C.H. NSO. i.e. Cy.S.CH2.CO2H. Formed from potassium sulphocyanide and sodium chloro-acetate (Claesson, B. 10, 1347). Thick oil, changing to a solid polymeride when heated.—NaA aq: prisms. Converted by AgNO₂ into HS.CH₂.CO₂Na. CuSO₄ Gonversed by Agrica metric 15.512,002,1a. cabout forms, after a time, a black pp. of cuprous thioglycollate. — KA' aq. — BaA'2 4aq: tables. — BaA'2 aq: prisms.—CaA'2 2aq.—MnA'2 2aq. —Ethyl ether EtA'. (225°). S.G. 1:174. Formed by boiling chloro-acetic ether with potas-

sium sulphocyanide (Heintz, A. 136, 223). Liquid. Yields thioglycollic acid and thioglycollic ether on distillation with phosphoric acid. Polymerised by repeated distillation, many other products being formed at the same time. Boiling dilute HClAq forms NH2.CO.S.CH2.CO2H MeA' [75°-80°] and CaA' 2aq, and is resolved by heat into cyanic and thioglycollic acids (Nencki, J. pr. [2] 16, 11). Et lat 120° forms ethyl sulphocyanide and iodo-acetic acid.

Isoamyl ether C₃H₁₁A'. (255°).

Amide CH₂(S.CN).CONH₄. Needles.

Polymeride (C₃H₃SNO₂)₃. [200°]. Formed from potassium sulphocyanurate and potassium sulphocyanurate and potassium chloro-acetate (Claesson, J. pr. [2] 33, 121; B. 14, 732). Needles, sol. alcohol and ether. Decomposed by HClAq at 100° into thioglycollic acid and cyanuric acid.—Ba,A'', aaq: small prisms, nearly insol. water.—BaHA''' 2aq: large prisms.—Et,A'''. [81°]. Formed by distilling sulphocyano-acctic ether. Needles, nearly insol. hot water.

Persulphocyano-diacetic acid

C₂N₂S(S.CH₂.CO₂H)₂. [177°]. Formed from sodium chloro-acetate, iso-persulphocyanic acid, and KOHAq (Klason, J. pr. [2] 38, 381). Plates.

—BaA" 3aq.—CaA" 3¦aq.—ZnA" aq.—CdA".—
CuA" 6aq.—Et_A". Öil.

Amide. [125"]. Prisms.

SULPHOCYANO-ACETIC ALDEHYDE

 $CH_2(SCy).COH.$ [below -20°]. S.G. 12 1.47. Formed by heating iodo-acetic aldehyde with AgSCy and ether (Chautard, A. Ch. [6] 16, 193; C. R. 106, 1169). Oil, miscible with alcohol Decomposed by distillation, by and other. treatment with Cl, and by HClAq. HNO, forms acetic acid, sulphocyano-acetic acid, and thiocarbimido-acetic acid [128°]. Resinified by alkalis.

SULPHOCYANO-ACETONE C.H. NSO i.e. CH, CO.CH, SCy. S.G. 2 1.2; 20 1.18. S. 7 at 15°. Formed from chloro-acetone and barium sulphocyanide (Tschnerniac, C. R. 96, 587; B. 16, 349; 25, 2607, 2623). Liquid, v. e. sol. ether, v. sl. sol. ligroin. Decomposed by heat. Dissolves in aqueous KHSO₃. Boiling dilute Dissolves in aqueous KHSO. Boiling dilute HCIAq converts it into oxy-methyl-thiazole. Ammonium sulphocyanide forms 'propimine sulphocyanide' CH,-C(NH).CH,SCy '42°] (231°), which yields B'₂H,PtCl_{*}, B'HNO_{*} [183°], B'H,SO, 2aq, B'HSCy [115°], B'MeI [160°], and CH,-C(NAc).CH,SCy [134°].

Oxim CH, C(NOH).CH, SCy. [135°]. Yellowish prisms (Arapides, A. 249, 18). Produces great irritation on the skin.

SULPHOCYANO-ACETOPHENONE v. PHEN. ACYL SULPHOCYANIDE

SULPHOCYANO-BARBITURIC ACID

C₅H₃N₅SO₃ i.e. CO ${\stackrel{\rm N\,II.CO}{\rm N\,H.CO}}$ CH.SCy. Formed from di-bromo-barbiturio acid and alcoholic KSCy in the cold (Trzeinski, B. 16, 1058). The free acid splits up into thiodialuric acid and other products. Hot KOHAq also forms thiodialuricacid.—NH, A'. -KA'; tables (from water).

-AgA': crystalline pp.

-Y-SULPHOCYANO-BUTYRICACID. Nitrile. CH₂(SCy).CH₂CH₂CN. (c. 195° at 40 mm.). Formed by boiling potassium sulphocyanide (1 pt.) with γ -chloro-butyronitrile (1 pt.) and alcohol (Gabriel, B. 23, 2190). Liquid. Partially decomposed by distillation under atmo-

sandy decomposed by distinguish thinds atmospheric pressure. Converted by cone. H₂SO₄ into S_{*}(CH_{**},CH_{**},CO.NH_{**}),

a *SULPHOCYANO - ISOBUTYRIC ALDE HYDE CMc₂(SCy).CHO. S.G. ²³ 1*63. Formed from a independent price of the superior of the from a-iodo-isobutyric aldehyde and AgSCy (Chautard, A. Ch. [6] 16, 198). • Liquid with nauscous odour, decomposed by heat, by acids. and by alkalis.

SULPHOCYANO - ETHANE - SULPHONIC ACID C₃H₃NS₂O₃ i.e. CH₂(SCy).CH₂SO₃H. Formed from CH₂(SCy).CH₂Cl and aqueous Na₂SO₃ in sunlight (James, J. pr. [2] 26, 381). SULPHOCYANO-FORMIC ETHER

CyS.CO, Et. The compound (CyS.CO, Et) EtOH is got by mixing chloro-formic ether with ammonium sulphocyanide and alcohol (Delitsch, J. pr. [2] 10, 118; cf. Henry, J. pr. [2] 9, 464). It crystallises in prisms [41°], insol. water, v. e. sol. alcohol. Alcoholic potash forms Callin KSNO erystallising from alcohol in plates. KOHAq forms KSCy, alcohol, and K.CO... SULPHOCYANO-HEPTOIC ALDEHYDE.

Formed from iodo-heptoic aldehyde and AgSCy in ether (Chautard, A. Ch. [6] 16, 198). Yellowish liquid with fætid odour. Decomposed by heat, by acids, and by alkalis.

 β - SULPHOCYANO - PROPIONIC HYDE CH2(SCy).CH2.CHO. Formed by treating β -iodo-propionic aldehyde dissolved in ether with AgSCy (Chautard, A. Ch. [6] 16, 197). Liquid with fatid odour. Decomposed by heat, and resinified by alkalis and by mineral acids.

ω.SULPHOCYANO-TOLUIC ACID. Nitrile. CH₂(SCy).C.H.,CN. [86°]. Formed from c-cyanobenzyl chloride and KSCy in alcohol (Gabriel a. Day, B. 23, 2179). Needles. Converted by conc. HClAq at 180° into thiophthalide C.H.SO [57°]. Conc. H₂SO₄ at 30°-70° forms eyano-benzyl-mercaptan C₄H.NS [62°].

SULPHOCYANO-ISOVALERIC ALDEHYDE. Formed from iodo-isovaleric aldehyde and AgSCy in ether (Chautard, A. Ch. [6] 16, 198). Liquid, with fætid odour, easily decomposed by heat, by HClAq, and by alkalis.

SULPHO-DURIDE v. DI-DURYL SULPHONE. SULPHO-ETHYL-BENZOIC ACID. Amic acid C.H., NSO, i.e. C.H.Et(SO,NH.).CO.H. [262° cor.]. Formed by oxidising the sulphonic amide of p-di-ethyl-benzene with CrO, (Remsen s. Noyes, Am. 4, 202). Needles.—Bah' Baq.

SULPHO-FUMARIC ACID C,H,SO, i.e. CO₂H.CH:C(SO₃H).CO₂H. Formed by the action of Br or of HNO₃ on the salts of (δ)-bromo-(β)-sulpho-pyromucio acid (Hill a. Palmer, Am. 10, 409).—Ba, A''', 2xaq: v. sl. sol. water.— Ag₈A''' xaq.

SULPHO-HIPPURIC ACID C,H,NSO, i.e. C,H,(SO,H).CO.NH.CH,.CO.H. Formed from hippuric acid and SO, (Schwanert, A. 112, 59). Amorphous, deliquescent mass. Converted by nitrous acid into sulpho-benzoic acid.-BaA" aq: needles -- Pb. OA"

SULPHO-ISATIC ACID v. ISATIC ACID.

SULPHO-TRIMELLITIC ACID C.H.SO, i.e. $C_0H_1(SO_3H)(CO_2H)_3[5:4:2:1]$. Formed, together with the amic acid $C_0H_1(SO_2NH_2)(CO_2H)_3$, by oxidation of $C_0H_2Me(SO_2NH_2)(CO_2H)_2$ [2:5:4:1] by KMnO₄ (Jacobsen a. H. Meyer, B. 16, 192).— KH, A' Baq: prisms, m. sol. cold water. Potashfusion yields oxy-trimellitic acid.

SULPHO-TRIMESIC ACID. C₈H₇NSO₈ i.e. C₀H₂(SO₂NH₂)(CO₂H)₃. [x:5:3:1]. Formed by oxidation of the amic acid of o- or p-sulpho-mesitylenic acid (Jacobsen, A. 2006, 203).—KH₂A" 2aq: crystalline mass, m. sol. cold water. Conc. HClAq at 210° forms NH₃, H₂SO₃, and trimesic acid. Potash-fusion gives

oxytrimesic acid.

a-SULPHO-MESITYLENIC ACID C.H. SO. i.e. C_oH_.Me_a(SO_aH).CO₂H. Formed, together with a (β)-isomeride which yields CaA' 4aq, by which a (5)-isomerine which yields oak and, by the action of SO₂ on mostlylenic acid (Remsen a. Brown, Am. 3, 218). Yields o-oxy-mesitylenic acid on fusion with potash. By successive treatment with PCl, and NH₃ it is converted into an amide [288°].—Cah" 4aq. Less solwater than the salt of the (β) -isomeride.

Sulpho-mesitylenic acid. Amic acid. C_vH₁₁NSO₄ i.e. C_vH₂Mc₂(SO₂NH₂).CO₂II [5:3:6:1]. [262° cor.]. Formed, together with the (5,3,4,1)-isomeride, by oxidising mesitylene sulphonic amid with abrowing acid mixture or alkalim. amide with chromic acid mixture or alkaline KMnO₄ (Hall a. Remsen, Am. 2, 131; B. 10, 1040; Jacobsen, B. 12, 604; A. 206, 167). Short prisms (from water), sl. sol. hot water, sol. alcohol and ether. Decomposed by heating with conc. HClAq at 200° into H₂SO₄ and mesitylenic acid. Soda-fusion forms mesitylenic acid and m-xylene sulphonic amide [137°].-CaA', 6aq: long flat plates.—CaA', 5aq.—BaA', 8aq. S. 3·3 at 0°; 14 at 21°.—CuA', 4aq: blue needles.—CuA', 3aq.—AgA': pp.

Sulpho-mesitylenic acid. Amic acid C_eH₂Me₂(SO₂NH₂).CO₂H [5:3:4:1]. [276⁵ cor.]. Formed as above (J.). Long needles, v. sol. alcohol and ether, more sol. hot water than its isomeride. Conc. HClAq at 200° forms mesitylenic acid. Soda-fusion gives oxy-mesitylenic acid.—BaA'₂ 2aq. S. 2·05 at 0°.—CaA'₂ 2aq: prisms.—CuA', aq: blue monoclinic prisms. SULPHO.DI.METHYL.BENZOIC ACID.

Amic acid C,H,, NSO, i.e. C,H,Me,(SO,NH,).CO,H[4:2:5:1]. [268°]. Formed by oxidation of the sulphonic amide of ψ -cumene (Jacobsen a. Meyer, B. 16, 190). Long needles (from water). Yields di-methyl-benzoic acid on

(from water). Trents al-methyl-nenzois aud on heating with conc. HClAq at 210°.—KA'aq.

Sulpho-di-methyl-henzoic scid. [180°-190°].

Amic acid C₄H₂Me₂(S₀2NH₂).Oc₂H [1:2:5:3].

(a) - Sulphamine - hemimellitic acid. [238°].

Formed, together with the more soluble (\$\beta\$):so

meride, by oxidising the sulphonic amide of hemimellithene with alkaline KMnO, (Jacobsen, B. 19, 2519). Needles, sl. sol. cold water. HClAq at 150° forms sulpho-di-methyl-benzoic acid and, finally, hemimellitic acid [144° Potash-fusion yields an oxy-hemimellitic acid. -BaA', 5aq: small tables, m. sol, water.

Sulpho-di-methyl-benzoic acid. Amic acid $C_6H_2Me_2(SO_2NH_2)$ $CO_2H[1:3:5:2]$. [174°]. Formed as above. Stellate groups of minute needles. Converted by heating with HClAq into a very soluble sulphonic acid, and finally into m-xylene. Potash-fusion gives an easily soluble oxyhemimellitic acid.—BaA'₂4aq: needles.

Isomeride v. Sulpho-Mesitylenic acid. SULPHO-METHYL-TEREPHTHALIC ACID. A mic acid $C_aH_aMe(SO_aNH_a)(CO_aH)_a$ [2:5:4:1]. [295°-300°]. Formed by oxidation of ψ -cumene sulphonic amide by alkaline KMnO, (Jacobsen a. H. Meyer, B. 16, 190). Small needles (from water).—BaA" 2, aq: stellate groups of prisms.

SULPHONAMIDE v. Sulphamide, p. 567; and IMIDO-SULPHONAMIDE v. SULPHIMIDO-AMIDE,

SULPHONAMIDES. Amides of sulphonic acids. They contain the group SO, NH, attached by S to carbon.

SULPHONAMIDO- compounds v. Amic acids derived from Sulpho- compounds.

SULPHO-NAPHTHALENE-AZO- compounds v. Azo- compounds.

(' α')-SULPHO-(α)-NAPHTHOIC ACID

 $C_{11}H_8SO_3$ i.e. $C_{10}H_4(SO_4H).CO_2H.$ [235°]. Formed, together with the (β) - and (γ) - isomerides, by warming (a)-naphthoic acid with fuming H₂SO, at 70° (Battershall, A. 168, 119; Stumpf, A. 188, 1). Prisms, v. sol. water. Not deliquescent. Yields (a)-oxy-naphthoic acid by potash fusion. — K₂A" 2aq. — CaA" 3aq. — BaA" 4aq. Monoclinic crystals, sl. sol. water.
—BaH₂A"₂ 2aq: prisms, more sol. than BaA".

(β)-Sulpho-(α)-naphthoic acid. [218³-222°]. Crystalline mass, v. e. sol. water.—BaA" 3½aq:

needles, m. sol. water.—BaH₂Λ"₂ 4aq. (γ)-Sulpho-(α)-naphthoic acid. [182°-185°].

(γ)-suipno-(a)-naphthoic acid. [182"-185"], Needles, v. sol. water.—K,A".—BaA" 1½nq: m. sol. water.—BaH_AA", aq: almost insol. cold Aq. Sulpho-(a)-naphthoic acid. Nitrile C₁₀H_aCy,SO₂H. Formed by sulphonating (a)-naphthonitrile (Dutt, B. 16, 1251; Armstrong a. Williamson, C. J. Proc. 3, 43).—BaA'₂6aq: glistening plates.—KA' 3aq: prisms. Chloride of the nitrile C₁₀H_aCy,SO₂Cl. Prisms sol hangen.

Prisms, sol. benzene.
('a')-Sulpho-(β)-naphthoic acid. Formed, together with the ('8')-isomeride, by sulphonating (β)-naphthoic acid (B.; S.). Crystalline.—BaA" aq.—BaA" ω̄laq.—BaH₂A"₂ 6 laq. ('β')-Sulpho-(β)-naphthoic acid.—BaA" 2aq.

Less sol, water than the acid salt.

Reference .- OXY-SULPHO-NAPHTHOIC ACID. SULPHO- NAPHTHYL ETHYL DI-THIO-CARBONATE. The salt SO, K.C., H., S.CS.OEt, formed from potassium xanthate and diazotised naphthonic acid, crystallises from water in colourless plates, converted by boiling dilute alcoholic potash into S₂(C₁₀H₀:SO₃K)₂ (Leuckart, J. pr. [2] 41, 218). The corresponding salt from (8) naphthylumine (9) sulphylic acid swrttlings. (β)-naphthylamine (β)-sulphonic acid crystallines in small plates.

SULPHO · (B) · WAPHTHYL - PHOSPHORIC ACID SO₂H.C.₁₀H₄.O.PO(OH)₂. Formed, together with the anhydride O(PO(OH).C.₁₀H₄.SO₃H)₂, by heating potassium (B)-naphthol sulphonate (1 mol.) with PCl₂ (2 mols.) at 100° (Claus a. Zimmermann, B. 14, 1482). Decomposed by boiling alkalis into phosphate and (B)-naphthol sulphonate. The Ba salt is a white powder, sl. sol. water.

SULPHONES. Compounds of the form R.SO, R' where R and R' are attached by means of C to S. They may be formed from the corresponding sulphides and sulphoxides by oxidation with KMnO₄ (Beckmann, J. pr. [2] 17, 475). Aromatic sulphones can be prepared by the action of AlCl, on a mixture of a sulphonic chloride and an aromatic hydrocarbon (Beckurts a. Otto, B. 11, 472, 2066), and by heating a sulphonic acid with a hydrocarbon and P.O. at 200° (Michael a. Adair, B. 10, 583). Sulphones are often formed by the action of sulphuric acid on aromatic hydrocarbons. The sulphones are volatile, and are not reduced by nascent hydrogen. They are not attacked by PCl, or KMnO,. Chlorine in daylight converts di-phenyl-sulphone into chloro-benzene (1 mol.) and C₆H₂,SO₂Cl, while in sunlight it yields chloro-benzene (2 mols.) and SO₂Cl₂. Disulphones CHR(SO₂R')₂ are not attacked by alcoholic potash at 140°, while disulphones of the form R'.SO, CH2.CH2.SO, R' are converted by alcoholic potash into a sulphinic acid and an oxy-sulphone (Otto a. Rösspnnine acid and an oxy-sulphone (Otto & Nossing, B. 20, 185). The disulphones CMe.(SO_Et)_(sulphonal), CHMe(SO_Me). CHEt(SO_Et)_2 (Etg(SO_Me)_2, CMeEt(SO_Et)_2 (trional), and CEt_4(SO_Et)_2 (tetronal) are powerful hypnotics (Baumann a. Kast, H. 14, 52).

SULPHONIC ACIDS (organic). Acids con-

taining the group SO. OH united to C by S. Fatty sulphonic acids may be formed by the action of silver sulphite on alkyl iodides, the resulting ether being saponitied. Fatty sulphonic acids may also be got by boiling alkyl icdides with K.SO₃ or (NII.).SO₃Aq for a long time. Both fatty and aromatic sulphonic acids may be got. by oxidation of the corresponding mercaptans, sulphides, and sulphocyanides. The sulphonic acids of fatty acids and alcohols are formed by the action of SO₃ or ClSO₃H on fatty acids and of SO₃ on alcohols; SO₃H taking the α-position (Hemilian, A. 176, 1). Aromatic compounds readily yield sulphonic acids on treatment with SO3, with H2SO4, or with ClSO3H. As a rule not more than two SO, H groups enter a benzene nucleus. Aromatic sulphonic acids may also be obtained by the action of SO, on diazo- com-pounds. On adding NaCl to the product of sulphonation of aromatic compounds, the Na salt of the sulphonic acid frequently separates in crystalline form (Gattermann, B. 24, 2121). Nitric acid does not attack fatty sulphonic acids, while usually it nitrates aromatic sulphonic acids, although it sometimes displaces SO,H by NO. PCl, forms sulphonic chlorides which are reduced by zinc and dilute H2SO, to mercaptans. Aromatic sulphonic acids are partially converted into the corresponding amido- compounds by fusion with NaNH. In this way benzene sulphonic acid yields 15 p.c. of aniline (Jackson a. Wing, Am. 9, 75). Aromatic sulphonic acids are decomposed by superheated steam at 200°-

210° into the hydrocarbon and H.SO. (Kelbe, B. 19, 92). Hydrolysis may also be effected by passing superheated steam into a solution of the sulphonic acid containing H.SO. or H.PO. (Armstrong; Friedel a. Crafts, C. R. 109, 95). Aromatic sulphonic acids when fused with potash yield K.SO. and phenols. Fusion with KCN or K.FeCy. yields the corresponding nitriles. Fusion with sodium formate displaces SO. H by CO. H.

SULPHONIC ACIDS AND DERIVATIVES. Several inorganic acids, and derivatives of these acids, will be described here, most of which are regarded as derived from SO₂.OH.OH by replacing one OH by a monovalent radicle -- such as Cl, F, or NH₂—or as derived from SO₂.OH.H by replacing H by a monovalent radicle. A few sulphonic acids must be formulated as derived from 2(SO,,OH,OH), or 2(SO,,OH,II), by replacing 2OH, or 2H, by a divalent radicle; and one as derived from 3(SO, OH.OH), or 3(SO, OH.H), by replacing 30H, or 3H, by a trivalent radicle (v. supra). The sulphonic acids, therefore, are all looked on as compounds of the monovalent radicle SO₂OH. The term sulphonic is also frequently applied to organic acids containing this radicle; but in this dictionary such acids are described as sulpho-acids, e.g. sulpho-benzoic acid C.H.(SO.,OII)CO.H. The compositions of the sulphonic acids are expressed by the formulæ R'SO₂.OH, R'(SO₂.OH)₂, and R''(SO₂.OH)₃, where R' = NH₂,Cl,F,NO₂,NH.OH, or N(NO.OH); $R^{11} = NH$, or N.OH; and $R^{111} - N$.

AMIDOSULPHONIC ACID AND SALTS NH₂(SO₂,OH) and NH₂(SO₂,OM). These compounds are described in the article Sulphamo acid and Sulphamates (q.v. p. 567).

CHLOROSULPHONIC ACID AND SALTS CI(SO, OH) and CI(SO, OM). The acid has also been called chlorhydrosulphurous acid, monochlorosulphuric acid, sulphuric chlorhydrate or hydrochloride, sulphuric chlorhydrin, and sulphuryl hydroxyl chloride.

Chlorosulphonic acid Cl(SO,OH).

Formation.—1. By the direct union of SO₄ and HCl (Williamson, Pr. 7, 11; Baumstark, A. 140, 75; Williams, C. J. [2] 7, 804; Dewar a. Cranston, C. N. 20, 174; Michaelis, J. Z. 6, 235, 292).—2. By the reaction of PCl., POCl., or PCl., with cone. H.SO, (Müller, B. 6, 227; Geuther, B. 5, 925; Thorpe, C. J. 37, 358).—3. By distilling fuming H.SO, with P.O. in a current of HCl (Müller, Lc.).—4. By the reaction of HCl with crystallised fuming H.SO, (Beckurts a. Otto, B. 11, 2058).—5. By the action of Cl, S₂Cl., or S₂O₂Cl., with cone. H₂SO₄; or of Cl with moist SO₂ in presence of Pt at a red heat. 6. By warming S₂O₂Cl₂ with water (Billitz a. Heumann, B. 10, 602).

Preparation.—1. Three parts of the most conc. H₂SO₄ (preferably the residue from preparing SO₃) are warmed in a long-necked flask, and two parts PCl₃ are added little by little; when HCl ceases to be given off the contents of the flask are fractionated, the part boiling between c. 152²-156⁹ being believed apart.—2. Very conc. oil of vitriol, 200 parts, is mixed with POCl₃, 226 parts, the mixture is gently heated and then distilled [2(SO₂OH.OH) + POCl₃ = 2(Cl.SO₂OH) + HPO₃ + HCl] (Thorpe, Lc.).—

3. A mixture of P2O, and fuming H2SO, is distilled in a current of HCl, and the product is fractionated; this method removes all traces of P chlorides (Müller, l.c.) .- 4. Commercial crystalline fuming H2SO4 (approximately pure H₂S₂O₃).is placed in a retort connected with a good condenser, dry HCl gas is passed in so long as absorption occurs, the liquid is distilled, and the product fractionated; the yield is very satisfactory (Beckurts a. Otto, B. 11, 2058).

Properties .- A colourless liquid, furning much in air, and having a powerful, penetrating odour. S.G. $\frac{0^{\circ}}{4^{\circ}} = 1.78474$ (Thorpe, C. J. 37, 358); Michaelis (J. Z. 6, 235, 292) gives 1.776 at 18°. Boils at 15:3° at 760 mm. pressure (T., l.c.; v. also M., l.c.; Clausnitzor, B. 11, 2008; Beckurts a. Otto, l.c.; Behrend, B. 8, 1004). Ogier (C. R. 96, 616) gives H.F. [SO³ solid, HCl] = 14,400. Baumstark (A. 140, 75) found V.D. 59.3 (calc. = 58.12) (temp. is not given); Williams (C. J. [2] 7, 304) found V.D. at 216° to be 32.8; Heumann a. Köchlin (B. 16, 602) found V.D. 34.7 at 184° and 30.4 at 410°. The gas is therefore dissociated at a temperature not much above its b.-p. When CISO, OH is repeatedly heated above 158° it is partly resolved into SO Cl2; distilled, it gives SO₂Cl₂ (Williamson, C. J. 10, 97). By boiling the compound for a long time with an inverted condenser, Clausnitzer (B. 11, 2008) obtained H₂SO₄, SO₂, and Cl; Beckurts a. Otto (l.c.) heated ClSO₂OH for a long time in a sealed tube at c. 170°, and found that part remained unchanged, and that Cl and SO₂ were produced. Heumann a. Köchlin (l.c.) think that the decomposition at c. 440 is represented as follows: 2(ClSO₂OH) = $SO_2 + SO_3 + Cl_2 + H_2O$; they regard the high value obtained by Baumstark for the V.D. as due to presence of S₂O₅Cl₂ (v. also Claesson, J. pr. [2] 19, 235).

Reactions .- 1. Action of heat, v. supra. Propertics.—2. Water produces HClAq and H_SO₄Aq.
3. Hydrogen sulphide reacts at ordinary temperatures, forming HCl, S₂Cl₂, S, and H_SO₄ (Prinz, A. 223, 371).—4. Carbon distulphide, at 100°, produces HCl, SO., S, and COS. -5. Phosphorus pentoxide or pentachloride produce S20, Cl2 C. R. 96, 1146).—6. Heating with silver nitrate torms AgCl and NO. SO. OH (Thorpe, C. J. 41, 297) .- 7. Fusion with potassium sulphate forms K.S.O, and HCl; heating with sodium chloride forms HCl and Cl.SO. ONa (Müller, B. 6, 227).

8. The reactions of ClSO₂.OH, with several elements were examined by Heumann a. Köchlin (B. 15, 416).

Chlorosulphonates. The salts of Cl.SO.OH. which reacts as a monobasic acid, are formed by the reaction of the acid with metallic chlorides. It is very difficult to obtain these salts pure. When heated they form sulphates, giving off SO, and Cl; with water they decompose to chlorides and acid sulphates; and with alcohol HCl and salts of Et.H.SO, are formed (Müller, B. 6, 227). No accurate description of any salts has yet been given.

SO₂.Cl SO₂.Cl CHLOROSULPHONIC ANHYDRIDE SULPHUR OXY-

Pyrosulphuryl chloride, under SHLORIDES, p. 618.

FLUOSULPHONIC ACID AND SALTS F.SO2.OH and F.SO2.OM. Only the acid has been isolated.

Fluosulphonic acid F.SO, OH. Isolated and examined by Thorpe a. Kirman (C. J. 61, 921 [1892]). Prepared by placing pure SO, in a Pt vessel, surrounded by ice and CaCl. (for description of apparatus v. Thorpe a. Hambly, C. J. 55, 163), leading in excess of pure HF (made by heating KHF2), and removing excess of HF by passing in a stream of dry CO₂ for many hours, the liquid being kept at 25°-35°. A thin, colourthe liquid being kept at 25°-35°. A thin, colour-less liquid, with a slightly pungent smell, and fuming in air; boils at 162.6°, a little being decomposed with formation of H₂SO₄, and probably also SO₂F₂. Reacts rapidly with Pb, forming PbSO₄ and PbF₂; slowly attacks glass. Reacts violently, and sometimes explosively, with

water, forming H.SO.Aq and HFAq.
IMIDOSULPHONIC ACID AND SALTS NH(SO₂OH)₂, NH(SO₂OM)₂, and NM(SO₂OM)₂. By passing dry NH, into SO₃, H. Rose (P. 32, 81; 47, 41; 49, 183 [1834-40]) obtained two compounds, which he named sulphatammon and parasulphatammon, and to both of which he assigned the composition 2NH₃.SO₃. These compounds were examined by Jacquelain (A. Ch. [3] 8, 293 [1843]), Woronin (J. R. 3, 273 [1859]) and others; in 1875 Berglund (Lunds Universitets Arsskrift, 12 and 13; Bl. [2] 25, 455; 29, 422) showed that Rose's parasulphatanimon was diammonium imidosulphonate NH(SO2ONH4)2 and that sulphatammon was probably the triammonium salt N.NII₄(SO₂ONH₄)₂. Berglund's conclusions were confirmed, partly by Raschig (A. 241, 161 [1887]), and Mente (A. 248, 232 [1888], and partly by Divers a. Haga (C. J. 61, 943 [1892]). A full discussion of the constitution of Rose's compounds, with reference to the work of other chemists and an historical summary of researches on the imidosulphonates, will be found in the memoir by D. a. II

Imidosulphonic acid NH(SO2.OH)2Aq. This acid is known only in solution, which is obtained by suspending lead imidosulphonate in water, decomposing by a stream of H,S, and rapidly filtering from PbS. The solution gives a pp. with excess of BaOAq, soluble in HNO₂Aq; and a pp. of NH(SO₂OK)₂ with K.C₂H₂O₂Aq. The acid solution is very unstable, soon becoming changed to NH₂(SO₂OH)₂Aq and H₂SO₂Aq. (Jacquelain, l.c.; Fremy, A. Ch. [3] 15, 408; D. a. H., l.c. p. 945).

Imidosulphonates. The normal salts are of the types NH(SO₂.OM)₂ and NM(SO₂.OM)₂; besides these many basic salts have been isolated. The di-alkali imidosulphonates are prepared by mixing solutions of alkali nitrites and sulphites, dissolving the pp. which forms in water, heating this solution for some time, allowing to crystallise, and then boiling the nitrilosulphonate, N(SO₂OM), thus obtained (v. p. 601, NITRILO-SULPHONATES) with acidified water (for instance N(SO₂OK), + H₂O = NH(SO₂OK)₂ + KHSO₄);

also by heating the alkali amidosulphonates (e.g. 2(NH₂SO₂OK) = NH(SO₂OK)₂+NH₃); the diammonium salt NH(SO₂ONH₃)₂ is also obtained by the reaction of NH₃ with SO₃, CISO₂OH, SO₂O₂, or S₂O₂O₁. Most of the other di-salts are obtained by double decomposition from the alkali salts. The tri-salts

are generally prepared by dissolving the di-salts in excess of an aqueous solution of the base and crystallising. A number of mixed salts, such as N(NH₄)(SO_xO)_xBa, have been prepared, generally by double decomposition. Basic salts, chiefly of such slightly positive metals as Pb or Hg, have also been isolated. For references v. Divers a. Haga (C. J. 61, 943). The di-alkali salts give off NH_s, N, and SO₂ when heated; water reacts to form amidosulphonates amidosulphonates NH₂(SO₂OM)₂ and sulphates.
The chief imidosulphonates are those of NH₂

Ba, Ca, Hg, Pb, K, Ag, and Na; basic salts of Pb and Hg are known; mixed salts containing NH and Na, NH, and Ba, Ba and Hg, Ba and Na, Ca and Na, Hg and K, and Ag and Na have been isolated; some of the imidosulphonates also form double compounds with KNO3 and NaNO3. Full accounts of the preparation and reactions of the chief imidosulphonates are given in the memoir

of D. a. H.

NITRILOSULPHONIC ACID AND SALTS N(SO,OII), and N(SO,OM). The acid has not been isolated, and only a few salts are known.

Potassium nitrilosulphonate N(SO, OK), Solutions of K2SO3 and KNO2 are mixed in the ratio 4K2SO3:KNO2; after crystallisation occurs the mixture is heated at 100° till the crystals dissolve, a little water is added, and heating at 100° is continued for a little; on cooling the salt crystallises in well-formed crystals with The water of crystallisation is removed at 100°-110°; at a higher temperature decomposition occurs to K2SO4, (NH1)2SO4, SO4, and SO₂. The salt may be crystallised from dilute KOHAq; it is decomposed by water at 40° to

NH(SO₂.OK), and KHSO₄. Claus prepared this salt in 1871 (B. 4, 186), giving it the formula NH2(SO3K)3 and the name potassium trisulphammonate; Raschig (B. 20, 584 [1887]) showed that the salt was probably N(SO2.OK)3, and this composition was confirmed both by the earlier work of Berglund (B. 9, 252, 1896 [1876]) and by the more recent work of Divers a. Haga (C. J. 61, 943).

For description of a salt NO(SO₃K), v. Raschig (A. 241, 225); this is the trisulphooxyazotate of Claus and Raschig. R. regards it

as $(SO_2.OK)_3N < {\atop O} > N(SO_2.OK)_3$.

Sodium nitrilosulphonate N(SO2.ONa)3. Formed by passing SO, into a solution of NaNO, and Na₂CO₃ (in the ratio 2NaNO,:3Na₂CO₃. 10aq) until the solution is feebly acid to litmus (v. D. a. H., l.c.).

NITROSULPHONIC ACID NO2(SO2.OH), AND DERIVATIVES. The acid and its potassium salt have been isolated. The anhydride SO₂(NO₂).O.(NO₂)SO₂, the chloride NO₂(SO₂.Cl), and an oxy-anhydride S2O5O(NO2)2 have also been obtained.

Nitrosulphonic acid NO₂(SO₂.OH). (Nitrosylsulphuric acid SO₂.OH.O(NO). Lead chamber crystals. Nitrosyl hydrogen sulphate NO.H.SO.) This acid is produced by the reaction be-Name of the reaction between H₂SO₄ and any oxide of nitrogen except N₂O (Henry, P. 7, 135; A. Rose, P. 50, 161; Reibling, J. 1861. 152; Kuhlmann, 4. Ch. [3] 1, 116; Sestini, Bl. [2] 10, 226). It is also formed in the leaden chambers in making H₂SO₄ (first observed by Clement a. Desormes,

A. Ch. [2] 59, 329). The acid is produced by A. Ch. [2] 59, 529. Ine acta is produced by the reaction of SO₂ with NO or NO₂ in presence of water (Davy); also by burning 1 part S mixed with 2.5-3 parts KNO₂ in moist air (Girard a. Pabst, Bl. [2] 30, 531; Reinsch, N. J. P. 12, 3). The acid is best prepared by leading No, into well-cooled fuming H.SO, till the whole solidifies, and then drying over H.SO, (Weber, J. pr. 85, 425; 100, 37; Tilden, C. J. 28, 630); or by adding NO, in excess to conc. H.SO, washing the crystals with liquid NO,, and drying in a stream of dry air at 20°-30° or in vacuo (Müller, A. 122,

1; Gaultier de Claubry, P. 20, 467).
Colourless rhombic plates, melting at 73° (Tilden, l.c., gives m.p. 85°-87°), and easily remaining liquid below this temperature (Weltzien, A. 115, 213; De la Provostaye, A. Ch. [2] 73, On melting in air the anhydride (S2O5(NO.)2) is formed, and the water given off (S₂O₃(NO₃)₂) is formed, and the water given on causes decomposition of part of the acid to H₂SO, and oxages of N (Michaelis a. Schumann, B. 7, 1075; Fremy, C. R. 70, 61). With dry and C reacts to give NaHSO, and NOCl; on heating for a little HCl is given off (Tilden, l.c.). Dissolves unchanged in H.SO₄ (Döbereiner, S. 8, 239; cf. Lunge, B. 12, 1058; 21, 67). SO₂ is without action on dry NO2(SO,OH), but in presence of water, or H2SO4Aq with S.G. less than 1.55, decomposition occurs with formation of H₂SO₄, N₂O₃, and other oxides of N, according to Lunge (l.c.).

Potassium nitrosulphonate NO2(SO2.OK) seems to be obtained by the reaction of SO, on KNO2, also by adding liquid SO2 to dry KNO2; the salt cannot be prepared by neutralising the acid by KOHAq. The salt is decomposed by water (Schultz-Sellack, B. 4, 113).

Nitrosulphonic anhydride

S.O.(NO.). $[O < \frac{SO.(NO.)}{SO.(NO.)}]$. Formed by heating NO.(SO.OH) (Michaelis a. Schumann, B. 7, 1075); also by the reaction of SO. with NO in absence of O and moisture (H. Rose, P. 47, 605; Brüning, A. 98, 377); also by adding liquid NO to liquid SO, without warming (De la Provostaye, A. Ch. [2] 73, 362); by passing electric sparks through a dry mixture of N, O, and SO, or of S vapour and N.O. or NO (Morren, A. Ch. [4] 4, 293; Chevrier, C. R. 69, 136). Hard, regular plates; S.G. 2·14; melts at 217°; may be distilled unchanged at c. 360°. Decomposed by water to NO, H.SO₄Aq, and HNO₄Aq. NO₂(SO₂OII) crystallises from a solution in

OXYNITROSULPHONIC ANHYDRIDE

 $S_2O_2O(NO_2)_2$ $\left[O < SO_2(NO_2) \atop SO_2(O(NO_2))\right]$. A white, fusible, crystalline solid; formed by leading vapour of NO₂ into SO₃ till saturated. Gives S₂O₃(NO₂)₂ when heated (Weber, P. 123, 333; cf. Thorpe, C. J. 41, 297).

Nitrosulphonic chloride NO2(SO2-Cl). (Nitrosulphuryl chloride.) A white, crystalline solid; formed by the action of SO, on NOCl in absence of moisture, also by the reaction of AgNO, with SOCl₂ (Thorpe, C. J. 41, 297); dissolves unchanged in funing H₂SO₄; dissolves in conc. H₂SO₄, giving off HCl, and forming Cl(SO₂OH) on heating; decomposed by moist air or by water, giving HClAq, H₂SO₄Aq, HNO₂Aq, and NO (Weber, l.c.).

NITROSO-OXY-AMIDOSULPHONIC ACID AND SALTS N(NO.OH)(SO, OH). (Nitrosohydroxylamine sulphonic acid nyaroxyummne supponta acta N(NO)(SO₂OH)OH. Dinitroso-sulphuric acid SO(NO)₂(OH)₂ or (SO₂OH)₂(NO)₂H.) The acid has not been isolated, but the NH₄, Ba, Pb, K, and Na salts are known. These salts are de-

scribed as Nitrososulphates under SULPHATES,

p. 581.

OXY-AMIDOSULPHONIC ACID (Hydroxylamine SALTS NH(OH)(SO2.OH). sulphonic acid [Raschig]. Sulphydroxylamic acid [Claus]. Sulphazidic acid [Fremy].) The K salt of the acid is obtained by the action of water on N(OH)(SO₂.OK)₂ (v. Oxy-IMIDOSUL-PHONIC AGID AND SALTS, infra). The acid itself is known only in aqueous solutions. Two Ba salts, a K salt, and a Na salt have been isolated. The alts have been investigated by Fremy (A. Ch. [8] 15, 408), Claus a. Koch (A. 152, 336; 158, 52, 194), Raschig (A. 241, 161), and Divers a. Haga (C. J. 55, 760).

Oxy-amidosulphonic acid NH(OH)(SO...OH)Aq. An aqueous solution of this acid (the acid has not been isolated) is this acid (the acid has not been isolated) is prepared by heating an aqueous solution of N(OH)(SO₂OK)₂ (v. infra) to boiling (whereby NH(OH)(SO₂OK)Aq, H₂SO₄Aq, and KHSO₄Aq are formed), neutralising by NH₂Aq, adding BaCl₄Aq, filtering off BaSO₁, adding BaOAq to ppt. Ba(N(OH)SO₂O)₂Ba.H₂O, washing this pp., adding enough H₂SO₄Aq to ppt. half the Ba in the salt as BaSO₄, filtering, and so getting a solution of the (soluble) salt (NH(OH)SO₂O₂O₃D.Ba. solution of the (soluble) salt (NH(OH)SO...O).Ba. On now heating this solution with an equivalent quantity of H.SO,Aq (the Ba in solution must be estimated) and filtering, a solution of the acid is obtained (Fromy, modified by D. a. H.). The solution of NH(OH)(SO.OH) is fairly stable, but slowly decomposes; in presence of hot acid the decomposition is more rapid, giving 2NH2OH.H2SO4Aq and H2SO4Aq (Raschig, confirmed by D. a. H.). Oxy-amidosulphonates. The normal salts

Oxy-amidosulphonates. The normal salts are of the form NH(OH)(SO₂OM¹) and (NH(OH)SO₂O)M¹, where M¹=K or Na, and M¹=Ba; there is also a dibarium salt Ba\(\text{N(OH)}.SO₂O\)Ba.H₂O. The salts are best obtained from the solution of the soluble salt (NH(OH).SO₂O).Ba.H₂O (v. supra) by adding the equivalent quantity of a sulphate. The dibarium salt is itself prepared as described under the acid (supra); the monobarium salt is btained by decomposing the di-salt by enough H₂SO₄Aq to ppt. half the Ba, filtering, and evaporating over H₂SO₄ (D. a. H.). The oxyamidosulphonates are fairly stable; they are decomposed by heating with acid into hydroxylamine sulphate and H₂SO₂Aq; caustic alkalis produce only sulphite and hyponitrites (the latter rapidly undergo further change, giving off N₂O) (D. a. H., l.c.; v. also C. J. 61, 988 note). Basic oxides, such as CuO and Ag₂O, in presence of alkali produce sulphite, sulphate, and N₂O and at the same time the basic oxide is reduced

(D. a. H., l.c., p. 770).
Raschig's sulphasinate (A. 241, 197)
(SO₂.OK)N(OH).O.(OK)N.(SO₂.OK) may be derived from 2NH(OH)(SO, OH) by replacing 2H

OXY-IMIDOSULPHONIC ACID SALTS N(OH)(SO₂OH)₂. (Hydroxylamine disulphonic acid N(SO₂OH)₃OH (Raschig). Disulphydroxy-azic acid (Claus).) Only the potassium salt has been isolated.

Potassium oxy-imidosulphonate

N(OH)(SO, OK), 2aq (Claus, A. 158, 83; Raschig, B. 20, 584; cf. Divers a. Haga, C. J. 51, 659). Prepared by passing a rapid stream of SO₂ through well cooled KNO₂Aq made strongly alkaline by KOHAq; allowing N(SO₂OK); (v. Nitrilosulphonates, p. 601) to crystallise out, pouring off, and allowing to stand. Large, lustrous crystals; almost insol. cold water, more sol. water at 40°-60°; heated with water gives KHSO₄Aq and NH(OH)(SO₂.OK)Aq (v. supra, Oxy-AMIDOSULPHONIC ACID). Three Na salts and several other oxy-imidosulphonates have been prepared by D. a. H. (C. J. Proc. 1893-4. 61).

The salts described by Fremy (l.c.) as sulph-The saits described by Fremy (i.e., as such-azotates, and further examined by Raschig (A. 241, 211), and formulated by him as N(OH)(SO₂.OK)₂.N(OM)(SO₂.OK)₂, where M = K or Na, and N(OK)(SO₂.OK)₂.N(OK)(SO₂.OK)₂. may be regarded as derived from oxy-imidosul-

phonic acid N(OH)(SO...OH).

The oxysulphazotate of Claus (sulphazilinate of Fremy) examined by Raschig (i.c., p. 223) and formulated by him as

 $(SO_2.OK)_2N < O > N(SO_2.OK)_2$, may be looked on as derived from oxy-imidosulphonic acid by the removal of 2H from 2N(OH)(SO₂.OH)₂... M. M. P. M.

SULPHONO-DI-ACETIC ACID v. DI-METHYL

SULPHONE DICARBOXYLIC ACID SULPHONO-DI-BUTYRIC ACID

SO₂(CHEt.CO₂H)₂. [152°]. Formed by oxidation of sulphido-dibutyric acid (5 g.) in neutral solution by KMnO, (5 g.) in water (500 g.). Its ether is got from SO_{*}(CH_{**}CO_{*}Et)_{**}, Na, and EtI (Lovén, J. pr. [2] 33, 104). Octahedra. Sulphono-di-isobutyric acid

SO₂(CMe₂.CO₂H)₂. [182°-186°]. Formed by oxidising S(CMe₂.CO₂H)₂ (Lovén). Plates.— BaA" 2½aq. Groups of needles (from hot water). SULPHONO DIPROPIONIC ACID v. Di-

ETHYL-SULPHONE DICARBOXYLIC ACID. SULPHONO-DI-ISOVALERIC ACID

SO.(C,H,,CO,H). Formed by oxidation of S(C,H,,CO,H), and by the action of PrI (2 mols.) on sulphono-di-acetic ether (1 mol.) and NaOEt (2 mols.) at 120°; the product being saponified by baryta (Lovén, J. pr. [2] 33, 114).—BaA" 7aq. SULPHO-OXY-BENZOIC ACID v. Oxy-

SULPHO-BENZOIC ACID.

SULPHO-PHENYL-ACETIC ACID C,H,SO, e. CHPh(SO₃H).CO₂H. Formed by saponifying the product of the action of K2SO3Aq on a-bromothe product of the action of K.SO.4q on a-bromophenyl-acetic ether (Papilsky, J. 1880, 856). Very deliquescent mass.—Salts: K.A".—CaA".

—BaA": plates, m. sol. hot water.—ZnA".—ChPh.(SO.NH.).CO.Et. Tables, v. sol. water.—CHPh.(SO.NH.).CO.Et. Tables, v. sol. water.—CHPh.(SO.NH.).CO.Et. Tables, v. sol. water.—CHPh.(SO.4K.).CO.Et. thin plates, v. e. sol. Ag. SULPHO-PHENYL-AMIDO-ACETIC ACID. SH. NSO. aq i.e. SO.H.C.H.,NH.CH. CO.H. [185°]. Formed by heating phenol (1 pt.) with hippuric acid (1 pt.) and H.SO.4 (3 pts.) at 140° (Zehenter, M. 5, 332; 6, 528). Monoclinic prisms (containing aq); a:bx=98:1:128. Sol.

prisms (containing aq); a:b:c = 93:1:1-28. Sol.

water and alcohol. Coloured violet by FeCl3. Decomposed by HCIAq at 140° into phenol, glycocoll, and H.SO,. Aqua regia gives $C_0H_2(OH)Ol(NO_2)_2$ [1:2:3:5].—BaH.A''₂ aq.— AgHA" Saq: concentric groups of needles

p-SULPHO-PHENYL-CARBAMIC ACID The acid ether C_eH_{*}(SO_sH).NH.CO_sMe [188°] is formed by dissolving methyl phenyl-carbamate in fuming H_{*}SO_{*} (Hentschel, B. 18, 979) and also by adding NaOH to a cooled mixture of CICO₂Me and aqueous p-amido-benzene sulphonic acid (Noelting, Bl. [2] 50, 622).

SULPHO-PHENYL-GLYCOCOLL v. SULPHO-

PHENYL-AMIDO-ACETIC ACID.

m-SULPHO-PHENYL-PROPIONIC ACID C.H.SO. i.e. C₆H₄(SO₃H).CH₂.CH₃.CO₃H₄ Formed by treating bromo-sulpho-phenyl-propionic acid with sodium-amalgam (Göring, C. C. 1877, 793, 808). Yields m-oxy-benzoic acid by potash fusion.

exo-Sulpho-phenyl-propionic acid C_aH_a.C₂H₃(SO₃H).CO₂H. Formed by boiling cinnamic acid with aqueous K2SO3 for 12 hours (Valet, A. 154,62). Cinnamic aldehyde is converted by K₂SO₃ into PhC₂H₃(SO₃K).CH(OH).SO₃K, which crystallises in needles (containing 2aq) and is converted by boiling dilute H.SO, into exo-sulpho-phenyl-propionic acid (Heusler, B. 24, 1805). Crystals, v. sol. water and alcohol. Converted by boiling conc. KOHAq into cinnamic acid. Not affected by boiling dilute II.SO₁.—
KHA". S. 4 at 15°.—K.A" xaq. Efflorescent crystals.— CaA" xaq. Plates.— BaA" aq.—
K₂ZnA".—Ag.A" aq: white crystalline pp.
SULPHO-PHENYL-THIO-CARBAMIC ACID.

Anhydride C,H,NS,O, i.e. C,H, <NH,CS [183°]. Formed from phenyl-thio-carbimide and SO₃ (Magatti, B. 11, 2267). Crystals (from benzene), insol. water, alcohol, and ether. Insol. acids and alkalis. Decomposed by water at 100° into H2S, CO2, and amido-benzene p-sulphonic acid.

SULPHO-PHLORETIC ACID C.H.SO. Formed from phloretic (oxy-phenyl-propionic), acid and SO, (Nachbaur, J. pr. 75, 45). Sour syrup. — Na,A" xaq. — BaA" 3aq. — MgA" 5aq. — CAA" 4aq. Crystalline.

c.SULPHO-PHTHALIC ACID

 $\mathbf{C_{\bullet}H_{\bullet}}(\mathbf{SO_{\bullet}H})(\mathbf{CO_{\circ}H})_{\circ}[3:2:1].$ (a)-Sulpho-phthalic Formed by oxidising naphthalene (a)-sulphonic amide by KMnO, (Remsen, Am. 5, 107), and got also, in small quantity, together with the (β) -acid, by the action of fuming H₂SO, on phthalic acid (Rée, C. J. 49, 514). Minute orystals, v. sol. water, m. sol. alcohol. Soda-fusion gives c-oxy-phthalic acid.—Ba,A'''₂ 8aq. Needles, sl. sol. hot water.—PbHA'''11aq.—Ag,KA'''2aq. Ppd. by adding AgNO, to a solu-tion of the K salt (Stokes, Am. 6, 280).

Amic acid C₄H₁NSO₄i.e.

C₅H₄(SO₂NH₂)(CO₂H)₂. [155°-160°]. Formed by oxidation of naphthalene (a) sulphonic applied by alkaline KMnO. Thick needles (containing aq). At 155° it splits up into H₂O and the anhydride. Conc. HClAq at 150° forms c-sulphophthalic acid.—KHA": slender needles, v. sl. sol. cold water.—K₂A". [300°]. Amorphous, v. e. sol. water. Vields, when heated, the compound $C_{e}H_{2}(COCl) < SO_{2} N.POCl_{2} [120^{\circ}-126^{\circ}]$ whence

MeOH produces $C_0H_1(CO_2Me) < \frac{SO_2}{C(OMe)} > NH$ [144°] (Stokes, Am. 6, 274).—PbA".—AgHA": needles.—AgA". Insol. hot water. Anhydride of the Amic Acid

C_eH_s(CO₂H) SO₂NH. Formed as above. Begins to sublime at 200°, but is not melted at 240°. Its silver salt C,H,AgNSO, is converted. by MeI into $C_0H_3(CO_2H) < SO_2 > NMe [191° cor.]$.

The compound C_aH_a(CO₂Me) < SO₂ NMe [180° cor.] has also been prepared.

i-Sulpho-phthalic acid CoH3(SO3H)(CO2H)2[4:2:1]. (B)-Sulpho-phthalic acid. (7)-Sulpho-phthalic acid. [140] (when hydrated). The chief product of the sulphonation of phthalic acid or anhydride at 100 - 2000 (Loew, A. 143, 257; Rée, B. 18, 1629). Formed also by oxidation of naphthalene (B)-sulphonic amide (Remsen, Am. 5, 110) and by the action of hot HNO, (S.G. 13) on potassium di-nitro-(a)-naphthol sulphonate (naphthol yellow S) (Graebe, B. 18, 1126; Rée, C. J. 49, 516). Crystalline (containing aq), very hygroscopic, v. sol. water and alcohol, insol. ether. At 180° it yields the anhydride C₈H₈SO₆. Soda-fusion forms i-oxyphthalic acid. The K salt fused with sodium formate yields trimellitic acid. Heated with resorcin it yields fluoresceïn sulphonic acid. PCl₅ forms C₆H₃(SO₂Cl)(CO₂H)₂ [170° $C_0H_3(SO_2CI)$ $C_{CCI_2}^{CO}$ > 0 and C_0H_3CI $C_{CCI_2}^{CO}$ > 0. The mono-chloride is converted by NH, into C.H.(SO.NH.)(CO.H). [192°-202°] which crystal-

lises in plates, sol. water, alcohol, and ethor.
Salts.—KH₂A''' 2aq. Needles, v. sol. water.
—K₂HA''' ²aq.—(NH₄).HA''' 1¹₂aq. At 200° it yields $C_0H_3(SO_3NH_4) < \stackrel{CO}{CO} > NH$ [c. 300°]. Crys. 4 tallising in monoclinic prisms. - Ba, A", 2aq. Ball, A''', 5aq. S. 5 at 15°; 50 at 100°. At 250° it yields Ba(C, H, SO,), BallA''' 2aq.

s-Sulpho-isophthalic acid C,H,(SO,H)(CO,H),[5:3:1]. $[258^{\circ}].$ by sulphonation of isophthalic acid (Aronstein a. Kramps, B. 13, 489; Lönnies, B. 13, 704). Long deliquescent needles (containing 2aq). Potash-fusion yields s-isophthalic acid. KH2A'" 3aq: long needles.—K3A'" xaq: prisms. -Ba₂A''₂8aq: needles, v. sol. water. i-Sulpho-isophthalic acid

 $C_8H_3(SO_3H)(CO_3H)_5[4:3:1].$ [244°]. Formed by oxidation of m-xylene (a) sulphonic acid (Jacobsen a. Lönnies, B.13, 1556), and by oxidation of C_aH₃Me(SO₂NH₂).CO₂H (Remsen a. Iles, Am. 1, 114; Remsen a. Coale, Am. 3, 206). Hygroscopic needles (containing 2aq), v. e. sol. water. Potashneedles (containing 2aq), v.e. sol. water. Potashfusion yields (a)-oxy-isophthalic acid.—Salts:
KH_A^M' 2aq: needles, sl. sol. cold water. S.
1-59 at 26°.—K_A^M'.—CaHA'' 4jaq. Crystals.—
BaHA'' 3aq: small needles. S. 073 at 23°.
—BaHA'' 4aq.—Ba_A^M'. 3aq.
Amic acid C,H,NSO, i.e.
C,H,(SO,NH,)(CO,H),. Formed by oxidation of
C,H,SO,NH,)(CO,H),. Leg. (Remsen, B.
11, 464; 12, 1436; Am. 1, 122; 3, 209). When
set free from its salts it changes at one to the.

set free from its salts it changes at once to the anhydride C_aH₂(CO₂H) < NH [284°], S. ·45

at 10°.—KHA" aq. S. 2·3 at 26°.— K_2A'' 4aq: v. e. sol. water.— Ca H_2A'' , 2aq.— CaA'' 5aq.—Ba H_2A'' , 2aq: monoclinic tables.—BaA'' 3aq.— $Ag_4C_8H_1$ NSO $_4$: crystalline pp. (Jacobsen, B. 12,

c-Sulpho-isophthalic acid. Amic acid C₆H₂(SO₂NH₂)(CO₂H)₂[2:3:1]. Formed by oxidation of the corresponding m-xylene sulphonic amide (Jacobsen, B. 11, 902). Its acid potassium salt is sl. sol. water.

a-SULPHO-PROPIONIC ACID C3H6SO, i.e. CH, CH(SO, H).CO, H. Formed by boiling a-chloro-propionyl chloride with aqueous ammonium sulphite and also by warming propionic acid with CISO₃H (Kurbatoff, B. 6, 563; A. 173, 5). Syrup, v. sol. water and alcohol.-K,A" aq: needles (Rosenthal, A. 233, 27).—(NH.), A" aq: prisms.—BaA" 2aq. S. (of BaA") 745 at 18°.
—CaA" 2aq.—CdA" 2aq.—Ag, A": small needles. Got also by mixing propionic anhydride with SO_8 (Franchimont, R. T. C. 7, 27).

B-Sulpho-propionic acid CH2(SO3H).CH2.CO3H. [68°]. Formed by boiling B-iodo-propionic acid with an aqueous solution of (NH₄)₂SO₃. Got also by the action of ammonia-cal AgNO₃ on the compound of acroleïn with NaHSO₃ (Rosenthal, A. 233, 15) and obtained likewise by the oxidation of thiohydantoic acid NH:C(NH).S.CH,.CH,.CO.H (Andreasch, M. 6, 838; 7, 169). Hygroscopic crystals, sol. water and alcohol. Decomposes at 150°. Successive

and alcohol. Decomposes at 150°. Successive treatment with PCl₂ and with tin and HClAq converts it into sulphydro-propionic acid.

Salts.— K₂A" aq.— KIIA" aq.—Na,A" aq.—(NH₄),A" 4aq. Hygroscopic.—HNH₄A".—BABA" 5aq.—BaH₂A"₂—SrA" 5aq.—CaA" 2½aq.—CaA" aq.—MgA" 4aq.—ZnA" 4aq.—CuAⁿ.—MnA" 4aq.—PbA".—CdA" aq.—Ag,A" ½aq.—HAAA" ½aq.—PhAA" 2aq.—PhAAA" 2aq.—PhAAA" 2aq.—PhAAA" 2aq.—PhAAA" 2aq.—PhAAA" 2aq.—PhAAA" 2aq.—PhAAA" 2aq.—PhAAAA" 2aq.—PhAAAA HAgA" 1 aq.

Ethyl ether Et,A". Liquid.

Sulpho-dipropionic acid is DI-ETHYL-SUL-PHONE DICARBOXYLIC ACID.

SULPHO-PROPYL-BENZOIC ACID v. SULPHO-CUMINIC ACID.

SULPHO-ISOPROPYL-SUCCINIC ACID

CMe2(SO3H).CH(CO2H).CH2.CO2H. Got by action of HNO₃ on sulphocamphylic acid (Königs a. Hoerlin, B. 26, 2044). When heated in vacuo at 170° it splits up into water, SO, and terebic acid. Tables (containing 3aq), v. a. sol.

SULPHO-PYROMUCIC ACID C.H.SO, i.e. CH:C(CO₂H) O. Formed by dissolving pyromucic acid in cold fuming H2SO4, and got also by the action of zinc-dust and ammonia on diby the action of since as and aminoma of the formo-sulpho-pyromuoic acid (Schwanert, A. 116, 268; Hill a. Palmer, B. 18, 2095; Am. 10, 373, 409). Deliquescent prisma.—K₂A"4aq.—KHA".—Na₂A"5aq.—NaHA"aq.—BaA"4aq. Small prisms. Yields fumaric acid when heated with excess of bromine.—Salts: BaH₂A"₂, 4aq.—

BaH₂A''₂ 6aq. - CaA'' 3aq. - PbA'' 2aq. - Ag₂A''.

A mide C₅H₂SO₄(NIL₂)₂ [213°]. Crystalline. (β)-Sulpho-pyromucic acid

C.H.O(SO.H)(CO.H). Formed by sulphonation of brome-pyromucic acid and debromination of st be product by zinc-dust and NH₂ (H. a. P.).—
Salts: K₂A"2½aq.—CaA"2aq.—BaH₂A"; 3aq.
—BaA"3aq.—BaA"aq: small concentric prisms.

SULPHO - PYROTARTARIC ACID C,H,SO. i.e. C3H3(SO2H)(CO2H)2. Formed by boiling k.s. c₃L₃(100₂L)(100₂L)₃. Formed by boiling ita-, citra-, and mesa- conic acids with aqueous K,SO, (Wieland, A. 157, 34). Crystalline, v. e. sol. water.—Ca₂A'''₂7aq. Sl. sol. cold water.—SULPHO-QUINOLINE CARBOXYLIC ACID

C,H,N(SO,H).CO,H. (a)-Sulpho-cinchoninic acid. Formed by heating cinchonic acid with SO₃ or with H₂SO₄ and P₂O₅ at 180° (Weidel a. Cobenzl, M. 1,844). Triclinic crystals (contain-

cinchoninic acid. Formed at the same time as the preceding acid (Weidel, M. 2, 565) and prepared by heating cinchoninio acid (1 pt.) with H₂SO₄ (7 pts.) at 300° (Von Georgievitch, M. 8, 639). The same acid (crystallising with aq) appears to be formed by oxidation of benzylidenelepidine sulphonic acid by alkaline KMnO, (Busch a. Koenigs, B. 23, 2683). Colourless needles (containing 2aq), v. sol. hot water. Very bitter. Potash-fusion yields (3)-oxy-cinchoninic acid.—(NII₁)HA'' 2aq.—BaA'' aq.—PbA'' 4aq.

SULPHO-SALICYLIC ACID v. Oxy-sulpho-

BENZOIC ACID.

SULPHO-SUCCINIC ACID C.H.SO. i.e.

CO,H.CH,CH(SO,H).CO,H. Formation.—1. By exposing cooled succinio acid to SO, vapour (Fehling, A. 38, 285; 49, 203).—2. By boiling fumaric and maleïc acids with aqueous K₂SO₃ (Credner, Z. [2] 6, 77; Strecker a. Messel, A. 157, 15; Z. [2] 6, 459, 671).-3. From succinyl chloride and Ag2SO4 (Carius a. Kümmerer, A. 131, 167). -4. By oxidation of thio-malic acid with HNO, (Carius, A.

Properties .- Deliquescent mass, v. e. sol. water, alcohol, and ether. Yields fumaric acid

water, alcohol, and other. Yields tumaric acid when fused with potash.

Salts.—K₃A'' aq: efflorescent crystals.—
K₃A''' 2 ½aq.—K₄A'' 1½aq. Crystals.—KH₂A'''.—
K₂A''' 2 ½aq.—K₄A'' 1½aq.—(NH₄),A''' aq.—(NH₄)H₂A''' aq.—(NH₄)H₂A''' aq.—(NH₄)H₂A''' aq. crystals.—Ba₂A'''₂ (dried at 100°).
Pp.—Ca₃A'''₂ 6aq.—Pb₂A'''₂ 4aq.—Pb₂A'''₂ 3aq.—
Pb₂OA'''₂—Pb₂OA'''₂—Ag₂A'': n. sol. water.

SULPHO-TEREPHTHALIC ACID C₈H₈SO,

i.e. $C_8H_3|SO_3H)|CO_3H|_2|2:4:1]$.

Formation.—1. By heating terephthalic acid with fuming H₃SO₄ at 250° (Ascher, A. 161, 2; Schoop, B. 14, 223).—2. By oxidation of sulphontoluic acid (Remsen a. Burney, Am. 2, 410; Weber B. 25, 17:40), of a vilence subposition of the supposition of the supp Weber, B. 25, 1740), of p-xylone sulphonic acid (Remsen a. Kuhara, Am. 2, 414), and of C_sH₂Me(SO₂NH₂).CO₂H (Hall a. Remsen, B. 12, 1432; Am. 2, 56).

Properties.—Hygroscopic needles or tables. Salts.—KH,A''' jaq. Needles (Remsen L. Approxes.— Aygroscopic needles of tables. Salts.—KH_A'" & qq. Needles (Remsen a. Keiser, Am. 5, 170).—KH_A'" aq (W.).—K_A'" aq.—BaHA'" aq.—CaHA'" ½ aq.—BaHA'" ¼ aq.—BaHA'" aq.—Ba_A'", 8aq.—BaH_A''', 5aq.—PbHA'' 2 aq.—Ag,HA'''.

Amic acid C_sH_s(SO,NH_s)(CO,H)_r. Formed by oxidising p-xylene sulphonic amide with alkaline K.FeCy. (Noves a. Walker Am. a all

line K.FeCy. (Noyes a. Walker, Am. 9, 94).

Consentric needles, sol. hot water. Not melted at 310°.—KHA" ½aq. —BaA" aq: nodules.

Imide C₈H₃(CO₂H) < CO NH. [284°] (W.); [299° cor.] (N. a. W.). Formed by oxidation of C₈H₃Me(SO₂NH₂),CO₂H by KMnO₄. Short thin prisms (from ether), in. sol. cold water. AgNO₃ gives a pp. insol. HNO₃.—KC₈H₄NSO₃ aq.—BaC₈H₃NSO₃ 3aq. Scales, v. sl. sol. water.—Ag₈C₈H₃NSO₃.
SULPHO-TOLUENE DICARBOXYLIC ACID.

**SULPHO-TOLUENE DICARBOXYLIC ACID.

*Amic acid C₈H₂Me(SO₂NH₂)(CO₂H)₂(1:4:3:5].

[c. 300°]. Formed by oxidation of ψ-cumene sulphonic amide (Jacobsen a. Meyer, B. 16, 190).

Needles, sol. water, alcohol, and ether. —

BaA" 2 jaq: small prisms, sl. sol. water.

SULPHO-o-TOLUIC ACID C₈H₄SO₅ i.e.

SULPHO-o-TOLUIC ACID C₈H₈SO₈ i.e. C₈H₈Me(SO₃H).CO₂H [2:3:1]. Formed by heating o-toluic acid with H_.SO₄ (5 pts.) for 3 hours at 160° (Jacobsen a. Wierss, B. 16, 1960). Crystalline, v. e. sol. water. Potash-fusion yields o-oxytoluic acid.

Sulpho-o-toluic acid. Amic acid

C₄H₁Me(SO₂NH₂).CO₄H [2:5:1]. [243°]. Formed, together with about an equal quantity of the (2,4,1)- isomeride, by oxidation of m-xylene o-sulphonic amide by alkaline KMnO₄ (Jacobsen, B. 14, 38). Long needles, sol. alcohol, ether, and water. Potash-fusion yields the corresponding oxy-toluic acid. Further oxidised by KMnO₄ to C.H.(SO.NH.)(CO.H).

C₄L₄(SO₂NH₂)(CO_.HI)₂.
Sulpho-o-toluic acid. Amic acid
C₄L₃Me(SO₂NH_.).CO_.H [2:4:1]. [217]. Formed as above. Long needles, sl. sol. cold water, v. sol. alcohol and ether.—KA': crystals.

s-Sulpho-m-toluic acid

C₂H₃Me(SO₃H).CO₂H [3:5:1]. Formed, together with the (3,4,1)- isomeride, by sulphonating m-toluic acid with fuming H₂SO₄ at 180° (Jacobson, B. 14, 2355).

Sulpho-m-toluic acid. Amic acid C₂H₁Me(SO₂NH₂).CO₂H [3:4:1]. [248⁻]. S. 2 at 15°. Formed by oxidation of m-xylene sulphonic amide (Remsen, Am. 1, 37; 3, 205; Jacobsen, B. 11, 895). Needles (from water), m. sol. alcohol, sl. sol. ether. Potash-fusion gives (4,3,1)-oxym-toluic acid. KMnO₁ yields sulpho-isophthalic acid.—CaA'₂1!aq: small concentric needles.— BaA'₂4aq.—BaA'₂5aq.—AgA': needles (from hot water).

Sulpho-m-toluic acid. Amic acid C_bH₂Me(SO₂NH₂).CO₂H [3:2:1]. [203°]. Formed by oxidation of the corresponding m-xylenc sulphonic amide [96°] (J.). Converted by potash-fusion into the corresponding oxy-toluic acid.

Sulpho-p-toluic acid $C_6H_3Me(SO_3H).CO_2H$ [4:3:1].

Formation. — 1. By oxidation of thio-carvacrol (Flesch, B. 6, 480; Bechler, J. pr. [2] 8, 170).—2. By oxidation of cymene sulphonic acid (Remsen, Am. 2, 411; R. Meyer a. Baur, A. 220, 18).—3. From p-toluic acid and SO, (Fischli, B. 12, 616).—4. By oxidation of p-xylene sulphonic acid (Remsen, Am. 8, 264). Needles (containing 2aq). Not hygroscopic. V. sol. water, insol. ether. Decomposes at 185°—190° without melting. Potash-fusion-gives oxyptoluic acid [204°]. Conc. HClAq at 190° forms p-toluic acid.

Salts. - KHA" 3aq. - KHA" 2aq.-

K,A"1 jaq. — MgA"8aq. — MgA"7aq. — BaA"8aq.—BaA"4aq.—PbA"aq.—PbA"8aq.—PbA"8aq.—PbA"8aq.—PbA"8jaq.—Ag,A"aq.

Amide C,H,Me(SO,NH.).CONH. jaq. [218°].

Amid & C.H., Me(SO,NH.). CONH., § aq. [218°].

Amid acid C., H., Me(SO,NH.). CO., H. [267°].

Formed by oxidation of dynene sulphonic amide and of p-xylene sulphonic amide by chromic acid mixture (Remsen a. Hall, Am. 2, 50; B. 11, 229; Noyes a. Walker, Am. 9, 98). Needles, sol. cold alcohol, insol. ether, sl. sol. cold water.—

BaA'_2 2aq. — CaA'_2 4aq. — MnA'_2 5aq: needles. Probably the same amic acid [242°] is formed by oxidising p-butyl-toluene sulphonic amide by KMnO_4 (Kelbe a. Baur, B. 16, 2505). Sl. sol. water, nearly insol. alcohol.

Sulpho-p-toluic acid C₆H₁Me(SO₃H).CO.H [4:2:1]. [182°] (W.); [190°] (F.). that by oxidising thio-thymol (Fittien, A. 172, 329) and by evaporating its imide with HClAq (Weber, B. 25, 1741). Crystals (containing 3aq).—NH.HA".—MgA".—Ag.A".

Anhydride C_eH₂Mo < CO SO₂ > O. [97°]. Got by treating the acid with AcCl.

Amic acid C₆H₃Me(SO₃H).CONH₂. [186°]. Prisms (containing aq).—NH₄A'. Got from the anhydride in benzene by the action of dry NH₃.—

AgA' aq: scales (from water).

A mic acid C₀H₃Me(SO₂NH₂).CO₂H. [185°].

Got by boiling the imide with water (Weber, B. 25, 1739). Yellowish crystals. Probably identical with the preceding amic acid.—BaA'₂2aq.—AgA'.—MeA'. [145°].—EtA'. [95°].

Imide C_aH₂Me ⟨SO₂⟩NII. Mcthyl-sac-charin. 1240°]. Got from p-toluidine sulphonic acid vid C_aH₄MeCy.SO₂H, C_aH₃Me(Cy.SO₂Cl, C_aH₃MeCy.SO₃NH₂, C_aH₃Me(Cy.SO₂NH₂), C_aH₃Me(Cy.SO₂NH₂), the last body being heated (Kreis, G. P. 48,583; B. 22, Ref. 719; Weber, B. 25, 1737). Sl. sol. cold water, v. sol. alcohol, ether, and alkalis. Yields C_aH₃Me ⟨SO₂⟩NAg, whence MeI forms

 $C_cH_2Me < {SO_2 \over CO} > NMe~~[153^\circ],~~while~~EtI~~gives$ $C_cH_2Me < {SO_2 \over CO} > NEt~~[106^\circ]~(Weber).~~The imide is converted by warming with aqueous KOCl into <math>p$ -toluidine sulphonic acid.

Di-sulpho-o-toluic acid C_uH₂Me(SO₃H)₂CO₂H [2:3:5:1]. Formed by sulphonation of o-toluic acid with H₂SO₄ containing SO₂ (Jacobsen a. Wierss, B. 16, 1960). Minute needles, v. e. sol water.—×Ba₂Δ'''₂: amorphous, v. sol. water. Di-sulpho-p-toluic acid C_aH₂Me(SO₃H)₂CO₂H.

Di-sulpho p-toluic acid C.H.Me(SO.H).CO.H. Formed by heating p-toluic acid with fuming H.SO. and P.O. (Weinreich, B. 20, 982).—BaHA''' 5aq. Crystals.

Reference.-NITRO-SULPHO-TOLUIC ACID.

SULPHO-UVITIC ACID C₅H₈SO, i.s. C₄H₈Me(SO,H)(CO,H)₂ [5:6:3:1]. Formed by evaporating its amic acid with conc. HClAq (Jacobsen, A. 206, 185). Needles (from dilute H.SO₄). Potash-lusion yields oxy-uvitic acid.— KH.A" 2ac.—Ba.A", S. 3:23 at 12:5°. Needles

(Jacobsen, A. 206, 185). Needles (from dilute H.SO₄). Potash-fusion yields oxy-uvitio acid.—
KH₂A" 2aq.—Ba₂A"'₂. S. 3·23 at 12·5°. Needles.
A mic a cid C_bH₂Me(SO₂NH₂)(CO₂H)₂. A product of oxidation of mesitylene sulphonio amide with KMnO₄ (Hall a. Remsen, Am. 2, 136; Jacobsen). When set free from its salts it changes at once into the anhydride C_bH₁NSO_a [270°], S. 5 at 100°.—KHA".—BaA"-BaA" 8aq.

SULPHO-ISOVALERIC ACID C₃H₁₀SO₅ i.e. C₄H₁₀(SO₅H),CO₂H. Formed by heating isovaleric acid (1 pt.) with CISO₃H (1 pt.) at 150° (De Varda, G. 18, 91). Deliquescent crystalline mass. Its aqueous solution partially decomposes when heated .- BaA" aq .- PbA" 2aq.

SULPHOXIDES. Organic compounds R.SO.R' formed by the action of conc. HNO, on sulphides. Decomposed by heat. Reduced by Zn and H₂SO₄ and by HI to sulphides. Attacked by PCl₃, sulphides being formed. They reduce KMnO₄, being converted into sulphones. Sulphoxides containing monovalent alcohol radicles form unstable

mg monovaries acono ranteres form district compounds with HNO₃, such as Et₂SO,HNO₃ (Beckmann, J. pr. [2] 17, 475).

SULPHO-XYLENE CARBOXYLIC ACID.

Amic acid C₆H₂Me₂(SO₂NH₂).CO₂H [1:3:4:5].

[268° cor.]. Formed by oxidising ψ-cumone sulphonic amide (Jacobsen a. Meyer, B. 16, 190). Long needles, sl. sol. hot water. - KA'aq.

BaA'₂2½aq.
SULPHUR. S. At. w. 31.98. Mol. w. 63.96; probably also 191.88 and 255.84 (v. infra). probably also 19188 and 25584 (v. infra). The following data apply to ordinary rhombic S. Melts at c. 115°; different observers give from 111° to 115° (v. Helff, Z. P. C. 12, 219; Spring, A. Ch. [5] 22, 170; Kopp, A. 93, 129; Brodie, J. pr. 62, 336; Gernez, C. R. 83, 217; for m.p. at high pressures v. Hopkins, J. 1854. 48). Boils at 440° (Dumas, A. Ch. [2] 36, 83; Troost a. Hautefeuille, C. R. 76, 76, 219). Callender a. Griffiths (T. 182, 119) give 44:453° as lendar a. Griffiths (T. 182, 119) give 444.53° as within '1° of the true temperature of the vapour of sulphur boiling freely under a pressure of 760 mm.' (This determination was made with Pt resistance thermometers with great care, but unfortunately no special precautions were taken to insure the purity of the S used. For other determinations v. Carnelley's Melting- and Boiling-point Tables, 1, 11. For b.p. under different pressures from 1 to 760 mm. v. Monckman, Pr. 46, 136.) S.G. c. 2.03 (for numerous data v. Clarke's Table of Specific Gravities, 2nd ed., 9). Clarke's Table of Specific (travities, 2nd ed., 9).
S.G. molten S 1:801 to 1:815 (Playfair a. Joule,
C. S. Mem. 3, 76); S.G. at b.p. 1:46 to 1:51
(Ramsay, C. J. 35, 471). V.D. varies from
c. 122 to c. 62; v. infra, Molecular Weight of S.
S.H. (17°-45°)·163 (Kopp, T. 1865, 71);
(0°-100°)·1776 (Bunsen, P. 141, 1). S.H.
(liquid)·2346 (Person, A. Ch. [3] 21, 295).
Latent heat of fusion = 9:368 (for 1g. S) (Person, L.c.). S.V.S. 15·9. S.V. of S in combination varies from 28·6 to 22·6; S.V. at b.p.
21·6 (Ramsay, C. J. 35, 471). , C.E. (linear)
00006418 (at 40°) (Fizcan, C. R. 68, 1125;
v. also Kopp, A. 93, 129; Pisati, G. 1874. 29;
Spring, J. 1881. 1085; Moitessier, J. 1866. 27, v. also Kopp, A. 93, 129; Pisati, G. 1874, 29; Spring, J. 1881, 1085; Moitessier, J. 1866, 27, who gives C.E. for each c. 20° from 110° to 440°). S. in CS₅; 16:54 at -11°, 18:75 at -6°, 23:99 at 0°, 87:15 at +15°, 41:65 at 18:5°, 46:05 at 22°, 94:57 at 38°, 146:21 at 48:5°, 181:94 at 55° (Cossa, B. I, 138; Payen, C. R. 84, 456, 508). For S.G. of solutions in CS₂ v. Macagno (C. N. 43, 192). For S. in C₆H₆ and other solvents v. Pelouze (C. R. 68, 1179; 79,

56). Refraction-equivalent $\left(\frac{\mu-1}{d}$. at.w.) for

D line 16.0 (solid), 16.47 (liquid), 16.1 (gaseous, for C line), 16.0 (in solution), 16.0 (calculated from data for SCl₂), 16.1 (from data for S₂Cl₂)

(Gladstone, P. M. [5] 35, 204). H.C. [8,07] = 71,080 (Th. 2, 247). The E.C. of S is very small; it varies much with temperature (v. Monckman, Pr. 46, 136). The fundamental form of rhombio S is a simple pyramid, or elongated octahedron; a:b:c=\$106:1:1*98. For emission-spectrum v. Salet, C. R. 68, 404; 78, 559; Bl. [2] 11, 302; Mulder, J. pr. 91, 112; Barrett, J. 1865. 138; Seguin, C. R. 53, 1272; Chautard, C. R. 79, 1123; Plücker a. Hittorf, J. 1863, 109. For absorption-spectrum of S vapour v. Salet, C. R. 74, 865; Gernez, C. R. 74, 803; Ciamician, W. A. B. 77 [2] 839. For vapour pressures of S vapour v. Regnault (J. 1863. 65). Ignition point c. 250° (Hill, C. N. 61, 125; Blount, C. N. 61, 153).

The following data apply to monoclinic S. Melts at 117.4° (Gernez, C. R. 83, 217); at 120° (Brodie, J. pr. 62, 336). S.G. 1.982 (Marchand a. Scheerer, J. pr. 24, 129); 1.958 (Deville, J. 1, 365). S.V.S. 16.4. H.C. [S,O'] = 71,720 (Th. 2, 247; Petersen, Z. P. C. 8, 601). For volumes occupied at different temperatures v. Toepler (W. 47, 169). Crystallises in secondary forms of a monoclinic prism; a:b:c=1.004:1:1.004, angle $b:c=84^{\circ}$ 14'. Sol. CS₂, from which solution rhombic S crystallises out.

Insoluble sulphur is amorphous; insol. CS,; S.G. c. 2.04 (Troost a. Hautefeuille, C. R. 69, 248); S.G. after compression at 8,000 atmos. 1.9556 at 0°, 1.9643 at 100° (Spring, Bl. Acad. Belg. [3] 2, 83).

Cf. Allotropy of Sulphur (p. 609). Occurrence. — Native, in beds, in Sicily, Mexico, New Zealand, &c.; in the lava fissures of volcanic districts; in small quantities in the mud from the sea-bottom (Buchanan, Pr. E. 1891. 1). Many metallic sulphides also occur native-e.g. sulphides of Sb, As, Cu, Fe, Pb, Hg, and Zn. Sulphates occur in large quantitiese.g. gypsum, celestine, heavy spar; these and other sulphates are found in the earth's crust, in the sea, and in many river and spring waters. (For more details v. Dictionary of Applied CHEMISTRY, iii. 682.) S is a constituent of albumen, hair, feathers, horn, and some other parts of animals; it is also found in many plants. Small quantities of S compounds are found in the atmosphere near volcanoes. According to Young sulphur occurs in the solar atmosphere (Am. S. [3] 4, 356).

Sulphur has been known from very early times. The quantitative work of Lavoisier, in 1772, on burning S showed this substance to be an element, but it was not finally placed on the list of elements until after the experiments of

Gay-Lussac and Thénard in 1809.

Formation.—1. By the interaction of SO_3 and H_2S ; $2SO_2+4H_2S=3S_2+4H_2O.$ —2. By the partial oxidation of H₂S, either by incomplete combustion or by exposure of H₂SAq to a limited quantity of air; $2H_2S + O_2 = 2H_2O + S_2$. Also by the oxidation of FeS by exposure to moist air; $2\text{FeS} + 3\text{O} = \text{Fe}_2\text{O}_3 + \text{S}_2 - 3$. By distilling certain metallic sulphides out of contact with air, e.g. $3F_0S_2 = F_0S_4 + S_2 - 4$. By decomposing solution

5r65_= re,5,+5,:-4. By decomposing solution of an alkali or alkaline polysulphide by acid; e.g. CaS,Aq + 2HClAq = CaCl₂Aq + H₂S = 2S₂. Also by adding acid to solution of a thiosulphate; e.g. Na,S₄O,Aq + 2HClAq = 2NaClAq + H₂O + SO₂Aq + S. — 5. By decom-

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posing S₂Cl₂ by water (2S₂Cl₂+2H₂O+Aq=4HClAq+SO₃+3S).—6. When sulphates, e.g. CaSO₄, are in prolonged contact with decaying organic matter (such as plant-leaves) they are reduced to sulphides, and if these come into contact with acids S is among the products of the reactions that occur. For a fuller account of some of these processes, whereby native S is probably formed, v. DICTIONARY OF APPLIED CHEMISTRY, iii. 683. For methods of forming the various varieties of S v. infra, Preparation.

Preparation .- 1. Ordinary S is dissolved in pure, dry CS,; a part of the CS, is distilled off, and the rest is allowed to deposit crystals of S. This process is repeated once or twice; the S crystals are powdered, kept in vacuo for some days to remove all CS, and then repeatedly distilled in vacuo, the middle portion of the distillate being collected each time.—2. Ppd. S is distilled several times in S₂Cl₂ to remove H compounds; the distillate is then repeatedly distilled in vacuo, the middle portion only being collected; the distilled S is finely powdered, repeatedly washed with water, dried, distilled over a few small pieces of pure Zn in vacuo (to remove traces of S_2Cl_2), and then repeatedly distilled in vacuo.—3. S is ppd. by adding HClAq to pure Na₂S₂O₃Aq, the pp. is repeatedly washed till free from chlorides, dried, distilled repeatedly, and finally distilled several times in vacuo (v. Monckman, Pr. 46, 149).

Ordinary rhombic sulphur is prepared by melting S and allowing to cool very slowly at 90° (Schützenberger, C. R. 66, 746), or by melting and throwing in a crystal of rhombic S when the liquid has cooled nearly to the crystallisation point (Gernez, C. R. 83, 217); also by crystallising from CS₂; and, in very well formed crystals, by saturating pyridine or picoline with H₂S and allowing to saand (Ahrens, B. 23, 2708).

Monoclinic sulphur is prepared by melting a considerable quantity of roll sulphur in a Hessian crucible, allowing to cool till a crust forms on the surface, piercing this crust, and pouring out the S that is still liquid; the walls of the crucible are covered with monoclinic crystals. This form of S can also be prepared by evaporating alcoholic solutions of (NH₄)₂S (Mallard, J. 1885. 383; Ruys, J. 1884. 336; Gernez, C. R. 100, 1539; 101, 312); also, along with rhombic crystals, from solution of S in boiling alcohol, benzene, &c. (Maquenne, Bl. [2] 41, 238). By melting S, and throwing in a crystal of the monoclinic form when the liquid is near the crystallisation point, the S solidifies in monoclinic crystals (Gernez, C. R. 83, 217).

Soft soluble sulphur is prepared by decomposing S.Cl., by water, or Na_S.O.Aq or a soluble polysulphide by a limited quantity of acid, or many metallic sulphides by fuming HNO, or SO.Aq by H.SAq (Weber, A. 141, 432, 180se, P. 47, 166; Deville, Ph. C. 1848, 200; Fordos a. Gélis, Ph. C. 1854, 294). This preparation is not homogeneous; it contains both soluble and insoluble S.

Insoluble sulphur (insol. in CS₂) is prepared by heating ordinary S nearly to boiling and then cooling rapidly (most easily by slowly pouring into a large quantity of cold water), rubbing the plastic mass so obtained with a glass rod, under water, till it becomes hard, and

removing soluble 8 by treatment with warm CS₂ (cf. Deville, Ph. C. 1848. 200). Insoluble 8 is generally present in 'flowers of sulphur' (which is formed by rapidly cooling vapour of S); by treating this with CS₂ the soluble S is removed, and the insoluble form remains. Soluble S becomes covered with a film of the insoluble variety by exposure to sunlight or electric light when melted (Berthelot, J. pr. 31, 396; Lallemand, C. R. 70, 182). Insoluble S is also said to be obtained by decomposing Na S2O, Aq by HClAq, dissolving the ppd. S in CHCl, evaporating, and keeping the crystals that separate for some time (for details v. Engel, C. R. 112, 866; Friedel, C. R. 112, 834). Insoluble S is also formed, mixed with the soluble variety, by the incomplete combustion of H.S or CS2; by decomposing H2S by fuming HNO2 aqua regia, Fe Cl, Aq, S2Cl2, or CrO, Aq; and by the reaction of HNO, Aq, SO,, or halogens with melted S (v. Wöhler, A. 86, 373; Vogel, J. Ph. [3] 29, 433; Schiff, A. 115, 68; Nöllner, A. 108, 19; Dietzenbacher, C. R. 56, 39). Insoluble S is also formed by decomposing thiosulphates by acid, or S2Cl2 or S2Br2 by water, &c., and washing the soft magma so obtained with C5, to remove soluble S (cf. Preparation of soft soluble sulphur, supra; and v. Weber, A. 141, 432; Rose, P. 47, 166; Deville, Ph. C. 1848, 200).

Colloidal sulphur, soluble in water, is prepared by passing H₂S into SO₂Aq at a little above 0° till all the SO₂ is decomposed, filtering, and concentrating over KOll in vacuo. The yellow solid so obtained is sol. water, but changes to ordinary S on keeping (Debus, C. J. 53, 282). According to Engel (C. R. 112, 866) this form of S exists in the solution obtained by adding 1 vol. Na₂SO₂Aq, saturated at the ordinary temperature, to 2 vols. HClAq saturated at 25°-30° and let cool to c. 10°, and filtering from NaCl that separates. This form of S has not been isolated in a state of purity.

Regarding the formation of the varieties of S one from the other, cf. Allotropy of sulphur, p. 609.

Properties.—S exists in several modifications. The chief are (1) soluble in CS_2 , (2) insoluble in CS_2 , (3) soluble in water.

1. Soluble sulphur exists in two, perhaps in three, varieties, differing in S.G., crystalline form, &c.

A. Ordinary rhombic (octahedral) sulphur is a pale-yellow, tasteless, very brittle solid. By crastallisation from CS, it forms clear, yellow, transparent, lustrous crystals; the colour becomes paler at low temperatures, until at -50° the crystals are almost colourless (Schönbein, J. pr. 55, 161); by immersion in boiling water it becomes easily powdered (Daguin, C. R. 20, 1667). The crystals are derived from the fundamental form of a rhombic pyramid; about thirty varieties are known. When held in the hand S emits a distinct adour, probably because of slight volatilisation; according to Berthelot (C. R. 100, 1826) S is wholly volatilisable at a temperature not much above the ordinary. Sis said to phosphoresce in air or O at 200° (Heurmann, B. 16, 139). When S is rubbed it becomes strongly (negatively) electrified. S is a bad conductor of heat, and a very bad conductor of electricity; the conductivity varies slightly,

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according as the light is or is not allowed to fall on the S (Monckman, Pr. 46, 136). Insoluble in water; easily sol. CS₂ (data at beginning of article); also sol. C₄H₆, CHCl₈, &c. Sol. warm conc. acetic acid (Liebermann, B. 10, 866); sol. liquid SO₂ (Sestipi, Z. 1868. 718). As octahedral S changes to prismatic S near the m.p. of the former, it is evident that hot solutions of the former, in solvents which boil near to, or above, the m.p. of S must contain some prismatic S. Rhombic S slowly changes to monoclinic S when kept near its m.p. (v. p. 609, Allotropy of sulphur); the change is accompanied by absorption of heat (c. 650 g.-units for 32 grams S) and expansion of volume (v. Petersen, Z. P. C. 8, 601). According to Gernez (C. R. 83, 217), if a fair quantity of rhombic S is heated till melting begins on the surface, the interior portions change to microscopic monoclinic crystals, and the surface parts solidify again; this occurs only if the m.p. of monoclinic S (117.4°) is not exceeded. S melts to a clear yellow liquid; at c. 150° the liquid begins to darken and thicken; between 170° and 200° it is black, and so viscid that it does not pour out when the vessel containing it is inverted; at 330°-340° the liquid becomes thin, but it remains dark coloured until it boils at c. 444°. These changes are accompanied by very considerable changes in the electrical conductivity of S: the conductivity is almost constant from 270°-290°: it increases considerably up to 340°-350°, and then very rapidly up to the b.p. (v. Monckman, Pr. 46, 136). The expansion-coefficient, for each interval of 10°, decreases from 110° to 180°, and then increases gradually, but not regularly, to the b.p. (v. Moitessier, J. 1806. 27). Melted S may be cooled below 95° without solidifying (cf. Gernez, C. R. 97, 1298, 1366, 1433). For S.G., S.H., and other physical properties of S, v. beginning of this article.

B. Monoclinic sulphur, obtained by cooling molten S, forms transparent, yellowish brown needles; as obtained by crystallisation from solutions the crystals are nearly colourless. The crystals gradually become pale yellow and opaque, due to change into the rhombic form. The crystals are secondary forms of a monoclinic prism. This form of S is sol. CS₂; rhombic S crystallises from this solution; it also dissolves in alcohol, C₆H₆, CHCl₃, &c. On evaporation, crystals, both of rhombic and monoclinic S, separate (Maquenne, Bl. [2] 41, 238); monoclinic S may be recrystallised from alcoholic solution of (NH₄), S (for references v. p. 607, Preparation of monoclinic S). The change of monoclinic to rhombic S is hastened by scratching with a glass rod, or by covering with CS₂; heated to 95.1° at 760 mm. pressure, monoclinic changes to rhombic S; the change is accompanied by appearance of heat and contraction of volume (v. p. 609, Allotropy of sulphur). For S.G. &c. of monoclinic S v. beginning of this article.

C. Soft soluble sulphur (v. Preparation of soft soluble sulphur, p. 607) is only partly sol. CS,; it contains both soluble and insoluble amorphous S; it is a very pale yellow, or nearly white, soft, amorphous, magma that gradually hardens; when heated it gives off H.S (Weber, A. 141, 432; Rose, P. 47, 166; Deville, Ph. C. 1848. 200; Fordos a. Gélis, Ph. C. 1854. 294).

2. Insoluble sulphur. It is doubtful whether more than one variety of this form of S exists, or whether substances described as varieties are not merely mixtures of ordinary insoluble S with impurities.

D. Plastic sulphur is a citron-yellow. soft, caoutchouc-like, amorphous solid, formed by suddenly cooling molten S (v. p. 607, Preparation of insoluble sulphur); as prepared from ordinary S it is dark brown, but Mitscherlich (J. pr. 67, 369) found that the dark colour is caused by the presence of small quantities of fatty substances (cf. Dietzenbacher, C. R. 56, 39). The S.G. of brown, plastic S is c. 1.91 to 1.96; but the substance is not homogeneous; it contains both soluble and insoluble S. Plastic S soon hardens and becomes yellow, more quickly when broken up and rubbed with a glass rod, or when immersed in turpentine, or when heated to c. 100°; heat is given out in this change (v. p. 609, Allotropy of sulphur). For determinations of the volumes occupied at different temperatures by plastic S v.

Toepler (W. 47, 169).

E. Amorphous yellow sulphur is prepared from plastic S, or flowers of S, or the S obtained by decomposing thionates by acid, or H2S by oxidisers &c. (v. p. 607, Preparation of insoluble sulphur), by washing with warm CS, till all soluble S is removed. This variety is an amorphous, buff-yellow powder; kept under CS, it seems white; when dried and rubbed it forms a loose, flocculent powder. Insol. CS₂; somewhat sol. CHCl₃, Et₂O, and alcohol, according to Deville (J. pr. 56, 359). Unchanged at the ordinary temperature, but slowly converted the ordinary temperature, but slowly converted to crystalline soluble S at 100° (v. Berthelot, J. pr. 70, 941; 71, 364; Favre, J. Ph. [3] 24, 344; F. a. Silbermann, A. Ch. [3] 34, 447). S.G. 2-046 (v. data at beginning of this article). H.C. [S,O²] = 71,990 (Petersen, Z. P. C. 8, 601). The accounts of this variety of S vary considerably.

F. Black sulphur. When S mixed with a very little oil is thrown into a hot Pt dish, a black substance is obtained which has been looked on as a modification of S (Magnus, P. 92, 367; 99, 145; Dietzenbacher, P. 124, 644; Gross, B. B. 1879. 788; Jones, C. N. 41, 244; Keller, Bl. [2] 4, 346). Knapp (J. pr. [2] 38, 48; 43, 305) has shown that the black substance contains c. 55 p.c. S and c. 33 p.c. carbonaceous matter; K. thinks it is probably a modification of S adhering to carbonised products of the oil. This substance is said to be non-volatile above the b.p. of S; it is a lustrous, amorphous, solid, insol. CS2, alcohol, Et2O, oils, H2SO4, &c.
3. Colloidal sulphur soluble

water. This form of S is said to exist in Wackenroder's solution (the milky liquid formed by passing H₂S into SO₂Aq), and also in the solution obtained by adding HClAq to Na₂S₂O₂Aq (v. p. 607. Preparation of colloidal sulphur). This p. 607, Preparation of colloidal sulphur). This form of S has not yet been obtained free from impurities; it is a plastic, gummy, pale-yellow solid; it dissolves in water, forming a turbid liquid. By ppg. by NaCl, filtering, drying on bibulous paper, shaking with water, and repeating this treatment, Debus (C. J. 53, 284) obtained colloidal S that dissolved in water so as to form an almost clear, opalescent liquid which became quite clear on warming, and turbic

on cooling. This solution yielded ordinary S on addition of several salts; evaporation left a viscous, transparent residue; the S in solution did not diffuse through a porous membrane.

did not diffuse through a porous membrane.

Other modifications of sulphur. Various experimenters have described forms of S different from those usually recognised, but there is much doubt as to whether any of these are really distinct varieties, or merely mixtures of known varieties (v. Maquenne, Bl. [2] 41, 238; Gernez, A. Ch. [6] 3, 266; C. R. 100, 1326; Engel, C. R. 112, 866; Berthelot, C. R. 100, 1328; Brame, C. R. 101, 533, 639).

Allotropy of sulphur. The following table presents the best established allotropic forms of S:—

Insoluble in water.

Soluble in CS₂

Rhombie; S_a

Monoclinie; S_b

Amorphous, soft

Insoluble in CS₂
Plastic; S_r
Amorphous, yellow

Soluble in water. Colloidal; S.

The amorphous forms of S (soft, soluble; yellow, insoluble; and plastic, insoluble) and colloidal S have not been obtained pure; the soluble amorphous always contains insoluble, and the insoluble forms always contain soluble S; the colloidal contains S insoluble in water (cf. Magnus, J. pr. 70, 215; 72, 48; Weber, J. pr. 70, 354). It would probably be more accurate to make only three divisions of amorphous S: soluble in water, insol. water but sol. CS2, insol. both water and CS. Berthelot (J. pr. 71, 364; 78, 244) holds that there are two main varieties of S: soluble in CS, and insoluble in CS, separated from compounds wherein it acts as the positive radicle, or part of the positive radicle (e.g. S₂Cl₂, SO₂Aq), is insoluble, according to B.; whereas when separated from compounds wherein it forms the negative radicle, or part of the negative radicle (e.g. H₂S, K₂S), S is soluble in CS₂. B. distinguishes the two varieties of S as electro-positive and electro-negative. Cloëz (J. pr. 74, 266; 78, 241) asserts that insoluble S is obtained from S.Cl., when this compound is rapidly shaken with water, but that soluble (crystalline) S separates from the same compound by the gradual action of moist air; and that insoluble S is obtained by electrolysing H.SAq provided the electrolysis is rapid (cf. Weber, P. 141, 432).

Any form of S changes gradually to the rhombic crystals (S_a); this change is hastened by raising the temperature within certain limits. Berthelot (J. pr. 71, 360) examined the amount of soluble (crystalline) S changed to insoluble at different temperatures; he found that rhombic S heated to 130° 140° and rapidly cooled was still wholly soluble in CS_a, that much insoluble S was formed by heating to c. 170°, and not much more at c. 230°. These results can be taken only as very roughly approximate, on account of difficulties in cooling, &c. (cf. Deville, J. pr. 56, 365; Frankenheim, J. pr. 54, 436). According to experiments of Gernez (C. R. 97, 1298, 1366, 1433; 100, 1343, 1882), Ruys (R. T. C. 8, 1), and Reicher (J. 1885, 247), monoclinic S(B_g) changes to rhombic (S_g) in c. 12 days at — 36° Vol. IV.

to -15°, and in c. 80 minutes at 40°. Reicher (R. T. C. 2, 246; Z. K. 8, 593) says that the temperature of change of S_s to S_s is 95.6° at the ordinary pressure, and rises 05° for each increase of 1 atmosphere pressure; at 96:1° S. changes to S., and at 95:1° S. changes to S.. The change of any form of S to rhombic crystals is accompanied by the appearance of heat and contraction of volume; the data for the heats of combination of Sa, SB, and amorphous insoluble S give c. 650 gram-units as the quantity of heat produced when 32 grams Ss change to S., and c. 900 gram-units for the change of 32 grams insoluble amorphous S to S. (cf. Berthelot, C. R. 70, 941; and Mitscherlich, P. 88, 328). By keeping S molten for some time at 100°, and then inducing crystallisation by dropping in a crystal of S, either rhombic or monoclinic crystals can be obtained, according as the crystal dropped in is rhombic or monoclinic. When rhombic S is melted and allowed to cool under ordinary conditions the solid contains both S, and S_s; if the cooling is rapid, some amorphous S (both soluble and insoluble) is also produced; hence ordinary 'flowers of sulphur,' formed by rapidly cooling S vapour, contains both soluble and insoluble S, and generally also, when freshly prepared, both rhombic and monoclinic crystals. The crystals of S that separate from solutions in CS, are rhombic; both forms of crystals separate from solutions in alcohol, OaHa, CHCla, &c.; and monoclinic crystals separate from solutions in alcoholic (NH4)2S. Light brings about the change of soluble into insoluble S; if bright sunlight, or light from the electric arc, falls on molton Sat c. 130°, a film of insoluble S is produced. Similarly, light concentrated by a lens and directed on to a conc. solution of S in CS, quickly causes the formation of a speck of insoluble S, which soon increases in size till the liquid becomes turbid (Berthelot, J. pr. 31, 396; Lallemand, C. R. 70, 182). No differences have been observed between the chemical behaviour of the soluble and insoluble varieties of S (v. Schmitz-Dumont, B. 25, 2659).

Atomic weight of sulphur. The at w. of S has been determined (1) by converting AgCl into Ag,B (Berzelius, P. 65, 319 [1845]; Svanberg a. Struve, J. pr. 44, 320 [1843]; (2) by reducing Ag,SO, to Ag by H (Struve, A. 80, 203 [1851]; Stas, Stas R. 125 [1860]); (3) by direct synthesis of Ag,S (Dumas, A. Ch. [3] 55, 147 [1859]; Stas, Stas R. 53 [1860]); (4) by determining S.H. of S (Kopp, T. 1865, 71); (5) by determining V.D. of, and analysing, SH, SO, S,Cl., &c.

Molecular weight of sulphur. The V.D. determinations of Dumas (A. Ch. [2] 50, 170) gave c. 95 at 450°-500°, pointing to the molecular formula Se,; Bineau (C. R. 49, 799) found V.D. 39 from 714° to 743°, and 34 between 840° and 1160°, indicating the molecular weight S_s. chemical behaviour of the soluble and insoluble

Molecular weight of sulphur. The V.D. determinations of Dumas (A. Ch. [2] 50, 170) gave c. 95 at 450°-500°, pointing to the molecular formula S₄; Bineau (C. R. 49, 799) found V.D. 39 from 714° to 743°, and 34 between 840° and 1160°, indicating the molecular weight S₄. The determinations by Deville a. Troost (C. R. 56, 891) at 860°-1040° confirmed the number 32 and the molecular weight S₄. Troost (C. R. 95, 30) got the number 42·5 at 665°, indicating a mol. w. of c. S₄ (V.D. corresponding to S₄—48). In 1888 Biltz determined V.D. of S at intervals from 468° to 606°, and got results ranging from 113·2 at the lower temperature to 68·4 at the higher (S₇=112; S₄=64). The V.D. constantly decreased as temperature rose; the V.D. was constant only between 502° and 524°, but the

values were between those calculated for S, and S. Biles concluded that the only molecules which exist as gas through any considerable range of temperature have the composition S2. Ramsay (Z. P. C. 3, 67 [1889]) thought that Biltz's results did not negative the existence of gaseous molecules more complex than S2. Schall (B. 23, 1701 [1890]) got numbers for V.D. varying from 115 to 122, at 573° and pressures from 10-20 mm., in an atmosphere of N or CO.; S. concluded that molecules S, probably exist in the vapour of S. Riecke (Z. P. C. 6, 430 [1890]) regarded the decrease of V.D. with increasing temperature as a dissociation of S, to S, and S,; by making certain assumptions, his calculated results agreed well with the experimental numbers of Biltz. In 1888 Paterno a. Nasini (B. 21, 2153) determined the depression in the freezing-point of benzene caused by dissolving S therein; their results indicated S_a as the molecular for-mula of S in solution in benzene. By determining the increase in the boiling-point of CS, produced by dissolving S in that solvent, Beck-nann (Z. P. C. 5, 76 [1889]) got values for the mol. w. of S varying from 245 to 280 (S_a = 256). Sakurai also used this method in 1892 (C. J. 61, 989); his values for mol. w. of S in CS, varied from 252.3 to 254.9. From observations of the effect of dissolving S in naphthalene on the f.p. of the solvent, Hertz (Z. P. C. 6, 358 [1890]) concluded that the mol. w. of S in solution in naphthalene is $256 = S_s$. Helff (Z. P. C. 12, 196) in 1893 also got S, for mol. w. of S in CS2, and in molten P. These results leave little doubt that molecules S, exist in solutions of S in CS, and in naphthalene, and S, in solutions in benzene; that molecules of greater complexity than S₂—probably as complex as S₃—exist in S vapour, but these are stable only through a small range of temperature, and gradually dissociate as temperature rises until all the molecules existing above c. 700° have the composition S₂. Biltz a. Meyer (B. 22, 725 [1889]) have shown that the V.D. of S corresponds with the mol. w. S₂ up to 1600°-1700°.

Reactions.—1. Reacts with water at 100° to form H.S. Cross a. Higgin (C. J. 35, 249; B. 16, 1195) found that the solution contained thionic acids; they supposed that these were produced by reactions between the H.S and SO. formed by the action of the S on the water (cf. Payen, J. Ph. 8, 371; Mulder, J. 1858, 84; Meyer, C. R. 74, 195; Gélis, C. R. 56, 1004). Senderens (Bl. [3] 6, 800) regarded the production of H.S as due to interactions between the S and the glass vessels employed; C. a. H. (C. J. 35, 252) found H.S was produced when dilute H.SO.Aq was used in place of water, and they concluded that the alkaline constituents of the glass were without influence. Becquerel (C. R. 56, 287) says that when water containing S in suspension is electrolysed, H.SO., forms at the positive, and H.S at the negative, electrode (cf. Colson, Bl. [2] 34, 66). When S is moistened with water and let stand in the air, H.SO., Aq is said to be produced (Polacci, C. C. 1884, 484; Böhm, M. 3, 224).—2. S is oxidised to H.SO., Aq by heating with nitric acid, aqua regia, or polassium chloruric acid is reduced, giving off SO.,—4. Cone, hydriodic acid gives H₃S and I (I de-

composes dilute H.SAq to HIAq + S) .- 5. Chlorosulphonic acid when heated with 8 produces S₂Cl₂, SO₂, and HCl (Heumann a. Köchlin, B. 15, 416).—6. S dissolves in boiling alkali solutions, also in molten alkalis and alkaline car. bonates, to form mixtures of polysulphides and thiosulphates. Boiling ammonia solution forms polysulphides; heated in a sealed tube above 100° some (NH),28,0,4A is produced (v. Brunner, D. P. J. 150, 371).—7. Sulphur trioxide dissolves S, forming a blue solution of S2O3 (v. SUL-PHUR OXIDES) .- 8. Carbon dioxide reacts with boiling S to form COS (Cossa, B. 1, 117; Berthelot, Bl. [2] 40, 364). The same compound is produced by volatilising S, by an electric current, in carbon monoxide (Chevrier, C. R. 69, 56) .- 9. PSCl. is formed by the interaction of S and phosphorus trichloride at 180° (Henry, Bl. 13, 495). Phosphorus pentachloride forms PCl. and S.Cl. (Goldschmidt, C. C. 1881. 489). 10. S decomposes many sulphates and carbonates at high temperatures, forming sulphides and SO₂, or CO₂ (v. Sestini, Bl. [2] 34, 490; Berthelot, Bl. [2] 40, 364).—11. Solutions of salts are very often reduced by boiling with S, sulphides being generally ppd. (v. Vortmann a. Padberg, B. 22, 2642; and, more fully, Senderens, Bl. [3] 6, 800; 7, 511).

Combinations.—1. Sulphur combines directly with most of the elements. The binary compounds of S—with the exception of those with Br, Cl, F, I, or O, and also compounds of S with more than one other element (except these be some of the five just mentioned)—are described under the least negative of the component elements; e.g. compounds of S with P and Cl are described (as sulphochlorides) under Phosphorus. For the conditions of formation of the binary compounds of S reference must be made to the various elements, except in the cases of bromide, chloride, fluoride, iodides, and oxides of S, which are described in this article in their proper (alphabetical) places.—2. Chlorine monoxide Cl,O is said to combine directly with S (suspended in S,Cl₂), at -12°, to form SOCl₂ (Wurtz, C. R. 62, 460).

Sulphur, acids of. Reference should be made to Hydrogen sulphide, vol. ip. p. 725; Sulphur oxyacids, this vol. p. 619; Sulphur oxyacids, nitrogen derivatives of, this vol. p. 619; Sulphogranic acid, vol. ii. p. 303; Sulphomo acids and derivatives, this vol. p. 599; Thiocarbonic acid, vol. i. p. 703. For acids, and salts of acids, containing S and P, and S, P and O, v. Phospidores sulphides, this vol. p. 145 (beginning of article); also Phosphorics sulphide, Reactions 7 and 8 (p. 146), Phosphoric sulphide, Reaction 8, and also end of that article (p. 147).

Reaction 8, and also end of that article (p. 147). Sulphur, bromides of. It is very doubtful whether any definite compound of S and Br exists. Powdered S dissolves in Br with evolution of a little heat; the deep ruby-red liquid begins to distil over at c. 60° and the thermometer rises steadily to c. 190°, when it secends slowly to c. 200°, after which it steadily rises till S remains; the fraction coming over at 190°-200° agrees fairly in composition with the formula S₂Br₂ (Pattison Muir, Ö. J. 28, 845). M. found that by passing CO₂ through a solution of S in excess of Br for some hours, at 15°, 50°, and 90°, the residual liquid had nearly the com-

position S.Br₂; Hannay, however, by passing air through such a liquid for 400-500 hours found that the whole of the Br was removed and that pure S remained (C. J. 33, 284; 35, 16). It is, however, possible that at the temperature of this experiment, c. 15°, dissociation of S.Br. was induced by the stream of air. H. also found that the vapour given off by the supposed S.Br., even at 0°, showed the absorption-spectrum of Br. Spring a Lecrenier (Bl. [2] 45, 867) examined the reaction of the supposed S₂B₂ with K₂SO₃. S. had before shown that S₂Cl₂ and K₂SO₃ produce KCl and K₂S₄O₄; but Cl and S acting as free elements produce K₂SO₄, KCl, K₂S₂O₃ and SO₄. S₂Br₂ ought then to produce KBr and K₂S₁O₅, whereas S and Br would form K.SO., KBr, K.S.O., and SO.; by determining the quantities of the products S. a. L. calculated that the supposed S.Br. contains c. 27 p.c. of the elements uncombined. Various reactions of the supposed S2Br2 are described in the memoirs already referred to (v. also Rose, p. 44, 327; Michaelis, J. Z. 6, 297; Ogier, C. R. 92, 922).

Sulphur, chlorides of. Three compounds of S and Cl are known: S₂Cl₂, SCl₂, and SCl₄. These compounds are liquids; S₂Cl₂ boils unchanged at c. 138°, SCl₂ begins to decompose to S₂Cl₂ and Cl at c. 10°, and the decomposition of SCl, to SCl, and Cl begins at c. - 20°.

Suiphur Monochioride S.Cl., (Sulphur protochloride, Sulphur sulphochloride, Sulphur thionyl chloride, Thio-thionyl chloride.) Mol. w. 134.7. Boils at 138.12°; S.G. 42 1.70941, S.G. at b.p. 149201 (Thorpe, C. J. 37, 356). S.V. 90.28 (T., l.c., p. 372). V.D. 68-4 (Dumas, A. Ch. [2] 49, 204; Marchand, J. pr. 22, 507). $\mu_{\rm in}$ = 1·64449 (Haagen, P. 131, 117). H.F. [S^{*},Cl^{*}] (from S_s) = 14,257 (Th. 2, 310); 17,600 (Ogier, C. R. 92, 922).

Formation .- 1. By the interaction of S and Cl.-2. By distilling S with 9 parts SnCl, or 8.5 parts HgCl₂.—3. By reacting on PCl, with S (Goldschmidt, C.C. 1881, 489).—4. By decomposing PSCl₂ by Cl or by heating to redness.—5. By the interaction of P₂S₂ and SOCl₂, the other product being P_2O_3 (Carius, A. 106, 331). – 6. By the action of CS_2 on ICl_3 (Weber, P. 128, 459).

Preparation.—A stream of dry Cl is passed into a flask, or retort, containing S (flowers or sticks) until most, but not quite all, S is dissolved to a yellowish red liquid, the vessel being gently warmed. The liquid is repeatedly distilled until it boils constantly at 138°-139°. If the passage of Cl is continued until the S is completely dissolved, the liquid must be distilled from a little 8 (to decompose SCl, quickly).

Properties. - A yellowish-red, oily liquid, with a very characteristic, rather disagreeable, odour and an acid taste; the vapour affects the mucous membranes rapidly, causing tears, and affecting the breathing. Does not become viscid at -75° (Haase, B. 26, 1052). Fumes in air. Dissolves in CS, and C,H, also in alcohol and ether with decomposition. S,Cl. dissolves large quantities of S; solution of S,Cl., containing free S, in CS, is used for vulcanising (v. Dictionary or APPLIED CHEMISTRY, vol. iii. p. 706).

SO,Aq, and S, with a little H,SAq, H,S,O,Aq, and some of the thionic acids.—2. Bydrogen sulphide produces HCl and S; hydrogen iodide reacts at the ordinary temperature to form HOl, I, S.I., and then H.S (Hautefeuille, Bl. [2] 7. 198). - 3. By passing S.Cl., vapour, mixed with and Cl are formed (Donny a. Mareska, C. R. 20, 817; Spring a. Lecrenier, 18. [2] 45, 867). A. Heating with phosphorus produces PCl_s, PSCl_a and S if a little P is used; or PCl_s, P sulphides, and red P if much P is used (Wöhler a. Hiller, A. 93, 274; Chevrier, C. R. 63, 1003) .- 5. Heated with many metals, S.Cl. gives metallic chlorides and S; the more volatile the metallic chloride the more readily does the reaction occur (v. Chevrier, C. R. 64, 302).-6. S.Cl. combines with chlorine, forming SCl. and SCl. (q.v., infra). Br and I are absorbed by S.Cl.; according to Evans a. Ramsay (C. J. 45,65) no compound is formed with Br. -7. With oxides of arsenic and antimony S.Cl. forms AsCl, and SbCl, giving off SO, and separating S; selenion dioxide produces Sc.Cl, and SO, oxides of phosphorus, boron, and silicon do not react (Prinz, A. 223, 355).—8. S₂Cl₂ absorbs sulphur trioxide, below 0°, forming a brownish-yellow liquid, from which excess of SO, crystallises out; a little above 6" SO, is given off, rapidly at 10°; S.O.Cl. is formed on distillation (Rose, P. 44, 291) .- 9. By passing vapour of S2Cl2 along with the vapours from sulphonic acid through a hot tube, SO., H.S., S. HCl, and Cl are produced (Brault a. Poggiale, J. Ph. 21, 140) .- 10. Heating S₂Cl, with sulphates generally produces SO,Cl₂ chlorides, S, and SO₂; heated with sulphuryl chloride to 250°, S,OCl, is formed (v. Schneider, J. pr. 104, 83; [2] 33, 18; Demarcay, C. R. 92, 720, 111, S,Cl, combines with supersystems 720).—11. S.Cl. combines with anumonia gas to form S.Cl. 4NH, stable in air, sol. alcohol, decomposed by water giving NH,ClAq, (NH,),S,O,Aq, and S (Brault a. Poggiale, J. Ph. 21, 140) .- 12. Reacts with organic compounds containing oxygen, generally forming Cl compounds and small quantities of S compounds, and also HCl, SO, and S .- 13. Combines with unsaturated hydrocarbons; e.g. with C.H. forms $\mathbf{C}_{2}\mathbf{H}_{4}\mathbf{S}_{2}\mathbf{Cl}_{2}.$

SULPHUR DICHLORIDE SCl. Mol. w. (in solution in benzene or acetic acid) 102.72. S.G. tion in benzene or acetic acid 102°72. S.tr. 1-6482 at 15·4° (Costa, G.20, 367). $\mu_{\rm Ha}$ =1·5716 (Costa, Lc). No constant b.p. (v.infra). This compound was prepared by H. Rose in 1831 (P. 21, 431; 27, 167); the experiments of Dumas (A. Ch. [2] 49, 204) and Marchand (J. pr. 22-507) led to its recognition as a definite compound (v. also Carius, A. 106, 291); Hübber a. Gueront (Z. 1870. 455) isolated the compound satisfactorily, and their results were confirmed satisfactorily, and their results were confirmed by Thorpe a. Dalzell, in 1871 (C. N. 24, 159). Costa, in 1890 (G. 20, 367), determined the mol. w. of the compound in solution.

Preparation.-Dry Cl is led into S2Cl, surrounded by a freezing mixture, until the liquid becomes deep red; excess of Cl is removed by a stream of dry CO₂. The temperature must not rise above 6°; the vessel containing the S_cCl₂ should be kept filled with Cl continually, and of Applied Chemistry, vol. iii. p. 700).

Reactions and Combinations.—1. S₂Cl₂ sinks in water, and then decomposes, giving HClAq,

A. Ch. [2] 67, 64; Michaelis, A. 170, 1). Properties. — A thin, dark, brownish-red, liquid, with smell and taste like S.Cl.; does not solidify at -30°; gives off Cl when exposed to sunlight, and should, therefore, be kept in a sealed tube in the dark. Easily decomposed by heat to S,Cl, and Cl; Michaelis (B. 6, 995) gives a table showing amount of dissociation from 20° to 130°; the temperature whereat 50 p.c. of the SCl, is dissociated is c. 86°. SCl, reddens dry litmus paper. The depression of the freezingpoint of benzene or glacial acetic acid by solution therein of SCl2, shows that the mol. w. agrees with the formula SCl₂ (Costa, G. 20, 367).

Reactions and Combinations .- 1. Heat, or direct sunlight, causes dissociation to S.Cl., and Cl (v. supra, Properties).—2. Water produces HClAq and H.S.O.AAq.—3. Oxidised violently by nitricacid to HClAq and H.SO.Aq.—4. Ammonia solution produces N₁ClAq, N, and S; ammonia gas combines to form SCl₂2NH₃ and SCl₂4NH₃, soluble, unchanged, in absolute alcohol and ether (Soubeiran, A. Ch. [2] 67, 74).—5. Thionyl chloride (SOCl₂), when heated with SCl₂, forms S₂OCl₄(Ogier, Bl. [2] 37, 293).—6. Alkali sulphites produce chlorides and trithionates (Spring a. Lecrenier, bl. [2] 45, 867).—7. Some inetals, e.g. Cu, Fe, K, react with SCl., with production of heat and light, and formation of chlorides and sulphides.—8. Combines with arsenious chloride, forming AsCl, SCl, according to H. Rose (P. 27, 107).—9. SCl, reacts with oxygenised carbon compounds similarly to, but more readily than, S₂Cl₂; it combines with several unsaturated hydrocarbons (v. Heintz, A. 100, 370; Guthrie, C. J. 12, 109).

SULPHUR TETRACULORIDE SCI,. This compound exists only at temperatures under -20°. The molecular weight is probably 173.46 (SCl.).

Preparation.—S₂Cl₂ is cooled to below -20°

Preparation.—S₂Cl₂ is cooled to below -20° (c. -22°) and a slow stream of dry Cl is passed in until absorption of Cl ceases. Michaelis a, Schifferdecker (B. 6, 993) found that 67.5 g, S₂Cl₂ kept at -20° to -22°, absorbed 106 g, Cl in 10 cm s - 20° (c. 10 cm s). 10 hours, that absorption of Cl then ceased, and that the liquid had the composition SCl.

Properties.—A mobile, yellowish-brown liquid; when removed from the freezing mixture used in the preparation, the liquid gives off Cl, and boils with an absorption of much heat. M. a. S. give the following data showing the dissociation of SCl₄ to SCl₂ and Cl:—

Temp.	P.c. SCl	P.c. SOL
- 22°	100.0	0.0
- 15	41.95	ີ 58⋅05
- 10	27.62	72:38
- 7	21.97	78·0 3
- 2	11.93	88.07
+0.7	8 ·8 7	91·13
+6.2	2.43	97.57

Reactions .- 1. Water causes rapid decomposition to HClAq and SO,Aq, with more or less S according to the mass and temperature of the water.—2. With sulphur trioxide, in the ratio SOI:SO, the products are SOCl, and S,O,Cl, in the ratio SCI,:2SO, the products are SOCI, SO, and Cl (M. a. S., Le.; also B. 5, 924). Sulphur dioxide does not react.—8. Chlorosulphonic acid reacts at a low temperature to form S.O.Cl. and HCl (M. a. S., B. 6, 996).—4. With some hydroxylic organic compounds, e.g. C.H.OH and

C.H. CO.OH, OH is replaced by Cl and SOCL is formed.

Combinations .- 1. Compounds of SCI, with several metallic chlorides are produced by warming the chlorides with S₂Cl₂ and passing in Cl; the compounds 2AlCl₂SCl₄ AuCl₂SCl₄ and 2TiCl₄SCl₄ are formed thus (Weber, P. 104, 421; Rose, P. 42, 517; Casselmann, A. 83, 267). The compound with AlCl, may be distilled in a closed shaped tube; the other two compounds A shaped tube; the other two compounds give off Cl when heated. The compounds SbCl, 3SCl, and SnCl, 2SCl, are produced by passing Cl over SnS, and Sb, s, respectively (R., l.c.; C., l.c.).—2. With iodine trichloride forms ICl, 3Cl, (Weber, P. 128, 459; cf. Jaillard, A. Ch. [3] 59, 451, who gives the composition SCl, 2ICl, Prepared by passing Cl into I dissolved in CS, till the liquid is wine-red, cooling, and drying the red-yellow, prismatic, very deliquescent, crystals, in a tube in a stream of dry Cl. Also formed by passing Cl into a mixture of 2 pts. S and 1 pt. I. Melts to a brown liquid when heated in a closed tube: heated in an open tube forms Cl, ICl, and S2Cl2; decomposed by water or dilute HNO, Aq.

Sulphur, chloro-iodide of, SCl.I(= SCl.,ICl.): v. supra, Sulphur Tetrachloride, Combinations, No. 2.

Sulphur, chloronitride of, S.CIN; v. NITROGEN SULPHOCHLORIDE, vol. iii. p. 571.

Sulphur, cyanides of, v. Cyanogen, sul-PHIDES, vol. ii. p. 358.

Sulphur, fluoride of. According to Gore (Pr. 20, 70 [1871]) the heavy colourless gas produced by fusing AgF with S is a fluoride of S. This gas is not liquefied at 0°, at the ordinary pressure; it fumes in the air, and attacks glass; no analyses are given by G.

Sulphur, haloid compounds of. The most stable of these compounds belong to the forms S₂X₂; where X = Cl. Br, or I. The chloride S₂Cl₂ may be distilled unchanged; the bromide, S.Br., is exceedingly easily decomposed if, indeed, it has been isolated; the iodide, S₂I₂, has been very slightly examined. The compounds SCl₂ and SCl, also exists; the former at temperatures below c. 10°, and the latter below c. -20°. The compound SI_s perhaps exists; it gives up I at the ordinary temperature. The only haloid compound of S that has been gasified unchanged is S₂Cl₂.

Sulphur, hydrides of, SH2 and (?) S3H2; v. HYDROGEN SULPHIDES, vol. ii. p. 725.

Sulphur, nitride of, SN; v. NITROGEN SUL-PHIDE, vol. iii. p. 570.

Sulphur, iodides of. S and I probably combine when heated together, but no definite compound has been isolated by this method (cf. Gay-Lussac, G. A. 48, 372; H. Rose, P. 27, 115; Lamers, J. pr. 84, 349; Sestini, J. 1863. 153; Wheeler a. Lüdeking, Fr. 26, 602).

SULPHUR MONO-IODIDE S.I.. Guthrie (C. J. 14, 57) obtained this compound by placing 2½ parts ÉtI and 1 part S₂Cl₂ in a sealed tube, opening after 12 hours, evaporating EtCl by warming with the hand and removing excess of Eti by gently warming; the S.L. crystallised out in lus-trous crystals resembling I. (One analysis is given, but no full description of properties.)

Ogier (O. R. 92, 922) gives H.F. $[S^2, I^2]$ (from gases) = 10,800.

SULPHUR HEXA-IODIDE SI. This compound is said to be formed by slowly evaporating, at a low temperature, a solution of I with slight expess of S in OS₂. Grey-black crystals; resembling, and isomorphous with, I; I evaporates on exposure to air and eventually only S remains; ticohol, conc. KOHAq, or KHAq, also withdraws all I (G. vom Rath, P. 110, 116; Lamers, J. pr. 84, 349). It is very doubtful whether the crystals examined by vom Rath were a compound or only I retaining a little S.

By passing H.S into a dilute solution of KCl.ICl₃, Lamers (l.c.) obtained an orange-red pp. which dried in an exsiccator to a brown amorphous mass containing S and I in the ratio S.I..

By subliming SnS₂ with I, Schneider (J. 1860. 186) obtained a compound to which he gave the composition SnSI₂.SI₂.

Sulphur, iodochloride of, SICl, (= SCl, ICl₃) v. Sulphur tetrachloride, Combinations No. 2.

Sulphur, oxides of. Four compounds have been isolated; S₂O₃, SO₂, SO₃, and S₂O₄. S and O combine directly to form SO₂ and SO₃; S dissolves in SO₃ to form S₂O₃; S₂O₃ is formed by the action of an electric discharge on a mixture of SO₂ and O, or SO₃ and O.

SULPRUR SESQUIONIDE S₂O₃ (Hyposulphurous anhydride). The production of a blue substance, on distilling funing H₂SO₄ and S, was noticed by Buchholz in 1804 (Gehlen's J. 3, 7); Vogel, in 1812, obtained the blue body by bringing together S and SO₃ (S. 4, 121); the substance was examined by Wach (S. 50, 1), Berzelius (Lehrbuch [5th edit.] 1, 485), and Stein (J. pr. [2] 6, 172). Weber, in 1875, isolated the compound and found its composition to be S₂O₃ (P. 156, 531).

S₂O₂ is prepared by adding well-dried flowers of sulphur, little by little, to SO₂ quite free from H₂SO₄, more S being added when the previous quantity has all combined. The process is conveniently conducted in a test tube, covered with a small porcelain crucible to exclude moisture, and plunged into water cooled to c. 12°; the S disappears in the SO₂ and blue drops are formed; the tube should be tilted so that the blue drops come into contact with the sides of the tube where they form a thin crust (if the drops solidify as they float in the SO₂, the solid S₂O₂ retains SO₃, from which it cannot be freed). When c. 1g. S has been added, excess of SO₄ (which should be colourless) is poured off, the last traces being removed by gently and carefully warming not above 35°; the solid S₂O₂ is seraped out of the tube by a glass roal

(which should be colourless) is poured off, the last traces being removed by gently and carefully warming not above 35°; the solid \$,0, is scraped out of the tube by a glass rod.

\$\(\text{S}_2\text{O}_2\) is a blue-green solid, consisting of a mass of microscopic crystals. Insoluble pure \$\text{S}_0\text{, if a little \$H_SO_1\) is present the \$S_0\text{, dissolves to a deep-blue liquid. Melts with decomposition; decomposes slowly in dry air, quickly on heating, to \$\text{S}_0\text{ and \$S}; deliquesces in moist air to a brown liquid from which \$S\text{ soon separates; reacts violently with water, giving \$H_SO_4\text{A}, \$H_S^2_0\text{Aq}, \$P_0\text{Aq}, \$P

S.O. may be regarded as the anhydride of H.S.O.; although the acid has not been ob-

tained from the oxide, nor the oxide from the acid.

For the compounds SSeO, and STeO, v. Sclenion thio oxide (p. 441) and Tellurium thio oxide (under Tellurium oxides).

SULPHUR DIOXIDE SO. (Sulphurous oxide. Sulphurous anhydride. Thionyl oxide.) Mol. w. 63-9. Melts at c. -76° (Faraday, T. 1845. 155); c. -80° (Mitchell, A. 37, 356). Boils at c. -10³ (Bunsen, P. 46, 97; Andréeff, J. 1859; Pictet, C. C. 1877. 81). S.G. (liquid) 1-4911 at -20-5°, 1-4384 at -2-20-8°, 1-4252 at +2-28°, 1-363 at 20°, 1-3258 at 38-65° (Andréeff, A. Ch. [3] 56, 317); 1-4338 at 0°, 1-2872 at 52°, 1-1845 at 82-4°, 1-1041 at 102-4°, 956 at 130-3°, 7317 at 151-75°, 52 at 156° (Cailletet a. Mathias, C. R. 104, 1563). S.G. (gas at 0° and 760 mm.) 2-2639 (Leduc, C. R. 117, 219). V.D. 32-23 (Gay-Lussac, Berzelius, Buff; Biltz, B. 21, 2769). S.H. (equal wt. water = 1) -1544; (equal volume air = 1) -3414 (Regnault, J. 1863, 84). Ratio of S.H. constant pressure to S.H. constant volume = 1-2562 (Müller, W. 18, 94). C.E. -00423 for 1° between 0° and 10°, 004005 10° to 20°, 003686 at 50°, 003757 at 160°, 003765 at 150°, 003795 at 200°, 003686 at 250° (Amagat, C. R. 73, 183; cf. C.R. 68, 1170). Leduc (C. R. 117, 219) gives C.E. between 0° and 20° as 00396. For C.E. of liquid SO₂ v. Drion (A. Ch. [3] 56, 5) and Andréeff (A. 110, 1). The

ratio PV >1; Amagat (l.c.) gives these values,

1.0185 at 15°, 1.0110 at 50°, 1.0054 at 100°, 1.0032 at 150°, 1.0021 at 200°, 1.0016 at 250°. II.F. [S,O²] = 71,070 from solid rhombic S; 71,720 from solid monoclinic S (Th. 2, 247). Heat of liquefaction of gaseous SO₂ = 5644 (Favre, A. Ch. [5] 1, 209). Critical temperature = 156° (Caillett a. Mathias, C. R. 104, 1563); 155·4° (Sajotscheffski, P. B. 1879. 741); 157°—161° (Ladenburg, B. 11, 821). Heat of vaporisation of liquid SO₂, at 0°, = 91·2, at 60° = 60 (C. a. M., l.c.; cf. Chappuis, C. R. 104, 897). Regnault (C. R. 50, 1063) gives vapour pressures as follows:

Temp.		Temp.	Vap. pressure	
- 25° - 20 - 10 0 + 10	373·79 mm. Hg 479·46 " 762·49 " 1165·06 " 1719·55 "	30° 40 50 60	3131·80 mm. Hg 4670·23 ", 6220·01 ", 8123·80 ",	•
20	2462.05 ,,	-	,, ,, ,,	

Vapour-pressure at critical temp. = 78-9 atmos. (Sajotscheffski, P.B. 1879. 741). \bullet S. in water between 0° and 20° (gaseous SO₂) = 79-789 - 2-60774 + 029349 t^* ; 1 vol. of the saturated SO₂Aq contains 68-861 - 1-87025t + 01225 t^* vols. SO₂; S. (water) between 21° and 40° = 75-182 - 2-1716t + 01903 t^* ; 1 vol. of the saturated SO_AQ contains 60-952 - 1-3889t + 0072 t^* vols. SO₃ (Bunsen a. Schönfeldt, A. 95, 2). S. in alcohol, at 760 mm. = 328-62 - 16-95t + 3119 t^* ; S.G. of solution = 1-1193t - 014091t + 00025 t^* (Carius, A. 94, 148). Sims (C.J. 14, 1) gives the table on the next page, which presents both the weight of SO₂ in grams and the volume of gaseous SO₂ in c.c. dissolved by unit weight of water at the normal pressure and different temperatures:

	Grams SO.	. o.c. SO,		
Temp.	absorbed by 1 g., vater			
8°	·168	58· 7		
12	.142	49.9		
16	·121	42.2		
20	·104	36.4		
24	.092	32.3		
28	.083	28.9		
82	.073	25.7		
86	.065	22.8		
40	.058	20.4		
44	.053	18.4		
48	.047	16.4		
60	•045	15.6		

The quantity of SO₂ dissolved by a given weight of water varies with pressure, and only at c. 40° and upwards is the quantity proportional to the partial pressure of the gas (v. Sims, C. J. 14, 1). For S.G. and composition from 5 to 10 p.c. of SO₂Aq v. Anthon (C. C. 1860, 744); also Giles a. Schearer (S. C. I. 4, 303). [SO²/3Aq] = 7,700 (gaseous SO₂) (Th. 2, 249); 1500 (liquid SO₂) (Berthelot, C. R. 96, 142, 208; Chappuis, A. Ch. [2] 19, 21). H₂SO₂Aq absorbs the following quantities of gaseous SO₂ (Kolb, D. P. J. 209, 270; cf. Dunn, C. N. 43, 121; 45, 270):—

B.G. H.SO.Aq	Kilos, SO ₂ per kilo, acid	litres SO, per litre acid
1.841	.009	5-8
1.839	.014	8.9
1.540	.021	11.2
1.407	.032	15.9
1.227	.068	29.7

SO₂ is absorbed by charcoal; 1 c.c. charcoal = 1·57 g. was found by Favre (A. Ch. [5] 1, 209) to absorb 165 c.c. SO₂. Camphor absorbs c. 308 times its vol., glacial acetic acid c. 318 times, SO₂Cl₂ c. 187 times, its volume of SO. (Schulze, J. pr. [2] 24, 168; Bineau, A. Ch. [3] 34, 326). $\mu_{\rm Na}=1\cdot35$ at 15° (Bleckrode, Pr. 37, 359). For surface tension of liquid SO₂ v. Clark (C. N. 38, 294; 40, 8). For absorption-spectrum v. Liveing a. Dewar (C. N. 47, 121).

Occurrence.—In volcanic gases, and in river and spring water near volcanoes (v. Ricciardi, G. 18, 38).

Formation.—1. By burning S in O. Baker (Pr. 45, 1; C. J. 47, 349) found that the combustion of S in O is retarded the drier the O is; using very carefully dried O there was no flame. According to Hempel (B. 23, 1456) c. 2 p.c. of the gas formed when S is burnt in O at the ordinary pressure is SO₃, 98 p.c. being SO; at a pressure of 40°-50° atmos. c. half the S is burnt to SO, and half to SO; at higher pressures c. 70 atmos. the proportion of SO, increases.—2. By heating S with oxide of Pb, Mn, Hg, Zn, Xc.—3. By heating various sulphates with S, also SO, with S, or cone. H, SO, with C, Cu, Hg, or S; by heating Na, SO, with charcoal and BiO₂.—4. By the decomposition, by acids, of alkali thiosulphate or polythionate solutions.—5. By burning H,S, CS, and various organic compounds containing S.—6. By decomposing cone. H, SO, by heat.—7. By the action of electric sparks on a mixture of sulphur with CO, NO, or N,O (Chevrier, C. R. 69, 136).

Preparation. -1. Pure H.SO, mixed with half to two-fifths its volume of water, is heated with pure Cu; the SO, that comes off is passed through water in a large flask, and then through a couple of bottles filled with pumice, broken into small pieces and moistened; the pumice should be twice moistened with pure H.SO, and heated to redness before being used, to remove chlorides and fluorides (Stas, Chem. Proport. chlorides and fluorides (Stas, Chem. Proport. 115). The SO₂ may be dried by passing it through pure conc. H₂SO₄, and then over CaCl₂.—2. A mixture of 3 parts pure CuO and 1 part S in powder is heated in a tube of hard glass; the anterior part of the tube contains CuO only, to oxidise S that may subline (Marchand, P. 42, 114).—3. Neumann (R. 20, 1584) obtains a require stream of any (B. 20, 1584) obtains a regular stream of ap-(B. 20, 1964) obtains a regima sardam of approximately pure SO₂ by placing a mixture of three parts CaSO₃ and 1 part CaSO₄, made into small cubes, in a Kipp's apparatus, and decomposing by ordinary oil of vitriol. The acid should be allowed to come into contact with sufficient cubes, and no more, to give the stream of gas that is required. Using c. 500 g. of the cubes, N. obtained a constant stream of SO₂ for 30 hours. The cubes are made by mixing the CaSO, and CaSO, moistening with water so that a semi-solid mass is obtained that can be worked with the fingers with some difficulty, pressing this in an iron mortar, hammering it into an iron frame c. 10-12 mm. in height, covering with oilcloth and pressing strongly, cutting into cubes while still in the frame, removing and drying at c. 20° (v. Winkler, B. 20,

Properties.—A colourless gas, at ordinary temperatures and pressures, with the strong penetrating, choking odour of burning S; causes coughing and blood-spitting if inhaled in any quantity. Incombustible in air, and extinguishes flame; when mixed with O and passed over heated spongy Pt it is oxidised to SO₃. Dry SO₃ is said not to redden litmus paper (Wilson, C. J. 1, 332). Bleaches many vegetable colours; the colours are generally restored by alkalis. Bad conductor of electricity (v. Bleekrode, P. M. [5] 5, 375, 439). Is not decomposed by passing through a red-hot, tube. Condensed at c.—10° under the ordinary pressure—by passing the dry gas into a tube surrounded by a mixture of snow and salt; may also be condensed at the ordinary temperature by evolving the gas (by warming charcoal saturated with SO₂, or a mixture of 1 part S and 5 parts SO₃ in one limb of a closed tube, the other limb being placed in cold water. Convenient apparatus for fiquefying SO₃ is described by Wohler (4. 137, 371) and Hofmann (B. 2, 262).

(B. 2, 262).

Liquid SO, is a colourlyss, mobile liquid. Exposed to air it evaporates very rapidly, with disappearance of much heat; an air thermometer placed in liquid SO, at 10°, in an open vessel, falls to -57°. Liquid SO, dissolves P, S, I, Br, and many gums. It is miscible in all proportions with liquid SO,; partially miscible with CS₂, Et,O, CHCl₃, and C,Ia, on warming; but immiscible with conc. H₂SO, (Sestini, Bl. [2] 10, 226). Liquid SO, is a n-on-conductor of electricity (Magnus, P. 104, 532).

By evaporating liquid SO, r'apidly in an airpump, part of it solidifies to a white, woolly

mass: the liquid may also be solidified by placing it in a mixture of solid CO, and ether.

Reactions and Combinations.-1. SO, is not decomposed by passing through a red-hot tube. But by heating to c. 1200° it is changed to SO. and S (3SO. = 2SO. + S); the action stops when the SO₂ attains a certain vapour pressure, but if the SO₂ is removed (by conc. H₂SO₄) the whole of the SO₂ is decomposed (Deville, C. R. 60, 317). Induction sparks effect the decomposition of SO, to SO, and S (v. Buff a. Hofmann, A. 113, 129); light acts similarly (Morren, C. R. 69, 397).—2. H₂O and S are produced by passing SO, mixed with hydrogen through a red hot tube.—3. Ohlorine combines with SO₂, in sunlight, to form SO₂Cl₂ (v. SULPHURYL CHLORIDE). SO₂Cl₃ is also formed by passing SO₂ and Cl into glacial acetic acid, even in the dark; also by passing SO₂ over charcoal saturated with Cl (Melsens, C. R. 76, 92),—4. Ozone produces SOs; the same compound is formed by passing SO₂ mixed with oxygen over heated spongy Pt, or by burning SO₂ in O under a pressure of several atmos. (v. supra; Formation, No. 1). According to Berthelot (A. Ch. [5] 12, 463), S.O. is formed by the action of the silent discharge on SO₂ mixed with oxygen. The compound S2O, N2 is said to be formed by passing electric sparks through a mixture of SO₂ and air. This compound is probably S₂O₅(NO₂)₂ (v. NITROSULPHONIC ANHYDRIDE, p. 601). -5. Passed over red-hot carbon the products are CO, CO, and S; COS and CS2 are also sometimes formed, probably by secondary reactions (Scheurer-Kestner, C. R. 114, 296; cf. Berthelot, Bl. [2] 40, 362; Eilsart, J. 1885. 457).—6. Potassium burns when heated in SO., giving K₂SO₄, K₂S₂O₃, and polysulphides.—7. Many other *metals*, especially when in fine powder, burn in SO2; Sb and Sn form oxides and sulphides; Fe, sulphide and sulphate; Pd and Pt, sulphides and SO3; Au, sulphate; Fa and Ft, sulphates and SO₃, I.a., S and SO₃; Mg, sulphate, sulphite, and sulphide; Al, Co, Ni, and Zn also burn; Bi and Hg do not react (Schiff, A. 67, 94; 117, 92; Uhl, B. 23, 2151).—8. Water dissolves SO₂, 9. Several metallic peroxides combine readily with SO, forming sulphates; e.g. PbO₂+SO₂ = PbSO4; in this reaction much heat is produced .- 10. Nitrogen dioxide is said to react ausea.—10. Nurogen aboxase is said to react with liquid SO, to form nitrosulphonic anhydride S₂O₅(NO₂)₂ (v. p. 601). With nitric oxide or dioxide, in presence of water, nitrosulphonic acid NO₂(SO₂OH) (q. v., p. 601) is formed. Nitric oxide in presence of alkali produces salts of SO₂OH(NO)₂H (v. NITROSOSUL-PHATES, p. 581).—11. Selenion dioxide does not react with SO (Schulze J. gr. [2] 32 not react with SO₂ (Schulze, J. pr. [2] 32, 890). -12. Dry hydrogen sulphide does not react; moist H₂S, at the ordinary temperature, produces H₂S, O₄, S, and H₂O (Cluzel a. Schmid, Chem. Zeitung, 11, 50); there is said to be no reaction in presence of water above 400° (Mulder, J. 1858. 84).—13. Phosphoretted hydrogen reacts at the ordinary temperature to form H₂O and P₂S₄ (C. a. S., l.c.).—14. Ammonia combines with SO₂ probably producing SO₂,NH₂ (= SO.OH.NH₂) and SO₂2NH₂ (= SO.ONH₂,NH₂) (v. Thionamio acid).—15. Hydrochloric or hydriodic acid produces H₂O, S, and Cl or I.—16. Many oxysails, e.g. nitrates and chlorates, react with

SO₂, when heated, to form sulphates and Noxides; at higher temperatures SO₃ is sometimes produced (v. Hodgkinson a. Young, C. N. 66, 199).—17. Alkali nitrites yield salts of nitrilosulphonic acid N(SO,OH), (q. v., p. 601), and salts of oxy-imidosulphonic acid N(OH)(SO,OH), (q. v., p. 602).—18. Combines with aluminium chloride at 50°-60°, forming AlCl. SO, which gives off SO, at a higher temperature (Adrianoffski, B. 12, 688). - 19. Phosphorus pentachloride produces POCl, and SOCl, (Kremers, A. 70, 297; Schiff, A. 102, 111).

SULPHUR THOMBS SO. (Sulphuric oxide. Sulphuric anhydride.) Mol. w. 79:86. Melts at 14:8° (Weber, B. 19, 3189; Rebs, A. 246, 356). Some other observers have given m.p. as high as 20.5° (v. Buff, A. Suppl. 4, 129; Bussy, A. Ch. [2] 26, 411; Fischer, P. 16, 119; Marignac, A. 88, 230). Boils at 46.2° (Weber, l.c.; v. also Buff, l.c.; Fischer, l.c.; Schultz-Sellack, P. 139, 480). S.G. 1.94 at 16° (Weber, Lc.); 197 at 203 (Bussy, Lc.); 19086 at 253 (Buff, Lc.). V.D. 3978 (Schultz-Schack, P. 139, 480; Perman, Pr. 48, 45). H.F. [S,0³]=103,240 (liquid SO, from solid S; Th. 2, 254); [SO³, O]=32,160 (liquid SO, from gaseous SO²; Th., l.c.); [SO³, Aq]=39,170 (liquid SO₃; Th., l.c.). For heat of vaporisation v. Berthelot (C. R. 90, 1510). Schultz Sellack gives vapour-pressure at 20° as 15°2 mm. Hg (P. 139, 480).

Formation.—1. By the interaction of ozone and SO.. Also by the action of an induction

current on a mixture of SO₂ and O₂ (Buff a. Hofmann, A. 113, 129; Deville, Bl. [2] 3, 366); Berthelot (C. R. 86, 20) says that the product is S.O .. -- 2. By burning S in O under a pressure of several atmos. (v. Sulphur Dioxide, Formation Nc. 1). Also by heating pyrites (Scheurer-Kestner, G. R. 99, 917; Lunge, B. 10, 1824). 3. By passing a mixture of SO, and O over heated Pt (Phillips a. Magnus, P. 24, 610), spongy Pt (Hodgkinson a. Lowndes, C. N. 57, 102) 193), or certain oxides, e.g. Fe₂O₃, GuO, Gr₂O₃ (Mahla a. Wöhler, A. 81, 255).—4. By heating certain sulphates or bisulphates, c.g. Fe2(SO4), Bi₂(SO₄)₃, Ag SO₄, or NaHSO₄.—5. By distilling Nordhausen sulphuric acid (v. Osann, D. P. J 151, 158); also by heating conc. H,SO, with P,O, (Barreswil, C. R. 25, 30; Evans, Ph. 8, 127).

Preparation.—1. Fuming sulphuric acid is

heated at as low a temperature as possible; the impure SO, is collected in a dry retort and redistilled once or twice, the most volatile portion being collected each time. The partially purified SO, is then distilled into a small tube, c. 8-10 mm. wide and about the length of a finger, containing some dry P.O.; this tube is narrowed at one end and fused on to a thick-walled tube c. 1-1.5 mm. wide, which is bent round and fused to a receiving tube c. 12-15 mm. wide and 300 mm. long; the tube containing the SO₃ and P₂O₅ is heated in a water-bath to 90°-100° for 6 or 8 hours, the receiving true projecting upwards, so that the distillate flows back again into the distilling-tube. The position of the apparatus is then changed, so that the receiving tube is lower than the distilling tube, and the SO is distilled from the P₂O₂ on a water-bath. When sufficient SO, has been collected, the narrow connecting tube is fused off, and the SO, is kept in the sealed receiving tube (Weber, B. 19, 3189).— 2. A mixture of SO₂ and O, in the ratio SO₂:O, is passed over platinised asbestos beated nearly to redness; the SO₂ is condensed in a small dry tube, in which it is sealed up. The mixture of SO₂ and O is obtained by strongly heating cone. H₂SO₂ and removing H₂O (H₂SO₄ + H₂O + SO₂ + O) by cooling and passing through coke moistened with 60 p.c. H₂SO₄Aq (Winkler, D. P. J. 218, 128). The asbestos is platinised by soaking in PtCl₁Aq made alkaline by soda, and mixed with sufficient HCO₂Na to reduce the Pt, drying at 100°, carefully washing out the salts with water, and drying (Thomsen, B. 3, 496). The SO₃ thus obtained is not quite pure. It may be purified by distillation with P₂O₃ (v. supra).

Properties.—A colourless, mobile liquid, so-

Properties.—A colourless, mobile liquid, solidifying at c. 15° to long, prismatic, transparent crystals, which melt at 14.8°. According to some observers (v. Marignac, Ar. Ph. 22, 225; 58, 228; Schultz-Sellack, P. 139, 480) the crystals of SO, slowly change to a mass of tough, opaque, lustrous needles, which melt above 50°, and constitute a distinct modification of SO, is but the experiments of Weber (P. 139, 480; B. 19, 3187; cf. Rebs, A. 246, 356) have shown that pure SO, exists only in one form, and that the substance with higher mp. is formed by the action of traces of H₂SO₄ in the SO₃; a small trace of moisture suffices to cause the gradual change. SO₄ is very acrid and poisonous; it chars paper, wood, and organic matter generally. SO₃ is extremely hygroscopic; it dissolves in water with a hissing sound and production of much heat ((SO³,Aq) = 39, 170), forming H₂SO₄Aq. Non-conductor of electricity (Magnus, P. 104, 558); not decomposed by electric sparks, but by passing through a red-hot tube gives SO₂ and O. SO₄ does not redden dry litmus. It is a strongly said-forming exide. Surehum care surface and surface surface and constitute surface and constitute and constitute surface and constitute surfac

acid-forming oxide (v. Sulphuric acid).

Reactions and Combinations.—1. Heated to redness (by passing through red-hot tube) gives SO₂+O.—2. Not decomposed by electric sparks (Magnus, P. 104, 553); electrolysis of SO₃ in H.SO₃ causes separation of S and O, and the solution becomes blue (Geuther, A. 109, 129).—3.

**Water reacts violently with SO₃ forming H.SO₄Aq (v. Sulphuric acid).—4. Hydrogen sulphide produces H.SO₃ and S.—5. A mixture of SO₃ and oxygen, in the ratio 2SO₃:O₃ forms S₂O₃ when submitted to the silent electric discharge (Berthelot, A. Ch. [5] 14, 345).—6. Sulphur dissolves in SO₃ forming S₂O₃; selenion and tellurium react similarly (v. Sulphur HIDO-OXIDS, BELENION THIO-OXIDS, And TELLURIUM THIO-OXIDS, PRICENION THIO-OXIDS, Torming P.O₃ and S.—8. Iodine dissolves in SO₃, apparently forming several compounds (v. Wach, S. 50, 37; Schultz-Sellack, B. 4, 109), Weber (J. pr. [2] 25, 224) describes the compounds I(SO₃), I(SO₃), and L(SO₃).—9. Iron and sinc react at red heat to give sulphides and coides; mercury produces sulphate and SO₄ (d'Heureuse, P. 75, 255).—10. Several metallic sulphides—e.g. of Sb, Pb, K.—form sulphates and SO₂ when heated with SO₃ (Weber, P. 130, 329).—11. Dry sulphur dioxide is absorbed by SO₂ at O', forming a thin, tuming liquid, approximately SO₂-2SO₂ (H. Rose, P. 89, 178), According to Schultz-Sellack, liquid SO₂ and SO₃ are miscible in all proportions (P. 189, 480).

(v. Selenion divide, Combinations, No. 4, 3, 441).—18. Nitric oxide, in absence of moisture, and O, forms S₂O₂N₂, which is generally called nitrosulphonic anhydride (q. v., p. 601) and written S₂O₂(NO₂)₂. Nitrogen dioxide (made by heating Pb(NO₂)₂) seems to form SO₂, NO₂, and on heating this and passing in more NO₂, O is given off and the compound S₂O₂N₂ remains (v. Weber P. 128, 337. Briging A. 98, 877). Weber, P. 123, 337; Brüning, A. 98, 377). The formula of the first of these compounds is generally doubled, and the compound regarded as $S_0 t_* O_* (NO_3)_2 = oxynitrosulphonic anhydride (q. v., p. 601); the second is described in some books as <math>S_0 O_1(NO)_2$ and is called nitrosyl pyrosulphate, but from the descriptions of Weber and Bruining it is evidently the same as the compound $S_1 O_2 N_2$ formed from NO and SO_3 , i.e. it is nitrosulphonic anhydride.—14. SO_3 combines with iodine pentoxide to form $SO_3 I_* O_3$ and $SO_3 \cdot S_1 O_3$ (Weber, B. 20, 86; Kämmerer, J. pr. 83, 72). With phosphorus pentoxide $SSO_3 \cdot P_2 O_3$, decomposing at $SO_3 \cdot SO_3 \cdot O_3 \cdot O_3$ and $SO_3 \cdot SO_3 \cdot O_3 \cdot O_3$ generally doubled, and the compound regarded oxide forms various unstable compounds (Adie. C. J. 55, 167; cf. Weber, B. 19, 3185; Schultz-Sellack, B. 4, 109; Reich, J. pr. 90, 176; Schafhaütl, B. J. 22, 113; and Pearce, Z. K. 20, 632). According to Baker (C. J. Proc. 1893. 130), dry SO, does not react with dry oxides of 130), dry SO₃ does not react with dry cxides of barrium, calcirum, or comper.—15. The compound SO₂.N.O₃.5H.SO₄ is said to be formed by passing SO₃ into pure, well-cooled, nitric acid (Weber, P. 123, 233; 142, 602).—16. Boric acid forms BH.O₂.8SO₃ [=B(HSO₄)₃] (D'Arcy, C. J. 55, 155; cf. Merz, J. pr. 99, 81; Schultz-Sellack, B. 4, 15).—17. Hydrobromic and hydriodic acids reported Broad Land town HSO₂ acid SO₂ separate Br, and I, and form H2SO, and SO2 --18. Hydrochloric and hydrofluoric acids form Cl(SO₂OH) and F(SO₂OH) (v. CHLOROSULPHONIO ACID, p. 599; and FLUOSULPHONIC ACID, p. 600). 19. Conc. sulphuric acid forms H,S_QO, (v. PYNO-SULPHURIC ACID, p. 625).—20. Ammonia produces NH₄(SO₂.OH) and salts of this acid (v. SULPIRMIC ACID AND SALTS, p. 567); and also salts of NH(SO₂.OH), (v. IMIDOSULPHONIC ACID AND SALTS, p. 600).—21. Phosphoretted hydrogen produces SO₂ and red P (H. Rose, P. 24, 140; Aimé, J. pr. 6, 79).—22. Phosphorus trichloride reacts violently, forming POGl, and SO₂ (Armstrong, B. 3, 732; Michaelis, J. Z. 6, 239). Phosphorus pentachloride produces pyrosulphuryl chloride S,O,Cl. (q. v. under Sulphur oxyglicheries, p. 617).—23. Boron chloride reacts at c. 120° to form S,O₃Cl₂ (Prudhomme, Bl. [2] 14, 385).—24. Nitrosyl chloride (produced by heating aqua regia) produces SO₂NOCl = NO₃(SO₂Cl) (v. NITROSULPHONIC GHLORIDE, p. 601).—25. Pyrosulphuryl bromide S,O₃Rr; (q. v., p. 617) is perhaps formed by the reaction 19. Conc. sulphuric acid forms H2S2O, (v. PYRO-(q, v., p. 617) is perhaps formed by the reaction of bromoform with SO₃.—26. Selenion tetrachloride produces SSeO₂Cl₄ (v. Selenion Thio-OXYCHLORIDE, p. 441).

SULPHURIO PEROXIDE S₂O₂. (Sulphur heptoxide. Persulphuric anhydride.) Mol. w. not known with certainty but probably 176-68 (S₂O₂). This oxide was prepared by Berthelot in 1877: (A. Ch. [5] 14, 345) by passing the 'silent' electric disoharge, for several hours, through a mixture of SO₂ and O in the ratio 2SO₂:0, or of SO₂ and O in the ratio 2SO₂:8O. (For apparatus used *e. B., A. Ch. [6] 12, 468.) Oily drops.

formed on the sides of the tube, and on redusing the temperature nearly to 0° they solidified to long, white, crystalline, needles. S₂O, resembles solid SO, in appearance; it remains schanged in a scaled tube for some days at 0°; when heated it gives SO, and O; dissolves in conc. H.SO, forming a fairly stable solution; fumes in the air; in water it rapidly decomposes forming H,SO,Aq and giving off a brisk stream of O; with BaOAq forms BaSO, and O; and also some Ba persulphate, according to Berthelot (La; no analyses given). By electrolysing H₂SO₄Aq, containing water and acid in the ratio 10H₂O:H₂SO₄, B. (C. R. 90, 269) obtained a quantity of persulphuric acid (H2S2O8; v. under Sul-PHURIC ACID, p. 625) equal to from 88 to 123 g. S₂O₂ per litre; using an acid of the concentra-tion H₂SO₄:2H₂O to II₂SO₄:3H₂O₄ B. (*l.c.*) says that a compound S2O, 2H2O2 is formed, which is decomposed by excess of conc. H₂SO₄ chiefly to H₂S₂O₈, and by dilution with water to H₂S₂O₈Aq and H₂O₂Aq which after a time decompose to H2SO, Aq, H2O, and O.

S₂O₇ is the anhydride of persulphuric acid H₂S₂O₈ (q. v., p. 625). Mendelceff (B. 15, 242) regards S₂O₇ as analogous in constitution to

 H_2O_2 , and writes the formula $\begin{vmatrix} OSO_2 \\ OSO_2 \end{vmatrix}$

looks on the corresponding acid as derived from H.O. by replacing 2H by 2SO.OH, thus: O.(SO.OH)

y (20 OH)

According to Traube (B. 22, 1518; 24, 1764; 25, 95), the liquid obtained by electrolysing 40 p.c. H₂SO₄Aq contains an oxide to which he gives the formula SO₄ and calls sulphuryl hyperoxide (or holoxide), SO_{...}O₂. Traube did not isolate this compound; his argument for its existence is based on the results of indirect analyses. In the light of the criticisms of Carnegie (C. N. 64, 158) it may be concluded that the existence of SO₄ is extremely improbable. In a later communication (B. 26, 1481) Traube thinks it is probable that SO₄ does not exist.

Sulphur, oxyacids of. For compositions of these acids, and references to articles where they are described, v. Sulphur, oxyacids of (p. 610)

Sulphur, oxyacids of, nitrogen derivatives of. For a general statement regarding these compounds, and roferences to the articles where they are described, v. Sulphub oxyacids, NITHOGEN DERIVATIVES OF (p. 619).
Sulphur, oxybromides of. There is very

Sulphur, oxybromides of. There is very little definite knowledge regarding the compounds of S, O, and Br. According to Michaelis (J. Z. 6, 239, 296) PBr, does not react with SO, and a mixture of PCl, and Br (in the ratio PCl, Br.) produces POCl, and S bromides. Rose (P. 44, 327) and Clausnizer (B. 11, 2012) could not obtain an oxybromide by the reaction of SO, and S bromide, nor by the action of SO, and HBr.

In his memoir on S₂O₂Cl, prepared by the reaction of SO₂ with CHCl₂, Armstrong (B. 2, 712) at that CHBr₂ reacts with SO₂ similarly to CHCl₂, but he does not describe the product. If the reaction of CHBr₂ with SO₂ is strictly similar

to that of CHCl, the product would be pyrosulphuryl bromide S.O.Br.. Odling (C. J. 7, 2) supposed that sulphuryl

Odling *C. J. 7, 2) supposed that sulphuryl oxy-bromide SO,Br, was formed by the action of sunlight on SO, and Br, but Sestini (Bl. [2] 10, 226) and Melsens (C. R. 76, 92) failed to obtain an oxybromide by this method.

THONYL BROWIDE SOBL. This compound was obtained, but not quite free from S bromides, by Hartog a. Sims (C. J. Proc. No. 118, 1898.

10) by the interaction of SOCL and NaBr; it is described as a very hygroscopic, orimson liquid, S.G. 268 at 18°, decomposing at 150° to Br, S bromides, &c.

Sulphur, oxychlorides of. Five compounds have been isolated, SOCl., SO₂Cl., S₂O₂Cl., S₂O₂Cl., and S₂O₄Cl.

THONUL CHLORIDE SOCI, (Sulphurous oxy chloride). Mol. w. 118-62. Boils at 78-8°; S.G. & 1-67673, S.G. at b.p. 1-52143 (Thorpe, C. J. 37, 354; for other data v. Carius, A. 106, 303; 111, 93; Wurtz, C. R. 62, 460). V.D. at c. 150° = 56; at c. 440° = 39 (Heumann a. Köchlin, B. 16, 1625). H.F. [S.O.Cl²] = 40,800; heat of vaporisation = 6,480 (Ogfer, C. R. 94, 82). S.V. 78-01 (Thorpe, L.).

Formation.—1. By the reaction of PCl, with SO₂ (Kremers, A. 70, 297; Schiff, A. 102, 111), SO₂Cl., C,H₂,SO₂Cl, and several other organic compounds containing S (v. Kekulé a, Barbaglia, B. 5, 875; Carius, J. pr. [2] 2, 262), sulphites, or thiosulphates; also by the reaction of POCl₃ with sulphates.—2. By the action of Cl₂O on CS₂, or on S in S₂Cl₂ at -12° (Wurtz, C. R. 62, 460).—3. By the interaction of SO₂ and SCl₁ (Michaelis a. Schilferdecker, B. 5, 924; 6, 993).—4. Along with SO₂Cl₂ by the gradual decomposition of S₂O₄Cl₄ (r. v. p. 619).

Preparation. -1. About 100 g. dry PCl, are placed in a retort connected with a reversed condenser, and a stream of dry SO, is led in till the PCI, has liquefied; another 100 g. PCI, is added and the stream of SO, is continued; when sufficient PCl, has thus been decomposed (PCl₅ + SO₂ = SOCl₂ + POCl₃) the liquid is heated for some time (the reversed condenser being still attached) to get rid of SO., and then fracson attached to get rid 180, and then have tionated repeatedly (SOCI, boils at 78.8° and POCI, at 107.2°) (Carius, A. 106, 303; 111, 98; Wurtz, A. 139, 375; Michaelis, A. 170, I Thorpe, C. J. 37, 354.—2. S.C.I is placed in a small flask, cooled to c. -20°, a stream of dry Cl is led in till the liquid is saturated, and then SO, is distilled into the flask from a solution in conc. H2SO,; the weights of S.Cl. and SO. used should be in the ratio S,Cl,:480, (=1:2:37) convenient quantities to use are 22 g. S.Cl., and 50 g. SO. (SCl. + 2SO. = SOCl. + S.O. Cl.). The liquid is fractionated finally from a small quantity of SO. (Michaelis a. Schifferdecker, B. S. O. C. G. O. C. 5, 924; 6, 993).

Properties.—A colourless, very refractive liquid, fuming in the air, with a very penetrating odour; vapour attacks the eyes and respiratory organs. V.D. 56 at c. 150°, but 39° at c. 440°; the smaller value corresponds with the decomposition 4SOCl₂ = S₂Cl₂ + 2SO₂ + 8Cl₂; these products are obtained by passing vapour of SOCl₂ through a red-hot tube (Heumann a Köchlin, B. 16, 1625).

Reactions and Combinations.—1. Moist air produces HOI and SO₂.—2. Water also forms HOIA4 and SO₂, warm water forming in addition H₂SO₂Aq and S (Garius, l.c.).—3. Hydrogen sulphide produces SO₂, HCl, and S (Prinz, A. 225, 371).—4. Phosphorus pentasulphide reacts to form SO₂, PSCl₃, and S, and some S₂Cl₂ (Prinz, l.c.).—5. With antimony trisulphide the products are SbCl₃, SO₂, and S.—6. Sulphur, heated to 180° with SOCl₂, forms S₂Cl₂ and SO₂; selenion forms S₂Cl₂ and SSeCl₂ (Prinz, l.c.).—7. Powdered antimony reacts without heating, forming SbCl. Reactions and Combinations .- 1. Moist air antimony reacts without heating, forming SbCl, Sb.S., and SO.—8. POCl., PSCl., and PCl., are formed by heating SOCl. with phosphorus trichloride (Michaelis, J. Z. 6, 239).—9. Heating chloride (Michaelis, J. Z. 6, 239).—9. Heating with sulphur dichloride produces S₂OCl, (q. v., p. 619) (Ögier, Bl. [2] 37, 293).—10. Ammonia does not produce thionylamide SO(NH₂)₂, but forms NS, NH₂Cl, (NH₂)₂O₃, and NH₄ polythionates (M., l.c.).—11. Reacts rapidly with silver mitrate, forming NO₂(SO₂Cl) (Thorpe, C. J. 41, 297).—12. SOCl₂ absorbs sulphur dioxide and chlorine freely (M., l.c.).—13. For reactions with various organic convocunds n reactions with various organic compounds v. Michaelis (l.c.); Heumann a. Köchlin (B. 16, 1625); Böttif ger (B. 11, 1407).

SULPHURYL CHLORDE SO₂Cl₂ (Sulphuric oxychloride). Mol. w. 134·58. Boils at 69·95° (Thorpe, C. J. 87, 859; for other determinations v. Regnault, J. pr. 19, 243; Clausnizer, B. 11, 2010; Ogier, C. R. 94, 82). S.G. 20 1.70814; at

b.p. 1-56025 (Thorpe, l.c.). V.D. 65 at 184°, 34 at 440° (Heumann a. Köchlin, B. 16, 602; cf. Regnault, J. pr. 18, 97; Behrend, J. pr. [2] 15, 23). S.V. 86'29 (Thorpe, l.c., p. 372). H.F. [S.O',Cl'] = 89,780; [SO',Cl'] = 18,700 (Th. 2, 810; cf. Ogier, C. R. 94, 82). S.H. (15°-63°) 233 (Ogier, l.c.). Heat of vaporisation 7,060 (O. l.c.).

(O., l.c.).

Formation.-1. By the direct combination of SO, and Cl in sunlight, or by reacting on a mixture of C₂H₄ and SO₂ by Cl in sunlight (Regnault, *J. pr.* 18, 93; 19, 243). Schulze (*J. pr.* [2] 23, 351; 24, 168) recommends to allow SO₂ and Cl to react in presence of camphor. Melsens and Cl to react in presence of camphor. Melsens (C. R. 76, 92) passes SO₂ and Cl into glacial acetic acid.—2. By passing SO₃ over charcoal saturated with Cl (M., l.c.).—3. By the interaction of PCl, with H₂SO₄ or SO₅ (Williamson, P. M. (4) 7, 865; Schiff, d. 102, 111); according to Michaelis (J. Z. 6, 233, 292), SO₃ and PCl₃ form 8₂O₄Ol₂—4. By heating SO₅ and BCl₃, in the ratio 2SO₂:BCl₃, to 120° in a closed tube (Gustavson, B. 6, 9).—5. By heating Cl(SO₂·OH) to a 200° for some time (Behrend, B. 8, 1004; cf. Otto a. Beckurts, B. 11, 2058). cf. Otto a. Beckurts, B. 11, 2058).
Preparation.—1. Cl and SO, are passed into

camphor, and the colourless liquid is fractionated (Schulze, l.c.).—2. Cl(SO₂.OH) (v. Chloro-sulphonic acid, p. 509) is heated to c. 200°, in a closed tube, for some hours, when it decomposes thus, $2[Cl(SO_*OH)] = SO_*Cl_2 + H_2SO_4$; the liquid

thus, $2[\mathrm{Cl}(\mathrm{SO_s,OH})] = \mathrm{SO_sCl_s} + \mathrm{H_sSO_s}$; the liquid is distilled, the portion coming over at 67° – 71° being collected separately and then repeatedly fractionated (Behrend, *l.c.*; cf. Thorpe, *l.c.*).

Properties and Reactions.—A colourless liquid, fuming slightly in air. 1. Decomposed by heating to dull redness into $\mathrm{SO_s}$ and Cl ; decomposition is complete at 440° (Heumann a. Kochlin, B. 16, 602); but does not begin at 250°

(Beckurts a. Otto, B. 11, 2060).—2. Water produces HClAq and H₂SO₄Aq; a small quantity of water is said to form Cl(SO2.OH)Aq. -3. Excess water is said to form U(SO₂, UH)Aq.—8. Excess of SO₂Cl₂ added to a little alcohol forms C((SO₂, OEt); with excess of alcohol SO₄(OEt)₂ is produced (Behrend, B. 9, 1834).—4. Phosphorus pentachloride reacts to form POCl₃, SOCl₂, and Cl (H. a. K., B. 15, 1736).—5. Phosphorus pentachloride and Collaboration and Cl (H. a. K., B. 15, 1736).—5. Phosphorus pentachloride and Collaboration and Colla SUUL, and UI (H. a. K., B. 15, 1736).—5. Phosphorus, arsenic, and antimony produce Pol, AsCl, and SbCl, respectively, and SO, (H. a. K., l.c.).—6. Ammonia forms NH₂Cl and SO₂NH₂ONH₄.—7. With many organic compounds SO₂Cl₂ reacts like PCl₃ or POCl, substituting Cl for H (v. Dubois, Z. [2] 2, 705; Michaelic 4 170 1) Michaelis, A. 170, 1).

PYROSULPHURYL CHLORIDE $S_2O_3Cl_2 = Cl.SO_2.O.SO_2.Cl.$ (Disulphuryl chloride. Pyrosulphuric oxychloride. Chlorosulphoric anhydride.) Mol. w. 214'38. Boils at 139'59' (Thorpe, C. J. 37, 360; for other determinations v. Rose, P. 44, 291; Michaelis, J. Z. 6, 235, 240, 292; Rosenstiehl, C. R. 53, 658; Schützenberger, C. R. 69, 352). S.G. 70 1.85846, at b.p. 1.60610 (Thorpe, l.c.). V.D. at slightly above b.p. = 104; between 160° and 240° = 54.8 (Heun.p. = 104; between 160° and 240° = 54°8 (Heumann a. Köchlin, B. 16, 470; Kanowaloff, B. 16, 1127; cf. Rosenstiehl, C. R. 53, 658; Rose, P. 44, 201; Ogier, C. R. 94, 82, 217; 96, 648). H.F. [S',O',Cl'] = 180,600 (Kanowaloff, l.c.); Ogier (l.c.) gives 159,400. Heat of vaporisation 7,570 (K., l.c.); 13,160 (O., l.c.). S.H. '258

(K., l.c.). Formation.—1. By the interaction of PCl_s and SO_s or Cl(SO₂.OH).—2. By heating P₂O_s and and SO₂ or Cl(SO₂.OH).—2. By heating P₂O₂ and Cl(SO₂.OH) (Billitz a. Heumann, B. 16, 483).—3. By heating SO₃ with NaCl (R., l.c.), with S₂Cl₂ (Rose, P. 44, 291), with CCl₄ (Schützenberger, C. R. 69, 352; Kanowaloff, C. R. 95, 1284), with C₂Cl₆ (Prudhomme, C. R. 70, 1137), with CHCl₄ (Armstrong, C. J. [2] 1, 244), or with SiCl₄ (Gustavson, B. 5, 332).—4. By the interaction of POCl₂ and SOCl₂ (Michaelis, J. Z. 6, 235, 240, 292). 235, 240, 292).

Preparation.-1. P2O3 and Cl(SO2.OH) are heated in a flask with a reversed condenser, using rather more Cl(SO₂OH) than P₂O₃; when HCl and SO₂ cease to be given off, the liquid is distilled, and the portion coming over between 135° and 145° is fractionated (B. a. H., l.c.).— 2. S.Cl2 in a flask is surrounded by a freezing mixture, and saturated with SO; the product is fractionated; $5SO_2 + S_2Cl_2 = 5SO_2 + S_2O_3Cl_2$ (Rose, P. 44, 291). Thorpe (C. J. 37, 360) found that the product of this reaction boiled almost wholly between 135° and 138°.

Properties and Reactions.—A colourless, mobile, very refractive liquid, fuming in the air with formation of Cl(SO₂,OH).—1. Decomposed by heat to SO₂, SO₂, and Cl (Rose, P. 44, 291); the V.D. determinations of Heumann a. Köchlin tne v.D. determinations of Heumann a. Köchlin (B. 16, 479) show that at 440° the decomposition is $S_2O_2O_1=SO_2+SO_2+Cl_2$.—2. Sinks in water, and is slowly decomposed to HClAq and H₂SO₄Aq; if a very little water is used Cl(SO₂OH) is formed, thus $S_2O_2Ol_2+H_2O$ = 2Cl(SO₂OH) (v. B. a. H., l.c.) — 3. Reacts with phosphorus suphus continuous with phosphorus, sulphur, antimony, copper, iron, sinc, and some other metals, to produce chlorides, SO, and SO, (Heumann a. Köchlin, B. 16, 479).—4. Phosphorus trichloride produces

PCl₃, POCl₃, and SO₂; phosphorus pentachloride forms POCl₃, Cl, and SO₂ (Genther, B. 5, 925). S. Selenion tetrachloride gives SSeO₂Cl₃ (Claus-nizer, B. 11, 2010).—6. Chromates react to form CrO₂Cl₂ (Rosenstiehl, C. R. 53, 658).-7. Ammonia forms a white solid, which dissolves in water, producing NH,Cl and a sulphamate of NH, (Rose, l.c.).

SULPHUR MONOXYTETRACHLORIDE S.OCI. heating equal weights of S₂Cl₂ and SO₂Cl₂ to 250° in a scaled tube, Ogier (Bl. [2] 37, 293) obtained a deep-red liquid resembling S₂Cl₂, S.G. 1.656 at 0°, decomposing under 100° to S₂Cl₂, SO2, and S, to which he gave the composition

S₂OCl₄. Decomposed by water to H₂SO₄Aq, SO₂Aq, HClAq, thionic acids, and S.

SULPHUR TRI-OXYTETRACHLORIDE SOLEHUR THI-OXYTETRACHLORIDE SOLEHUR MOI. w. not determined. This compound was obtained by Millon (A. Ch. [3] 29, 327) by the action of moist Cl on S₂Cl₂ (cf. Marchand, J. pr. 22, 507; Carius, A. 106, 295). It is conveniently propared by the reaction SCl₄+Cl(SO₂OH) = HCl+S2O2Cl; a stream of dry Cl is led into a mixture, in the ratio of equal numbers of molecules, of S2Cl2 and Cl(SO2OH), kept at c. - 20°, until a semi-solid mass is obtained (a very wide tube must be used to lead in Cl); the temperature is then kept at c. -13° and the Cl is continued till the mass gets quite solid; the freezing mixture is then removed, and the Cl is continued till the mass is white, when the excess of Cl is removed by a stream of dry CO, (Michaelis a. Schifferdecker, B. 6, 996).

S2O3Cl4 is a white, crystalline solid, with a most disagreeable odour; the vapour acts on the eyes. Melts at 57°, giving off SO, and Cl, the eyes. Ments at or, giving on 1902 and or, and leaving a liquid that solidifies chiefly to SOCl₂ and S₂O₃Cl₂; a portion sublimes in fine white needles. Ice-cold water produces SO₂Aq, H.SO.Aq, and HClAq; water at the ordinary temperature also separates S. Deliquesces in a partially closed vessel, giving off HCl, Cl, and SO₂, and leaving a liquid that gives SOCl₂ and S₂O₃Cl₂ on distillation. Conc. H₂SO₄ reacts violently, forming HCl, SO₂ and Cl(SO₂OH); CS₂ reacts violently, forming HCl, SO₂ and Cl(SO₂OH); CS₂ produces very rapid decomposition to COCl₂, CO, SO₂, S.Cl₂, and SOCl₂. On long standing in a closed tube S₂O₃Cl₄ separates into equal numbers of molecules of SOCl₂ and SO₂Cl₂ (M. a. Mathias, B. 6, 1452).

Sulphur, phosphides of, v. Phosphonus sul-phides, p. 145.

Sulphur, selenides of, v. Selenion sul-purdes, p. 442. Sulphur, silicides of, v. Silicon sulphides,

Sulphur, tellurides of, v. Tellurium sul-

M. M. P. M. PHIDES, p. 655. SULPHUR, OXYACIDS OF. Several acids have been isolated, and salts of some others are known. The following list gives the names and compositions of the oxyacids of sulphur and their salts, with references to the articles where these compounds are described :-

HYPOSULPHUROUS ACID AND SALTS H2S2O4 and M.S.O.; v. Hyposulphurous acid under Sulphurous Acid (p. 627), and hyposulphites under Sul-

ритив (р. 592).

SULPHUBOUS ACID AND SALTS H2SO, MHSO, and M.SO.; v. SULPHUROUS ACID (p. 626), and Виденетая (р. 587).

SULPHUBIC ACID AND SALTS H,SO, MHSO, and M2SO4; v. Sulphuric acid (p. 620) and Sulphares (p. 567).

THIOSULPHURIO ACID AND SALTS $H_2S_2O_2$, MHS_2O_3 , and $M_2S_2O_3$; v. THIOSULPHURIO ACID (p. 708) and THIOSULPHATES (p. 705).

THIONIC ACIDS AND SALTS H.S.O., H.S.O. $H_2S_1O_6$, $H_2S_3O_6$ (and salts); v. Thionic acids (p. 698) and Thionates (p. 695).

Pyrosulphuric acid and salts H.S.O., MHS.O., and M.S.O.; v. Pyrosulphuric acid under Sulphumo Acid (p. 625), and Pyrosulphates under Sulphates (p. 583).

PERSULPHURIC ACID AND SALTS H.S.O.Ag. M.S.O., and MS.O.; v. Persulphuric acid under Sulphuric acid (p. 625), and Persulphates under Sulphates (p. 582). M. M. P. M.

SULPHUR OXYACIDS, NITROGEN DERI-VATIVES OF. In 1845 Fremy (A. Ch. [3] 15, 408) described the K salts of a number of acids obtained by the interaction of KNO,Aq and K,SO,Aq, and by boiling the products of this interaction with slightly acidified water; he called the compounds salts of sulphazotised acids. The examination of these salts was prosecuted by Claus a. Koch (A. 152, 336 [1874], and by Claus (A. 158, 52, 194 [1876]); Berglund (Bl [2] 25, 455; B. 9, 252, 1896 [1875]); and Raschig (A. 241, 161; B. 20, 584 [1887]) also investigated the sulphazotised acids of Fremy; and the researches of Divers and Haga (C. J. Trans. 1885, 1886, 1889, 1892) have thrown much light on many classes of these compounds. The more recent investigations noted above have shown many of the formulæ given by Fremy to be inaccurate, and they have also led to a considerable revision of Claus's results. As the compounds that have been fairly thoroughly examined are noticed under the heading Sulphonic ACIDS AND DERIVATIVES (p. 509), it does not seem necessary to give an account of the other salts of sulphazotised acids, especially as it is very probable that the formula assigned to these compounds will require modification, and that some of the compounds will be found not to exist.

The chief sulphazotised compounds that have been investigated sufficiently to establish their composition satisfactorily are the following:-

Amidosulphonic acid and salts NH2(SO2.OH) described as Sulphamic acid (p. 567).

Imidosulphonic acid and salts NH(80,0H), (p. 600).

Nitrilosulphonates N(SO, OM), (p. 601).

Nitrosulphonic acid and salts NO2(SO2.OH) (p. 601).

Nitrosulphonic anhydride (NO₂), 8,0, (p. 601). Nitrosulphonic chloride NO₂(SO₂Cl) (p. 601). Nitroso-oxy-amidosulphonates N(NO.OH)(SO2-OM); described nitroso.

sulphates under Sulphates (p. 581).

Oxy-amidosulphor:c acid and salts (and salts derived therefrom) NH(OH)(SO₂OH)

(p. 602).

Oxy-inidosulphonates (and salts derived therefrom) N(OH)(SO₂OM)₂ (p. 602).
Oxy-nitrosulphonic anhydride (NO₂2OS₂O. (p. 601).

Sulphamide (NH₂)₂SO₂ (p. 567). Sulphimide NH₂SO₂ (p. 587).

Sulphimido amide NH(SO₂.NH₂)₂ (p. 587).

Thionamic acid and salts NH₂(SO.OH)

695).

M. M. P. M.

(p. 695). M. M. P. M. SULPHURETTED HYDROGEN v. Hydrogen sulphide, vol. ii. p. 725.

SULPHURIC ACID; also PERSULPHURIC ACID and PYROSULPHURIC ACID.

SULPHURIC ACID H₂SO₄ (Oil of vitriol).

Mol. w. probably 97.76. Melts at 10.35° (Pickering, C. J. 57, 331); 10.5° (Thilo, Chem. Zeitung, 16, 1688). Boiling begins at c. 290°, SO₄ and H₂O with some H₂SO₄xH₂O passing off; b.p. rises till 338° is reached, when it becomes constant and complete dissociation to SO₄ and H₂O occurs; for b.p. of H₂SO₄Aq from 95 to 5 p.c. H₂SO₄ v. Lunge (B. 11, 370). S.G. ¹⁸⁵_{12°} 1.8884 (Perkin, C. J. 63, 59; cf. Pickering, C. J. 57, 73, note; Rohlrausch, W. 17, 69; Schertel, J. pr. [2] 26, 246; Mendeléeff, B. 17, 30, 2536; Lunge a. Isler, Zeit. für anorg. Chemie, 1890. 129). V.D. 25 at 440°, corresponding with dissociation to SO₄ + H₂O (Deville a. Troost, C. R. 56, 891; Wanklyn a. Robinson, Pr. 12, 507). SH. (22° tq 80°) 355; (22° to 170°) 37 (Pfaundler, B. 3, 798); (16° to 20°) 3315 (Marignao, Ar. Sc. 39, 217, 273). C.E. 0005585 at 20° (Marignac, Lo.). H.F. [H²S,O⁴] = 192,920; [H²O, SO³] = 21,320 (formation of liquid H₂SO₂) (Th. 2, 255). Heat of fusion = 860 g. units (for 98 g. H₂SO₂) (Berthelot, C. R. 78, 716). T. C. v. Beetz (W. 7, 435), Weber (J. 1885. 121). μ-1. Mol. w. = 32.45 (Gladstone, P. M. [4] 36, 311). For further data v. infra.

Occurrence. — Small quantities of H.SO., from 1 to 5 p.c., are found in some rivers and springs in volcanic districts; in a pool in Texas, Mallet (C. N. 26, 147) found 5 29 g. H.SO. per litre of water. The acid is also found in certain animal secretions; the salivary glands of some molluses are said to contain c. 2 p.c. (Bödeker a. Troschel, B. B. 1854. 486; De Luca a. Panceri, Bl. [2] 9, 400; Maly, M. 1, 205). The salts of splutneric acid occur in large quantities (v. Sulphares, p. 567).

Formation.—The formation of an oily liquid by heating alum is spoken of by Geber in the eighth century; a similar liquid was formed in the fifteenth century by burning sulphur with saltpetre. These liquids were shown to be identical towards the end of the sixteenth century. Oil of vitriol seems to have been manufactured in fair quantities by heating ferrous sulphate from about the early part of the eighteenth century; the first manufactory for making the acid from sulphur was started at Richmond by Ward about 1740. The composition of sulphuric acid was determined by Lavoisier.

1. By long exposure of flowers of sulphur in the air (John, S. 14, 417; Wagenmann, P. 24, 601).—2. By heating S with H_{*}O to c. 200°; by electrolysing H_{*}O, using Pt electrodes with pieces of S attached, the H_{*}SO, forms at the positive pole (Becquerel, C. R. 56, 237).—3. By the oxidation of S in presence of H_{*}O by Cl, HNO_{*}, HCl and KClO_{*}, aqua regia, &c.; also by certain metallic salts (v. Wicke, A. 82, 146; Parkmann, Am. S. [2] 33, 328).—4. By oxidising SOAq or SO_{*} in presence of water, by Cl, Br, H_{*}O_{*}Aq,

NO., HNO., &c.; by passing moist SO., and air over hot Pt black (Phillips, A. 4, 171), through a red-hot tube containing pieces of glass (Magnus, P. 24, 610), or over red-hot sand (Blondeau, C. R. 29, 405).—5. By the oxidation of H_sS and polythionic acids (v. Cloëz a. Guignet, C. R. 46, 1110).—6. By the interaction of water and SO., SO.₂Cl., SO., Cl.OH, &c.

Preparation.—Commercial oil of vitriol is diluted until the S.G. is 1.53 (=50° Beaumé, or 106° Twaddell, =62.5 p.c. H₂SO, by weight); the acid is heated to 70°-80°, and Na₂S₂O₃ is added in quantity sufficient to decompose the As2O, present (which should be estimated beforehand), according to the equation $3Na_2S_2O_3 + As_2O_3 = 3Na_2SO_4 + As_2S_4$; the acid is stirred until the As, S, separates in flocks (Thorn, D. P. J. 217, 495); the acid is filtered from As S. through asbestos or glass-wool, and is then concentrated by evaporation in a Pt dish till it begins to fume, and then in a retort of Pt or hard glass. The cone, acid is now heated with a little pure (NH₁)₂SO₁, whereby HNO₂ and HNO₃ are decomposed (NH₄,NO₂ and NH, NO₃ are formed, and then decomposed to N and H₂O, and N₂O and H₂O). The acid is then distilled from a glass refort, heated by a ring-burner placed around the retort at about two-thirds of the distance from the level of the acid to the bottom of the retort. The distillate is re-distilled in small quantities from a Pt retort into a Pt receiver; the condenser being formed of Pt tubes, soldered with gold and fitting closely one into the other, and the temperature being such that the acid does not boil during the distillation (cf. Stas, Chem. Proport. 112). Various other methods for removing As have been proposed; for the preparation of H2SO, free from As for chemico-medical use v. Bloxam (C. J. 15, 52), also Buignet a. Bussy (J. Ph. [3] 44, 177; 46, 252).

Commercial oil of vitriol is prepared by passing SO₂, mixed with a little IINO₃, into large leaden chambers into which jets of steam are also sent. The SO₂ is prepared by burning S or pyrites in a stream of air; the hot gas is passed over HNO₃, or over pots containing KNO₂ and H₂SO₄, so that it sweeps into the leaden chambers a certain quantity of HNO₂. The interactions between the hot SO₂ and HNO₃ probably produceNO and N₂O₃(3SO₂ + 2HNO₄ + 2H O = 3H₂SO₄ + 2NO; and also 2SO₂ + 2HNO₄ + 2H O = 2H₂SO₄ + N₂O₃); the NO then combines with O in the air of the chambers to form N₂O₄(4NO + O₂ = 2N₂O₃), which interacts with SO₂ and H₂O to produce H₂SO₃ and NO(N₂O₄ + SO₄ + H₂O = H₂SO₄ + 2NO) :—if N₂O₄ is produced in the primary reaction of SO₂ with HNO₃, this N₂O₃ may take up O to form N₂O₃, which in turn may react with SO₂ and H₂O to produce H₂SO₃ and NO(N₂O₄ + 2NO). These cycles of changes proceed as long as SO₄ is sent into the chambers, and there is present a sufficient Of O₂, and SO₂ (or N₂O₃ and SO₂ (or N₂O₄ + 4NO; or SN₂O₄ + 4SO₂ + 2H₂O = 4NO₄(SO₂OH) —is formed as a solid on the sides of the chamber (3N₂O₄ + 2SO₂ + H₂O = 2NO₂(SO₂OH) + 2NO₄ (SN₂O₄OH) + 2NO₄ SN₂O₄ + 4SO₄ + 2H₂O = 4NO₄(SO₂OH) + 2NO₄

when steam is now sent into the chamber the nitrosulphonic acid is decomposed to H,SO_3 and N_2O_3 ($2NO_3$ (SO_2 .OH) + $H_2O=2H_3SO_4+N_2O_3$). It is possible that the formation of NO_3 (SO_2 .OH) and the interaction of this with water may form normal stages in the series of reactions that occur in the chambers. Lunge (C.J.47, 405) regards N_2O_3 as the chief carrier of O from the air to the SO_3 ; he formulates the two main interactions as

$$\begin{array}{ll} \textbf{(1)} & 2SO_2 + N_2O_3 + O_2 + H_2O = 2NO_2(SO_2.OH), \\ \textbf{(2)} & 2NO_2(SO_2.OH) + H_2O = 2H_2SO_4 + N_2O_3; \end{array}$$

moreover, he insists that the interactions take place for the most part between gases in contact with the surface of the vesicles of liquid water formed by the condensation of the steam sent into the chamber. (A fuller discussion of the reactions that occur in the leaden chambers will be found in the DICTIONARY OF APPLIED CHEMISTRY, vol. iii, p. 726.)

Some portion of the oxides of N is swept through the chambers and so lost (part of this is recovered in the Gay-Lussac towers); some is lost by leakage, solution in the acid formed in the chambers, and in other mechanical ways; but some portion of the available oxides of N is also destroyed by secondary reactions that occur in the chambers, and result in the formation of N₂O and sometimes of N or NH₃(v. Weber, P. 130, 329; Pelouze, A. Ch. [2] 60, 162; Lungo, B. 14, 2196; cf. Dictionary of Applied Chemistry, vol. iii. p. 729).

Properties .- A clear, colourless, oily, hygroscopic liquid; solidifying at c. 10.5°. The liquid may be cooled much below its freezing-point without solidifying, but addition of a crystal of H2SO, or a small quantity of SO, causes crystallisation; the presence of a trace of water lowers the freezing-point to c.0°. II SO, is exceedingly acrid and burning, and is a violent poison. H2SO, fumes very slightly in air at the ordinary temperature: at 30°-40° it fumes much, giving off SO₃; according to Colefax (C. N. 63, 179), H₂SO₄ is probably slightly volatilised at ordinary temperatures. The mol. w. of H₂SO₄ has not been determined directly, but from the mol. weights of such derivatives as SO2Cl2, SO, (OMe), &c., the formula H.SO, is most probably molecular. H,SO, is decomposed when heated, and does not show a definite b.p.; boiling begins at c. 290°, and the temperature gradually rises to 338°, at which temperature dissociation to H₂O and SO₂ is complete. The residue has the composition H₂SO₄-T₂H₂O; acid with this composition is obtained by boiling down either H.SO., 2H.O or H.SO., 2SO. (Marignac, A. Ch. [3] 89, 184; Dittmar, C. J. [2] 7, 446). The sp. tr. of the vapour given off at c. 440° corresponds with that calculated for the dissociation of H₂SO, into SO₁+H₂O (Deville a. Troost, C. R. 56, 891; Wanklyn a. Robinson, Pr. 12, 507). The b.p. of H₂SO₄A₁ containing from 95 p.c. H₂SO₄ (b.p. 295°), to 5 p.c. H₂SO₄ (b.p. 101°) is given by Lunge (B. 11, 370). H₂SO₄ freezes at 10·352° (v. Pickering, C. J. 57, 10°). 831; where a long series of determinations is given of f.p. of H₂SO₄Aq containing from 005 to 100 p.c. H₂SO₄). The S.H. and mol. heat $(=8.H.\times98)$ are given by Pfaundler (B. 8, 798) às follows :

Temp. interval	and the second	222 5
from 22° to	8.H.	Mol. neat.
80°•	·855	84.790
90	·856	84.888
100	·858	85.084
110	•359	85.182
120	•860	85.280
130	·362	85.476
140	.864	85.672
150	•365	85.770
160	-367	85.966
170	.870	86:260

For S.H. of H.SO, xH,O from 16° to 20°, varying from 0 to 400, v. Marignac (Ar. Sc. 8) 217, 273); Bode (Zeit. filr anorg. Chemie, 1885. 244) gives S.H. of H₂SO₄Aq from S.G. 1.842 to 1.037; Pickering (C. J. 57, 160) gives S.H. of H₂SO₄Aq from c. 2 to c. 12 p.c. H₂SO₄ dissolves in water in all proportions; much heat is produced, and contraction occurs; for thermal measurements v. Thomson (Th. 3, 44), Favre a. Silbermann (C. R. 24, 1081), F. a. Quaillard (C. R. 50, 1150), Plaundler (J. 1869, 122), and, especially, Pickering (C. J. 57, 164). According to Pickering (C. N. 64, 14), the maximum contraction, calculated for unit weight of solution, changes from 67 p.c. at 8°, to 70.1 p.c. at 38°; but the maximum is constant at 76 p.c., from 8° to 38°, if calculated for unit volume; for fuller data v. P. (C. J. 57, 148). The expansion to 400, xH₂O, at 20°, when x varies from 0 to 400, is given by Marignac (Ar. Sc. 39, 217, 273). The refractive indices and dispersion of H₂SO₂Aq containing from 93.87 to 088 p.c. II.SO, are given by Pickering (C. J. 63, 99; cf. van der Willingen, Ar. N. 3, 122). Perkir (C. J. 63, 57) gives Mol. R. for H.SO, Aq from 99.92 to 9.18 p.c. H₂SO₄ (= from H₂SO₄ + 53.87 H₂O to H₂SO₄ + .004 H₂O).

The electrical conductivities of H_sSO_sAq of different concentrations have been measured by Kohlrausch (P. 154, 215, 159; 233; W. 6, 1; 17, 69), also by Pickering (C. J. 57, 158), who gives determinations for H_sSO_sAq containing from 1 to 100 p.c. H_sSO_s (v. also Bouty, C. R. 108, 393; also Grotrian, P. 151, 378).

The S.G. and composition of H₂SO₄Aq of varying concentrations have been determined by many observers. Pickering (C. J. 57, 152) gives S.G. and composition of H₂SO₄Aq containing from 5 to 100 p.c. H₂SO₄ at 0°, 2°, 4°, and each 2° up to 40°. Lunge a. Isler (Zeit. flur anorg. Chemic, 1890. 129) give the following tables (cf. Mendeléeff, ZeP. C. 1887, 273; Pickering, C. N. 64, 311; Lunge, C. N. 65, 13):—

s.g. 15°	Degrees Beaumé	Degrees Twaddell	we	arts by right stain	1 litre contains kilos.		
in vacua	ÄÄ	ÄŽ	P.c. 80,	P.c. H,80	80,	H,80,	
1.000	0	0	0.07	0.09	0.001	0.001	
1.005	0.7	1	0.68	0.83	0.007	0.008	
1.010	1.4	2	1.28	1.57	0.018	0.016	
1.015	2.1	3	1.88	2.30	0.019	0.028	
1.020	2.7	4	2.47	8.03	0.025	0.081	
1.025	3.4	5	8.07	8.76	0.082	0-089	
1.030	4.1	6	3.67	4.49	0.038	0.046	
1.035	4.7	7	4.27	5.23	0.044	0.054	
1-040	5.4	8	4.87	5.96	0.051	0.068	

692	SULPHURIC ACID.																	
8.G. 15°	Degrees Beaumé	Degrees Twaddell		rts by ight tain	1 litre contains kilos.		8.G. 15°		S.G. 15° Socue in vacuo		8.G. 15°		Degrees Twaddell	100 parts by weight contain		1 litre d	1 litre contains kilos.	
in vacuo	ÄÄ	ďμ	P.c. BOs	P.c. H.SO.	80,	H,SO.	in vacuo	ឝ៓ឝ៓	åå	P.c. 80,	P.c. H ₂ SO ₄	SO,	H ₂ SO ₄					
1·045 1·050	6.0	9	5·45 6·02	6.67	0.057	0.071	1.365	38.6	73	37.89	46.41	0.517	0.633					
1.055	6·7 7·4	10 11	6.59	7·37 8·07	0.068 0.070	0·077 0·085	1·370 1·375	39·0 39·4	74 75	38·32 38·75	46·94 47·47	0.525	0.643 0.653					
1.060	8.0	12	7.16	8.77	0.076	0.093	1.380	39.8	76	39.18	48.00	0.541	0.662					
1.065	8.7	13	7.73	9.47	0.082	0.102	1.385	40.1	77	39.62	48.53	0.549	0.672					
1·070 1·075	9·4 10·0	14 15	8·32 8·90	10·19 10·90	0.089	0.109	1·390 1·395	40.5	78 79	40.05	49.06	0.557	0.682					
1.080	10.6	16	9.47	11.60	0.103	0·117 0·125	1.400	40·8 41·2	80	40.48	49·59 50·11	0·564 0·573	0·692 0·702					
1.085	11.2	17	10.04		0.109	0.133	1.405	41.6	81	41.33	50.63	0.581	0.711					
1.090	11.9	18	10.60		0.116	0.142	1.410	42.0	82	41.76	51.15	0.589	0.721					
1.095	12.4	19	11.16		0.122	0.150	1.415	42.3	83	42.17		0.597	0.730					
1·100 1·105	18·6	20 21	11·71 12·27	14·35 15·03	0.129	0·158 0·166	1·420 1·425	42.7	84	42.57 42.96	52·15 52·63	0.604 0.612	0·740 0·750					
1.110	14.2	22	12.82	15.71	0.143	0.175	1.430	43.4	86	43.36	53.11	0.620	0.759					
1.115	14.9	23	13.36		0.149	0.183	1.435	43.8	87	43.75		0.628	0.769					
1·120 1·125	15·4 16·0	24 25	13.89 14.42		0·156 0·162	0.191	1·440 1·445	44.1	88	44.14	54·07 54·55	0.636 0.643	0·779 0·789					
1.130	16.5	26	14.95		0.162	0.199	1.450	44.4	90	44.93	55.03	0.651	0.798					
1.185	179	27	15.48		0.176	0.215	1.455	45.1	91	45.31	55.50	0.659	0.808					
1.140	17.7	28	16.01	19.61	0.183	0.223	1.460	45.4	92	45.69	55.97	0.667	0.811					
1·145 1·150	18·3 18·8	29 30	16.54 17.07		0·189 0·196	0·231 0·239	1·465 1·470	45·8 46·1	93 94	46.07 46.45	56·43 56·90	0.675 0.683	0·827 0·837					
1.155	19.3	31	17.59		0.203	0.239	1.475	46.4	95	46.83	57.37	0.691	0.846					
1.160	19.8	32	18.11		0.210	0.257	1.480	46.8	96	47.21	57.83	0.699	0.856					
1.165	20.3	83	18.64		0.217	0.266	1.485	47.1	97	47.57	58.28	0.707	0.865					
1·170 1·175	$\substack{20.9 \\ 21.4}$	84 85	19·16 19·69		0·224 0·231	0·275 0·283	1·490 1·495	47·4 47·8	98	47.95 48.34	58·74 59·22	0·715 0·723	0·876 0·885					
1.180	22.0	86	20.21	24.76	0.231	0.292	1.500	48.1	100	48 73	59.70	0.731	0.896					
1.185	22.5	87	20.73	25.40	0.246	0.301	1.505	48.4	101	49.12	60.18	0.739	0.906					
1.190	23.0	38	21.26		0.253	0.310	1.510	48.7	102	49.51	60.65	0.748	0.916					
1·195 1·200	28·5 24·0	39 40	21·78 22·30	26.68 27.32	0.260 0.268	0·319 0·328	1.515 1.520	49·0 49·4	103 104	49·89 50·28	$61.12 \\ 61.59$	0·756 0·764	0·926 0·936					
1.205	24.5	41	22.82		0.275	0.337	1.525	49.7	105	50.66	62.06	0.773	0.946					
1.210	25.0	42	23.33	28.58	0.282	0.346	1.530	50.0	106	51.04	62.53	0.781	0.957					
1·215 1·220	25.5	43	23.84		0.290	0·355 0·364	1.535 1.540	50·3	107	51·43 51·78	63·00 63·43	0·789 0·797	0·967 0·977					
1.225	26·0 26·4	44	24·36 24·88	29.84 30.48	0.297	0.304	1.545	50.0	108 109	52.12	63.85	0.805	0.987					
1.230	26.9	46	25.39	31.11	0.312	0.382	. 1.550	51.2	110	52.46	64.26	0.813	0.996					
1.235	27.4	47	25.88		0.320	0.391	1.555	51.5	111	52.79	64.67	0.821	1.006					
1·240 1·245	27·9 28·4	48	26·35 26·83	32·28 32·86	0.327	0·400 0·409	1.560 1.565	51·8 52·1	$\frac{112}{113}$	53·12 53·46	65·08 65·49	0·829 0·837	1·015 1·025					
1.250	28.8	50	27.29	83.43	0.341	0.418	1.570	52.4	114	53.80	65.90	0.845	1.035					
1.255	29.3	51	27.76	84.00	0.348	0.426	1.575	52.7	115	54.13	66.30	0.853	1.044					
1.260	29.7	52	28·22 28·69	84·57 85•14	0.356	0.485	1.580 1.585	53·3 53·3	116	54.46	66.71	0.861	1·054 1·064					
1·265 1·270	80·2 80·6	53 54	29.15	35.71	0.363 0.370	0·444 0·454	1.590	53.6	117 118	54·80 55·18	67·13 67·59	0.869	1.075					
1.275	81.1	55	29.62	36.29	.0.377	0.462	1.595	53.9	119	55.55	68.05	0.886	1.085					
1.280	81.5	56	30.10	36.87	0.385	0.472	1.600	54.1	120	55.93	68.51	0.895	1.096					
1·285 1 290	82·0 82·4	57 58	30·57 31·04	87·45 88:03	0.393	0·481 0·490	1.605 1.610	54·4 54·7	121 122	56·30 56·68	68·97 69·43	0.904 0.913	1·107 1·118					
1.295	32.8	59	31.52	38-61	0.408	0.500	1.615	55.0	123	57.05	69.89	0.921	1.128					
1.800	83.8	60	31.99	89.19	0.416	0.510	1.620	55.2	124	57.40	70.32	0.930	1.139					
1.805	88.7	61	82.46	39.77	0.424	0.519	1.625	55.5	125	57.75	70.74	0.938 0.947	1·150 1·160					
1·810 1·815	84·2 84·6	62 63	82·94 83·41	40·35 40·93	0·432 0·439	0·529 0·538	1.630 1.635	55·8 56·0	$\frac{126}{127}$	58·09 58·43	71·16 71·57	0.955	1.170					
1.820	85.0	64	83.88	41.50	0.447	0.548	1.640	56.3	128	58.77	71.99	0.964	1.181					
1.825	85.4	65	84.35	42.08	0.455	0.557	1.645	56.6	129	59.10	72.40	0.972	1.192					
1.880	85.8	66	84·80 85·27	42.66 43.20	0·462 0·471	0·567 0·577	1.650 1.655	56·9 57·1	130 131	59·45 59·78	72·82 73·23	0.981 0.989	1·202 1·212					
1·885 1·840	86·2	67 68	85.71	48.74	0.471	0.586	1.660	57.4	132	60.11	78.64	0.998	1.222					
1.845	87.0	69	36-14	44.28	0.486	0.596	1.665	57.6	183	60.46	74.07	1.007	1.233					
1.850	87.4	70	36.58	44.82	0.494	0.605	1.670	57.9	134	60.82	74.51	1.016	1.244					
1.855 1.860	87·8 88·2	71	87·02 87·45	45·87 45·88	0·502 0·509	0.614 0.624	1·675 1· 680	58·2 58·4	135 186	61·20 61·57	74·97 75·42	1·025 1·034	1·256 1·267					

1-685	8.G. 15°	Degrees Besums	Degrees Twaddell	we	arte by ight itain	1 litre c	ontains os.
1-690		AA	T De	P.o. 80,	P.o. H ₂ SO.	SO.	H,80,
1-695	1.685	58.7	137	61.93	75.86	1.043	1.278
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For the properties of fuming H₂SO₄ v. Pyrosulphuric acid, p. 625.

For a test for small quantities of free H₂SO₄ v. Carey Lea (Am. S. [8] 45, 478; abstract in C. J. 64 (ii.), 566).

Reactions. -1. Conc. H2SO4 is decomposed

by heat; at c. 440° the products are SO, and H₂O, and by passing through a red-hot tube SO,, O, and H₂O are formed (Deville a. Troest, C. R. 56, S91; Wanklyn a. Robinson, Pr. 12, 507, Redwood, Ph. [2] 5, 601; Deville a. Debray, A. Ch. [3] 61, 125),—2. Decomposed by the electric current; with conc. H₂SO, and a raised temperature O separates at the positive pulc temperature O separates at the positive pole, and H and S at the nogative; at 0° only H and O are given off (Faraday, T. 1834; Warburg, P. 135, 114; Luckow, Fr. 1880, 1; Berthelot, C. R. 86, 71; 90, 269). Gladstone a. Tribe (C. J. 85, 176; 43, 345) found that a little SO, was formed when the electrolysis of 98 2 p.c. H₂SO, was very slow. According to the concentration of the II.SO.Aq electrolysed, the strength of the current, and the current density, ozone, H2O2, and S2O, are formed, besides H and O. For an examination of the conditions favourable to the production of ozone v. McLeod (C. J. 49, 591, where references are given to earlier memoirs). According to Botty (C. R. 108, 393), acid of the concentration H₂SO₄ + H₂O always gives H₂O₂ on electrolysis; Richarz (A. Ch. [2] 24, 183) obtained with acid of the concentration $H_2SO_4 + 1.347H_2O$; with acid more dilute than O p.c. H_2SO_4 very little H_2O_2 is obtained, but considerable quantities of S_2O_2 and ozone (Bouty, l.c.; cf. Kuriloff, J. R. 23, 235). In connection with the electrolysis of H₂SO₄Aq, and the conditions of production of H and O only, or of Holo, coone, and S₂O, also, v. Armstrong (C. J. Proc. 1893-4. 188 [No. 127]).—3. By passing a mixture of the vapour of H₂SO₄ mixed with hydrogen through a red-hot tube, H₂O is obtained along with SO₂, S₁ or H₂S₂ according to the quantity of H (v. Warner, C. N. 28, 18). Hydrogen occluded by palladium or platinum Hydrogen occurate of pattachem or patterns partially reduces 98.2 p.c. H₂SO₃, giving SO₄ (G. a. T., l.c. p. 177).—4. SO₃, CO₄, and H₄O are formed by heating conc. H₂SO₄ with carbon; and SO₂ and H₂O by heating with sulphur.—5. Phosphorus takes fire in boiling H₂SO₄ with separation of S; red phosphorus reacts with the conc. acid when hot, forming SO, and H.PO. -6. Chlorine reacts with conc. H2SO, to form Cl(SO₂.OH) (v. Chlorosulphonic acid, p. 509).—7. Most metals interact; K and Nagive off H, Zn and Fe and several other metals also give off H with more or less dilute H.SO.Aq at ordinary temperatures; on raising the temperaordinary temperatures; on raising the tempera-ture SO₂ and H₂S are generally evolved and S is often separated. Some metals, such as Sb, Bi, Cu, Hg, react only with warm fairly cone. H₂SO₄. Cu, Hg, react only with warm fairly cone. H₂SO₂, giving off SO₂, and often also H₂S. Au, Ir, Pt, Rh, and W do not interact with H₂SO₄. Regarding the conditions of the interaction of H₂SO₄ad with metals—concentration, temperature, and products—v. Ditte (A. Ch. [6] 19, 68). Pattison Muir a. Adie (C. J. 53, 47) found that the only products of the interaction of approximately pure zinc and dilute H₂SO₄Aq (c. H₂SO₄.12H₂O to c. H₂SO₄.15H₂O) were ZnSO₂Aq and H; that with cone. acid (c. H₂SO₄.H₂O to c. H₂SO₃ SO₂ was the chief gaseous product, and that H₂S was also produced at higher temperatures; and that with acid of intermediate concentration (c. H₂SO₄.2H₂O) both SO₂ and H₂S were formed in considerable quantities at c. 160°. For experiments on the rate of action of H₂SO₄Aq ox periments on the rate of action of H.SO.Ag on

different specimens of zinc v. Divers a. Shimidzu (C. J. 47, 598), who have also examined the production of NH₂OH by the interaction of zino with H₂SO₂Aq and HNO₂Aq together (cf. Hydroxymanne, vol. ii. p. 734). For qualitative the control of the control of the superscript of the sup tive experiments on the interaction of H₂SO₄ and tin, v. Pattison Muir a. Robbs (C. N. 45, 69, where references to other memoirs are given). Pullinger (C. J. 59, 815) found that pure zinc was not acted on by H₂SO₂Aq (1 part conc. acid + 3 parts water by weight) provided the acid had been boiled for a long time before use and the surface of the zinc was quite smooth; if the surface was rough some of the zinc was dissolved. P. also found that oxidisers increased the rate of solution of zinc, and reducers, if not containing S, almost stopped the solution. P. concluded that when the surface of the zinc was rough S₂O₇ was probably formed, and then the action proceeded. Weeren (B. 24, 1785) noticed that there was scarcely any reaction between pure zinc and H₂SO₄Aq (c. 20 parts water); he supposed that a layer of H was condensed on the surface of the metal. W. thought that with impure zinc the H is given off from the surface of the more negative metal present, and so the surface of the zinc is left exposed to the action of the acid. W. found that the evolution of H proceeded more rapidly in vacuo, and that it was hastened by brushing the surface of the metal. The weight of pure zinc dissolved in 30 mins. was 2·1 mgm. at 0°, 9·3 mgm. at 98°, and 122·1 mgm. at the b.p. of the acid used. W. obtained similar results with Al, Cd, Co, and Fe. Sodium amalgam or zinc amalgam, with conc. HaSO, amalgam or zinc amalgam, with conc. H.,SO,, gives off H, then quantities of H.,S, then SO, and S, and finally only SO, (Walz, C. N. 23, 245). The interaction of H.,SO, and copper has been fully examined by Pickering (C. J. [2] 18, 112; of. Copper, vol. ii. p. 253).—8. H.,SO, reacts with the caides of nitrogen (not with N.,O) to form NO, (SO, OH) (v. NITROSULPHONIC ACID, p. 601).—9. Phosphoretted hydrogen reacts slowly with H.SO. at the ordinary temperature, giving SO, S. Phosphotetet hydrogen teach slowly with H₂SO₂ at the ordinary temperature, giving SO₂, S, and H₂PO₄ (Rose, P. 24, 139)—10. With sulphuretted hydrogen, H₂O₅ S, and SO₂ are formed .- 11. Phosphorus pentoxide withdraws H₂O from hot conc. H₂SO₄, producing P₂O₃.H₂O and SO₄ (Barreswil, C. R. 25, 30; Evans, Ph. 8, 127); phosphorus pentaciloride or trichloride forms 80, and POCl, also 80, Cl, when PCl, is used (Williamson, P. M. [4] 7, 365; Schiff, A. 202, 111; cf. Michaelis, J. Z. 6, 233, 292), and also Ol(80, OH) (Müller, B. 6, 277; Ceuther, B. 5, 278) 925; Thorpe, C. J. 37, 358).—12. H₂SO, reacts with most salts to form sulphates, and set free the said of the salt if that said is more volatile than H.SO.. In several cases secondary reactions occur between the acid set free and the H.SO.; thus, with bromides and iodides, Br and I, and SO, or H.B, are produced. The interaction of H.BO.Aq and KBr has been examined by Addyman (C. J. 61, 94), who found that the percentage of HBr decomposed varied almost directly with the quantity of H₂SO₄ used, and that when so much H₂SO₂ was present that the water produced in the reaction 2HBr + H₂SO₄ = 2H₂O + SO₂ + Br₂ caused no sensible dilution of the H₂SO₄ all the HBr was decomposed; with dilute acid, c. 30 p.c. H.SO, using excess of acid, scarcely a trace of HBr was decomposed (cf. Feit a. Kubierschki,

J. Ph. [5] 24, 159). Jackson (C. J. 43, 839) finds that the interaction of conc. H.SO, and KI varies according as the acid is present in large excess, or in quantity just sufficient for the KI used. In the first case all the I of the KI is set free along with an equivalent quantity of SO; in the second case all the I is liberated with the equivalent quantity of H2S. Many salts of acids containing much oxygen, e.g. dichromates and permanganates, are decomposed by hot conc. H.SO, with evolution of O. The reaction of H.SO, Aq with KMnO, Aq has been examined by Gooch a. Danner (Am. S. [3] 44, 301), who found that the quantity of O given off increased with (1) concentration of H.SO.Aq, (2) time, (3) temperature; no O was given off after a few hours with 20 p.c. acid at the ordinary temperature, but a considerable quantity of O was produced after five days' action, and c. the same result was obtained by heating to 80° for one and a half hours (cf. Jones, C. J. 33, 95).— 13. Conc. H.SO, reacts with many oxygenated organic compounds, withdrawing H,O; with benzenoid hydrocarbons it forms sulpho-acids; many organic compounds, such as sugar, starch, &c., are charred by warm H₂SO₄.—14. Pictet (C. R. 115, 708, 814) has examined the reactions of sulphuric acid at low temperatures, using acid of 89 p.c. H.SO.; no action occurred below -125° with such bodies as NaOH, NaCl, NH., Na₂CO₃, Na, K; in most cases action began suddenly at temperatures varying from - 120° to -60°.—15. H₂SO₄ combines with water; the hydrates H₂SO₄.H₂O₅ H₂SO₄.2H₂O₅ and hydrates H₂SO₄.3H₂O have been isolated as solids (v. infra).—16. Conc. H.SO, combines with sulphur trioxide to form H.SO, SO, and other compounds (v. Pyrosulphuric acid).

For the reactions of fuming H.SO, v. Pyro-SULPHURIC ACID (p. 625). The salts of H2SO4 are described under Sulphates (p. 567). Both amides of H2SO, viz. SO2OH.NH2 and SO2(NH2)2, have of H.SO., VIZ. 502.0H.MI. Bull SO.(H.H.), have been isolated (v. SULPHAMIC ACTD, p. 567, and SULPHAMICA CUT), p. 567, and SULPHAMIDE, p. 567); the imide SO.,NH is also known, v. SULPHAMIDE, p. 587; cf. also SULPHAMIDE NH(SO.,NH.), p. 587, and IMIDO-MULPHONIO ACID NH(SO.,NH.), p. 587, and IMIDO-SULPHONIO ACID NH(SO.,NH.), p. 600.

Constitution of sulphuric acid.—The reactions of H₂SO₄ with Cl and with PCl₃, and the reactions of the products with water, also the formation of SO₂.OH.NH₂, SO₂(NH₂)₂, and SO₂NH, show that H₂SO₄ contains two OH groups. The fact that only one compound, SO. OEt.OMe, can be formed from H.SO. shows that the two OH groups in SO2(OH), are related to the rest of the molecule in the same way; hence the formula for the acid is to be written $\rm S{<}^{O.OH}_{O.OH}$ or $\rm O_2S{<}^{OH}_{OH}$. Inasmuch as $\rm SO_2Cl_2$

is formed from SO₂(OH)₂ by the reaction of PCl₃, as certain hydrocarbons interact with SO₂Cl₂ to form SO₂R₂ (where R = Me, Ph, &c.), and as these compounds SO₂R₂ are reduced to SR, where the radicles R are certainly in direct union with S, it is extremely probable that the OH groups in SO₂(OH)₂ are in direct union with

S, and hence the formula O₂S CH is to be pre-

ferred to S < O.OH for sulphuric acid. It is

HYDRATES OF SULPHURIC ACID. Two solid hydrates have been isolated; a liquid hydrate has probably also been isolated.

Monohydrate H.SO. H.O (Tetrahydroxy-sulphuric acid SO(OH),). Large, colourless, six-sided tablets; formed by mixing 1 part conc. H.SO, with rather less than one-fifth part water (by weight), and surrounding with a freezing mixture. The crystals melt at 7.5° (Pierre a. Puchot, A. Ch. [5] 2, 164). The hydrate readily remains liquid considerably below its m. p. S.G. $\frac{1}{20}$ = 1.7943 (for the liquid) (Mendelceff, B. 19. 880); 1.77806 at 15°, 1.77423 at 20°, 1.77071 at 25° (Perkin, C. J. 49, 777; determinations made with liquid, and referred to water at same temperatures). Thomsen gives H.F. from liquid H₂SO₄ and H₂O [H²SO',H²O] = 6,379 (Th. 3, 54); Berthelot gives 6,120 (C. R. 78, 716). Heat of fusion = 3680 g. units (for 116 g.) H₂SO₄H₂O (Berthelot, C. R. 78, 716). For vapour pressures from 143° to 204° v. Tate (P. M. [4] 26. 502).

Dihydrate H₂SO₄.2H₂O (Perhydroxysulphuric acid S(OH)_d). Formed by adding 368 parts H₂O to 1 part pure H₂SO₄, by weight. This hydrate has not been obtained as a solid; the S.G. of the liquid at 60 is given by Mendelceff

(B. 19, 380) as 1.6655 (cf. Perkin, C. J. 49, 777). It is stated (v. Mendelceff, B. 19, 388) that the maximum contraction when H₂SO₄ and H₂O are mixed occurs when the compounds are present in the ratio H.SO,:2H.O, but Pickering (C. J. 57, 84) says that the maximum does not correspond with the composition of any hydrate the existence of which is indicated in other

ways.

Tetrahydrate H.SO.,4H.O. Obtained by Pickering (C. J. 57, 339) as a crystalline solid, melting at -25°, by cooling H.SO.,4q containing 57.6 p.o. H.SO., (H.SO.,2H.O corresponds with 57.66 p.o. H.SO.). The crystals are large and well defined, and resemble H.SO.,H.O.; the compound may be kept liquid at 20° to 25° below its freezing point.

Hydrates of sulphuric acid in aqueous solution .-- According to Mendeleeff (B. 19, 380; cf. his Principles of Chemistry, vol. ii. p. 234), an examination of the connections between the concentration of H.SO.Aq and the S.G. indicates the existence of hydrates that have not yet been isolated. Pickering (C. J. 57, 64) comes to the same general conclusion from an extended examination of the connections between the changes of composition of H2SO, Aq and the changes of S.G., heat capacity, electrical conductivity, heat of solution, and expansion by heat of the solution. Pickering's reasoning is a special case of that explained in the article Solutions (part ii. p. 492); for the detailed argument, and criticisms of it, v. Peckering, C. J. 57, 64; Rücker, P. M. [5] 32, 304; 33, 204; P., P. M. [5] 33, 132, 463; cf. Mendeleeft, Z. P. C. 1, 275; and Crompton, C. J. 53, 116.

PERSULPHURIC ACID H.S.O.Aq. seid is present in the solution obtained by elec-You IV.

undecided whether the group SO₂ in O₂S.OH.OH | trolysing H₂SO₂Aq of certain concentrations; Berthelot (O. R. 90, 269; 112, 1461) obtained a quantity of the soid equal to from 88 to 123 g. S₂O, per litre by electrolysing H₂SO₂Aq containing water and acid in the ratio 10H₂O:H₂SO₄ (cf. SULPHURIC PEROXIDE, p. 616; and SULPHURIC ACID, Reactions, No. 2, p. 623). According to Traube (B. 22, 1518, 1528) a solution of H₂SO₂ in H₂SO₄ does not oxidise H₂CO₂, HNO₂ CO₃ or Cr₂(SO₄); Richarz, however (B. 21, 1670), says that oxadic and nitrous acids are oxidised. The acid has and introus acids are existing. The acid has not been isolated; by electrolysing at temperatures below 0°, and then adding BaOAq or KOHAq, the Ba or K salt is obtained. The formula H.S.O. is given rather than HSO. because of the results of Bredig's measurement of the conductivities of solutions of the K salt. For salts of this acid v. Persulphates.

> PYROSULPHURIC ACID ILS.O. sulphuric acid). A solution of this acid in H.SO, is know, as funing sulphuric acid, or Mordhausen acid. This acid is obtained by adding rather more SO, to H.SO, than the proportion SO,:H.SO, cooling, and spreading out the crystals that form over meanly conc. H.SO, under a bell-jar till the excess of SO, is removed (Schultz-Sellack, B. 4, 109). Forms large crystals, melting at 35°. Easily decomposed by heat to H₂SO, and SO, H₂S₂O, is dibasic, forming salts MHS₂O, and M₂S₂O, (v. PYROSULPHATES, p. 583). Funing sulphuric acid is a solution of H₂S₂O, in H₂SO₄; it is prepared by heating dry FeSO, in fireday vessels and collecting the oily, fuming liquid that distils over. The acid fumes strongly in the air, and gives off SO₃ whon warmed. But few of the reactions described for pyrosulphuric acid, or for fuming sulphuric acid, can be set down as belonging to a definite compound, but rather to belonging to a definite compound, but rather to solutions of H.S.Q., (and perhaps other compounds of H.S.Q., and SO.) in H.SQ. Finely-divided silver dissolves easily; the solution poured into water gives Ag.SO. and SO.; mercury reacts similarly; spongy copper has a slight reaction, giving Cu.S and CuSO. (Divers a. Shimidzu, C. J. 47, 636). Distilled with phosphorus pentoxide in a stream of hydrogen chloride, Cl(SO.,OH) is formed; the same soid is formed by heating with PCl. and also hy heating chloride, Cl(SO₂OH) is formed; the same soid is formed by heating with PCl₃, and also by heating 'crystallised funing sulphuric soid 'with HCl (v. Силовозиленоми аси, р. 509). Nitrogen dioxide passed into well-cooled pyrosulphuric acid gives NO₂(SO₂OH) (v. Nitrosoulphuric acid gives NO₂(SO₂OH) (v. Nitrosoulphuric acid, p. 601). By saturating ordinary conc. H₂SO₄ with SO₃ (Jacquelain, A. Ch. [3] 30, 343), or by cooling fuming H₂SO₄ to -10° (Wackenroder, Ar. Ph. [3] 87, 267), the compound H₂SO₂,2H₂SO₄ (-3H₂SO₄,SO₉) is said to be obtained in transparent crystals. Schultz-Sellack tained in transparent crystals. Schultz-Sellack (B. 4, 109) failed to obtain any compound of H₂SO₄ and SO₃, except H₂SO₄. Crystals of the composition H₂SO₄.3SO₄ (=H₂S₁O₁) melting at 8°-10° are said by Weber (P. 159, 313) to be formed by adding cooled conc. H_SO₄, little by little, to SO₄.
>
> M. M. P. M. little, to SO.

SULPHURIC ANHYDRIDE SO. v. Sul-PHUR TRIOXIDE, p. 615.

Persulphuric anhydride S.O. v. Sulphuric PEBOXIDE, p. 616,

SULPHURIC-NITROSYL CHLORIDE

SO. NOCI v. NITEOSULPHONIC CHLORIDE, p. 601. SULPHURIC OXIDE SO, v. SULPHUB TRI-OXIDE, p. 615. SULPHURIC PEROXIDE S.O. v. p. 616.

SULPHURIC PEROXIDE S₂O, v. p. 616. SULPHUROSAMIC ACID SO.OH.NH₂ v

THIONAMIC ACID, p. 695. SULPHUROUS ACID and HYPOSUL-

PHUROUS ACID.

SULPHUROUS ACID H₂SO₄Aq. The acid has not been isolated; a solution of SO₂ in water reacts as a weak dibasic acid, forming salts of the types M'HSO₃, M'₂SO₃, and M'HSO₃ (v. SULPHITES, p. 587). H.F. [H'₂S,O'₂Aq] = 147,130; [H'₂O,S,O'₂Aq] = 78,780 (from rhombic S; Th. 2, 251).

The methods of formation and preparation of H₂SO₂Aq are sufficiently detailed under SUL-PHUE DIOXIDE (p. 613); it is only necessary to add water to the SO₂ obtained.

Properties.—An aqueous solution of H₂SO₃ readily decomposes, giving off C'₃; on standing for some time in the air, and more quickly by warming, H₂SO₄Aq is formed with production of much heat; [H'SO'Aq, O] = 63,634 (Th. 2, 253). H₂SO₃Aq is altered by the action of light, so that after exposure to light for some time the solution ppts. Ag₂S from AgNO₂Aq, and reduces silver haloid compounds, forming some Ag₂S; the solution after exposure to light behaves like a dilute solution of a polythionic acid (Stas, Chem. Proport. 64). Löw (L'Institut, 1873. 67) says that dilute H₂SO₄Aq is changed to H₂SO₄Aq is changed to H₂SO₄Aq is changed to H₂SO₄Aq

and S by long exposure to light.

Reactions.—1. Heated in a closed tube to 170°—180°, H.SO,Aq and S are formed, and after a time also H.S (Geitner, A. 129, 350).—2. Decomposed by an electric current, giving H.SO,Aq at the positive pole and S at the negative; with a weak current H.S.O,Aq is probably formed at first at the negative pole (Guéroult, C. R. 85, 225).—3. Phosphorus pentachloride produces SOCU, and POCI, (Kremers, A. 70, 297; Schiff, A. 102, 111).—4. Sulphurous chloride with H.SO,Aq produces polythionic acids (v. Debus, C. J. 53, 345).—5. Vapour obtained by heating H.SO,Aq produces with chlorine, when passed over red-hot Pt, to form Cl(SO,OH) (v. Chlorosulphonic acid, p. 599).—6. NO₂(SO₂,OH) (v. NITROSULPHONIC ACID, p. 601) is formed by the interaction of moist SO₂, i.e. H.SO,Aq, with mitric oxide or mitrogen dioxide.—7. H.SO,Aq is oxidised to H.SO,Aq by oxygen, the halogens, and many other oxidisers.—8. Heated with phosphorus in a closed tube to 200°, H.S is produced (Oppenheim, Bl. [2] 1, 163).—9. Reduced by sinc and dilute sulphuric acid to H.S (v. Reinsch, D. P. J. 168, 286; 181, 382); with sinc alone, H.SO,Aq is partly reduced, probably giving H.S.O,Aq (v. Hyrosulphuroos ACID, p. 627).—10. Many metals which evolve H from H.SO,Aq or HClAq react with H.SO,Aq to form sulphites and sulphides, with evolution of little or no H (v. Federoff, Chem. Zeitung, 5, 16). For a fairly full qualitative examination of the interaction of Al, Cd, Mg, Ni, and Zn with H.SO,Aq, w. Schweitzer (C. N. 23, 293).—11. Many of the oxyacids of the halogens are reduced to hydracids by H.SO,Aq and H.S.; then S, and thionic acids (Wöhler, A. 89, 252; Maquenne, Chem. Zeitung.

1890 [1] 511).—18. Phosphoretted hydrogen produces H₂PO₄Aq, and S (Cavazzi, G. 16, 169).
14. Hydrogen sulphids passed into H₂SO₄Aq forms a solution containing H₂SO₄, H₂S₂O₆, H₂S₂O₆, probably H₂S₂O₆, S in suspension, and a colloidal form of S in solution; if the passage of H.S is continued until reaction ceases the final products are S and H,O (Debus, C. J. 53, 282; cf. Thionic acids, p. 698).—15. Many metallic salts are reduced, in aqueous solutions, by H2SO3Aq; salts of Ag and Hg to the metals, ferric to ferrous salts, &c. According to Divers a. Shimidzu (C. J. 49, 575), the reduction does not consist in the withdrawal of O by H₂SO₃Aq and the oxidation of that acid thereby to H₂SO₄Aq. The first step is looked on by D. a. S. as probably the formation of a sulphite of the metal of the salt, and this is followed by either the decomposition of this sulphite by water to metal and H₂SO₄Aq, or the reaction of the sulphite with some of the original, unthe surprise with some of the original, anchanged, salt to form metal and a persulphite (or -ic sulphite) of the metal.—16. With polassium thiosulphate H₂SO₂Aq forms K tri- tetra- and penta-thionates, and S (Debus, C. J. 53, 343).—12. ISSO As 2 includes when trackly and are 17. H₂SO₂Aq dissolves many freshly ppd. metallic sulphides, e.g. MnS, FeS, ZnS, forming thiosulphates (Schönbein, P. 104, 300; Heldt, J. pr. 83, 20).-18. Alkali nitrites give salts of nitrilosulphonic acid N(SO₂.OH)₃ (q. v., p. 601), and also salts of oxy-imidosulphonic acid and also state of oxy-inmostiphome acid N(OH)(SO_{...}OH)_{...} (q. v., p. 602). Using a dilute, ice-cold solution of H₂SO₄ (=5 p.c. SO₂), and adding 40 g. KNO_{...} in 1,000 c.c. water to 3 litres of this H₂SO₂Aq, Raschig (A. 241, 234) obtained NH₂(SO₂.OK) (cf. SULPHAMIC ACID, p. 567). Under certain conditions of concentration and temperature NO and N₂O, also NH₂ and sometimes NH₂OH, are produced. With nitrous acid the final products are NH₃, NO, N₂O, and H₂SO,Aq; according to Raschig (l.c.), NH₂(SO₂OH) is always formed, and the gaseous products are to be looked on as resulting from secondary reactions between nitrous acid and NH2(SO2OH) or other nitrogenised sulphonic acids formed in the primary reaction between the nitrous and sulphurous acids. With silver and mercurous nitrites Divers a. Haga (C. J. 51, 659) found that sulphites were produced, along with some NO and H₂SO₄, and more or less NH₂OH.— 19. For the reaction of H.SO, Aq with potassium platinochloride v. Platino-sulphonates, this vol.. p. 285.

Neither the amide SO(NH₂)₂ (v. the heading Thionamide), nor the imide SO.NH, of H₂SO₂ has been isolated; and it is doubtful whether the acid SO.OH.NH₂ or SO₂.NH₂.H is known v. Thionamic acid.

Constitution of sulphurous acid. The fact that many haloid derivatives of hydrocarbons interact with NaHSO, to form sulphonic acids—e.g. EtI+NaHSO,=EtSO,H+NaI—makesit probable that the Na in NaHSO, is in direct union with the S, because the S in sulphonic acids is almost certainly in direct union with the hydrocarbon radicle; hence it is likely that one H atom in H,SO, is directly combined with the S atom, and hence the formula for H,SO, is probably H,SO,OH. This view of the constitution of H,SO, is insisted on, and illustrated, by Divers (C. J. 47, 205).

Hydrates of sulphurous acid. Colourless, ice-like crystals are obtained by passing SO, into water surrounded by ice, by cooling saturated SO,Aq, or by passing moist SO, through a tube kept at a low temperature. After filtering quickly in a covered filter, and pressing between ditter paper at 8°, the crystals have the composition H.SO, xH₂O; Dopping (Petersburg Acad. Bull., 7, 100) found x = 10, Pierre (A. Ch. [3] 23, 416) found x = 8, Schönfeld (A. 95, 22) found x = 14, Roozeboom (R. T. C. 3, 29, 59, 75, 84: 4, 65) found x = 6, and this was confirmed by Geuther (A. 224, 218). Roozeboom (l.c.) gives S.G. of the crystals as 1.21 (referred to water at 4°); Geuther (l.c.) gives 1.147 as the S.G. after melting at 14°, and 14° as the m.p. with separation of some liquid SO, under the layer of SO, Aq. R. (l.c.) gives the following dissociation-pressures, which are independent of the quantity of the hydrate: 303 mm. at 0°, 754 mm. at 7.05°, 1177 mm. at 10°, 1773 mm. at 12·1°. According to R. the critical temperature of decomposition is 7.1° in an open vessel and 12.1° in a closed vessel.

HYPOSULPHUROUS H.S.O.Aq. ACID This acid has not been isolated. An aqueous solution is probably formed by decomposing the Na salt by dilute H.SO.Aq or H.C.O.Aq, and also perhaps by digesting H.SO.Aq with zinc clippings till the liquid is brownish red; but neither the aqueous solution of the acid, nor any of its calts, has been obtained free from impurities. For preparation of the sodium salt, and for references, v. Hyposulphites (p. 592). M. M. P. M.

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CHLORIDES, p. 618. SULPHURYL HYDROXYLCHLORIDE v.

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FLUOSULPHONIC ACID, p. 600. SULPHURYLIMIDE v. SULPHIMIDE.

SULPHURYL IMIDO-AMIDE v. SULPHIMIDO-AMIDE, p. 587. SULPHYDRATES v. Hydrosulphides, vol. ii.

p. 733.

SULPHYDRIC ACID v. Hydrogen sul-PRIDE, vol. ii. p. 725. SULPHUVINURIC ACID C4H4N2SO2, i.e.

S-C(NH.) CH:C(CO.H) N (Strende, A. 261, 26). Formed from di-bromo-pyruvic acid and a conc. solution of thio-urea (Nencki a. Sieber, J. pr. [2] 25, 74).
Crystals (containing 2aq), sl. sol. cold water.
Reduces Fehling's solution in the cold. FeCl. gives a deep violet colour.—Salts: MgA' .-

ZnA'2: minute needles.-HA'HCl.-HA'HBr.-HA'HNO, aq: needles, sl. sol. water. SULPHYDRO-ACETIC ACID v. THIOGLY-

COLLIC ACID.

SULPHYDRO-ACETONE CH., CO.CH., SH.

Ethul derivative EtS.CH, Ac. Ethyl derivative EtS.CH,Ac. (171°). Formed from chloro-acetone and NaSEt (Autencieth, B. 24, 165). Yields a phenyl hydrazide [57].

[360] Phenyl derivative Phs.CH.Ac. [36°]. (266°). Formed from CH.CO.CH.Cl and NasPh in alcohol in the cold. Crystals. Yields a phenyl-hydrazide [87] (A., cf. Delisle, A. 260, 250). Combines with KHSO, and NaHSO.

SULPHYDRO-ACETOPHENONE. Phenul derivative C_{1,}H₂SO, i.e. C₆H₃S.CH₂CO.O₆H₃. [53°]. Formed from ω -bromo-acetophenone and NaOPh (Delisle, B. 22, 309). Needles (from alcohol), v. sol. ether

and acetone. SULPHYDRO-ACETYL-PROPIONIC ETHER. Phenyl derivative C13H16SO, i.e. C.H.S.CH.CO.CH.CO.Et. (197° at 18

min.). Formed from bromo-acetyl-propionic ether and NaSPh (Delisle, B. 22, 309). SULPHYDRO-ALLYL-QUINAZOLINE. Di-

hydride C.H. CII.N.C.H., [91's]. Formed from w-oxy-tolyl-allyl-thio-urea and HClAq at 100° (Söderbaum a. Widman, B. 22, 1670). Needles, v. c. sol. alcohol and benzene.

Reference. - OXY SULPHYDRO-ALLYL QUINAZO

DISULPHYDRO-DI-ALLYL-TRIAZOLE

NH CS.N.C.H. Formed from allyl-thio-ures and HNO, (Hector, J. pr. [2] 44, 505). Oil. B',H.PtCl,: crystalline pp.
o-SULPHYDRO-BENZOIC ACID

C. H. (SH). CO.H. Thio-salicylic acid. Formed by reducing o-sulpho benzoic chloride with zinedust and H.SO. (Delisle, B. 22, 2206). Amorphous powder, sl. sol. hot water, v. sol. alcohol. Not volatile with steam. - AgA'.

Thio-amide C₄H₄(SH).CS.NH₂. Formed by heating o-oxy-benzamide with P₂S₅ (Spilker, B.

22, 2771). Minute dark-red crystals.

Phonyl derivative Collos. Collos. Formed from o-diazobenzoic acid, phenyl mercaptan, and NaOHAq at 50° (Graebe a. Schultess, A. 263, 4). Plates (from alcohol) or needles (from HOAc); sl. sol. water. - NH.A.

-KA': needles, v. sol. water. -EtA'. [151°].
m-Sulphydro-benzoic acid C,H,(SH).CO,H. "Nounpy de De La Caracter and Active and Hollag on C.H.(SO,Cl).COCl (Frerichs, B. 7, 793). Colourless plates, m. sol. water.—Bah', 2¹,aq.—HgA'.,—PbC.H.SO, 3aq.—Cu(OH)A'.—AgA'.

a.SULPHYDRO-BUTYRIC ACID

CHEt(SH).CO.II. Formed from a-bromo-butyric

acid and alcoholic KSH (Duvillier, Bl. [2] 80, 507). Sol. water, alcohol, and ether.

Sulphydro-isobutyric acid HS.CMe, CO.H. Formed from a-brome isobutyric ether by successive treatment with alcoholic K₂S and alcoholic KOH (Lovén, J. pr. [2] 33, 109). a-SULPHYDRO-CINNAMIC ACID

C.H..CH:C(SH).CO₂H. [119°]. Formed, together with sulphocyanic acid, by heating benzylidene-rhodanic acid C,H,:CH:C(SH).CO.S.CN with baryta-water (Ginsburg a. Bondzynski, B. 19, 128; M. 8, 350). Yellowish crystals. V. sol. alcohol, ether, benzene, and CS₂, nearly insol. water. By treatment with iodine in alcoholic solution it is oxidised to di-sulphido-di-cinnamic

acid S₂(C₂HPh.CO₂H)₂.

Reference.—NTRO-SULPHYDRO-CINNAMIC ACID.

BSULPHYDRO-CROTONIC ACID. Ethyl

derivative CH₃-C(SEt):CH.CO.H. [113°].

Formed from β-chloro-crotonic acid [94·5°], mercaptan, and Na (Autenrieth, A. 254, 235; B. 20, 3189). Crystals, insol. water, v. sol. ether and alcohol. Gives a dark-green colour on warming with isatin and H₂SO₄. Yields CH₃-C(SEt):CH₂ (110°) on heating above its melting-point.—

BaA'₂ aq.—AgA': silky needles, not decomposed by hot water. Ac₂O forms the compound CH₄-C(SEt):CH.CO.OAc, a brownish oil.

Isomeride of the ethyl derivative CH₊C(SEt):CH₊CO₊H. [92°]. S. (alcohol) 20. Formed in like manner from the isomeric β-chloro-crotonic acid (A.). Crystals, nearly insolwater. Forms a dark-green liquid on warming with isatin and H_sSO₊. Where heated alone it yields the same ethyl-sulphydro-propylene (110°) as its isomeride.—BaA'₂ aq: thin plates (from Aq).

as its isomeride.—BaA', aq: thin plates (from Aq).

Phenyl derivative v. Phenyl-sulphydroCROTONIC Agid.

SULPHYDRO-ETHYL ALCOHOL

HO.O.H.SH. Formed from glycolic chlorhydrin and alcoholic KSH (Carius, A. 124, 258). Oil, v. e. sol. alcohol. Oxidised by HNO₂ to isethionic acid.—Hg(O₂H₃OS)₂. Needles (from warm alcohol).

SULPHYDRO - ETHYL - QUINAZOLINE.

Dihyàride C.H. CH. NEt [103°]. Formed by warming \(\omega\)-tolyl-ethyl-thio-urea with HCl (Söderbaum a. Widman, B. 22, 2936). Needles.

B'HAUCI. [118°].—B'_HPtCl. [208°].

SULPHYDRO - METHANE DISULPHONIC

SULPHYDRO METHANE DISULPHONIC ACID HS.CH(SO.H), Formed by boiling the trisulphonic acid with HOAc (Albrecht, A. 161, 134). Gives a blue colour with FeCl₃.—K.A." ½ aq.—Pb₃(CHS₂O₆)₂ 8aq. Small needles.

-Pb₃(CHS₃O₆)₂ Saq. Small needles.
Sulphydro-methane trisulphonic acid

HS.C(SO.H). Formed by boiling CS₂ or CSCl, with K.SO.Aq.— K.A''' 2aq: triclinic crystals. S. 2 at 12°. Gives a blue colour with FeCl₂.— (NH.).A'' aq. Thin plates.

SULPHYDRO-METHENYL-AMIDO-CRESOL

[4 1/2] C₀H₃Me<0>C.SH. [217°]. Formed by
heating benzene-azo-p-cresol with CS₂ at 200°
(Jacobsen a. Schenke, B. 22, 3235). Needles.

SULPHYDRO - METHENYL, AMIDO - (a) - NAPHTHOL C₁₀H₂ N C.SH. [above 220°]. Formed by heating an alcoholic solution of S₂(C₁₀H₂,NH₂[1:2]), with CS₂ (Jacobson, B. 21, 2624). Needles. Oxidised by K₂FeCy, to a crystalline disulphide.

Sulphydro methenyl - amido - (β) - naphthol. [249°]. Formed by heating benzene-azo.(β)-naphthol with OS₂ at 250° (Jacobson, B. 21, 414). Needles, sl. sol. benzene. HClAq at 170° yields amido-(β)-naphthol. An alcoholio solution of iodine forms crystalline (C₁₀H₂CN)>C)₂S₂-

SULPHYDRO . METHENYL . α - AMIDO-WAPHTHYL MERCAPTAN $C_{10}H_{\bullet} < {N \atop S} > C.SH.$ [above 240°]. Formed by heating α -naphthyl

thiocarbimide with S at 225°, and got also by the action of CS₂ on di-amido-di-naphthyl disulphide (Jacobson, B. 21, 2625; 24, 1406). Minute rosettes, sol. alcohol. Oxidised by

 K_sFeCy_s to $(C_{10}H_s < N_S)_2S_2 - B'HgCl_2$. [210°].

Sulphydro - methenyl - amido - (\$\beta\$) - naphthyl mercaptan [232°]. Formed by heating (\$\beta\$)-naphthyl thiocarbimide with S. Minute needles, Yields a methyl ether [74°], crystallising in needles.

SULPHYDRO . METHENYL . o . AMIDO-PHENOL $C_0H_4 < \stackrel{N}{<} > C.SH$. Thiocarbamido .

phenol. [196°]. Formed by boiling an alcoholic solution of o-amido-phenol for several days with CS₂ in a current of H as long as H₄S is given off (Dünner, B. 9, 465). Formed also by heating oxy-phenyl-thio-urea, and by heating o-oxy-phenyl-allyl-thio-urea with HCl at 130° (Von Chelmicki, J. pr. [2] 42, 442; B. 20, 177). Obtained also by adding dilute alcohol to a mixture of potassium xanthogenate and amido-phenol hydrochloride (Kalckhoff, B, 16, 1825). Needles (from water), sl. sol. cold water. Sol. NH₃Aq, crystallising therefrom unaltered.

Reactions.—1. Converted in o-amido-phenol by HClAq at 170°, and by NH₂Aq at 200°.—

2. Ac₂O yields C₆H₄ $\stackrel{\sim}{O}$ C.SAc [120°].—3. BzCl forms benzenyl - amido - phenol and C₈H₄(NHBz).OBz.—4. An alcoholic solution of iodine, added to its solution in NaOHAq, forms (C₆H₄ $\stackrel{\sim}{O}$ C)₂S₂ [110°], which is reconverted by hot dilute NaOHAq into sulphydromethenyl-amido-phenol.—5. Boiling methylaniline forms a base (? C₈H₄ $\stackrel{\sim}{O}$ C.NPhMe)

which yields B'.H.,PtCla. Salt.—AgC,H.,NSO. Amorphous.

Salt.—AgĈ,H,NSÖ. Amorphous. Ethyl ether EtC,H,NSÖ. (c. 267°). Solid, melting below 35°; volatile with steam.

SULPHYDRO-METHENYL-AMIDO-PHENYL-MERCAPTAN $C_6H_4 < S > C.SH.$ [179°] (H.); [174°] (J. a. F.).

Fornation.—1. By digesting o-amido-phenol with CS₂ (Hofmann, B. 20, 1789).—2. By heating C₀H₅.N₂.C₀H₅ with CS₂ at 265° (Jacobson a. Frankenbacher, B. 24, 1403).—3. By heating phenyl thiocarbimide with sulphur.

Properties.—Needles or plates, v. sol. alcohol and ether. Forms B'HgCl₂. Oxidised by $K_2Cr_2O_7$ to $(C_0H_4 {\stackrel{N}{\le}} C)_2S_2$, which yields $B'K_2Cr_2O_7$

[180°]. MeI yields C₆H₄<\(\sigma\)\sigma\(\circ\)C.SMe [52°],
which forms B'₂H₂PtCl₈, crystallising in plates.
SULPHYDRO - METHENYL - BENZENYL -

THIO-AMIDOXIM $C_0H_3.C < N.S > C.SH.$ [162°]. Formed by the action of CS_2 on an alkaline alcoholic solution of benzenyl-amidoxim (Crayen, B. 24, 388). Needles, nearly insol. water and cold alcohol. Conc. HClAq at 150° decomposes it into benzoic acid, CO_2 , NH_3 , H_2S , and S. NaOEt and EtI yield $C_2H_3.C < N.S > CEt$ [49°].

while benzyl chloride forms, in like manner, C.H.O.N.S.O.CH.Ph [79°].

SULPHYDRO - METHENYL - p - TOLYL - METHENYL-THIO-AMIDOXIM C.H.sN.2S. i.e. C.H.Me.C NSSC.SH. [166°]. Formed from CS2 and tolyl-methenyl-amidoxim (Crayen, B. 24, 391). Crystals (from alcohol acidulated with HOAc), insol. water, sl. sol. ether. Forms salts with bases. p-Tolyl-methenyl-amidine forms the salt C₆H₄Me.C(NH₂):NHHA' [172]. Boiling EtI and NaOEt yield C_eH₁Mc.C \ll ^{N,S}_NC.SEt [37°].

SULPHYDRO - METHYL - GLYOXALINE

 $C_4H_6SN_2$ i.e. CH.NMe C.SH. [142°]. (c. 280°). Formed by boiling CH(OEt), CH₂NH₂ with methyl thiocarbimide, alcohol, and dilute (30) Plates, v. sol. water, sol. alcohol. B'₂PtCl₁.

B'AuCl₂.—C₄H₂AgSN₂.—B'McI. [148²]. Needles.

derivative CH.NMe CSMe. Methylimidazolyl methyl sulphide. (225° uncor.). Formed by treatment with MeI and alkalis. Liquid, miscible with water, alcohol, and ether. Boiling dilute HNO, forms C₃H₁(NO₂)SN₂ (85°), which yields B'₂H₂PtCl₄ [197°). C₃H₂SN₂MeI. [173°]. Needles, v. sol. Aq.

Reference. - OXY-SULPHYDRO-DI-METHYL-GLY-

SULPHYDRO-DI-METHYL-PYRIDINE

CS CH: CMe NH. [210°-215°]. Formed by heating oxy-di-methyl-pyridine with P.S. at about 160° (Guthzeit a. Epstein, B. 20, 2113). Needles, v. sol. hot water and alcohol.

SULPHYDRO - METHYL - QUINAZOLINE. Dihydride C,H, CH, NMe

Formed by warming ω -oxy-tolyl-methyl-thiourea with HClAq (Söderbaum a. Widman, B. 22, 2935). Needles.—B',H,PtCl, [195°].—B'HAuCl, [153°]. Minute needles.

SULPHYDRO-METHYL-QUINOLINE

 $C_{io}H_{o}NS$ i.e. $C_{o}H_{o} < C_{N}E:CH$ [253°]. Formed by heating (Py. 3, 1)-oxy-methyl-quinoline with P_2S_3 (Roos, B. 21, 625). Small brown needles (from alcohol). Tastes bitter. Insol. cold water. Does not react with hydroxylamine and phenylhydrazine. H₂O₂ forms C₂₀H₁₀N₂S₂ [167°] crystallising from benzene in plates. EtI and alcohol at 100° form C₆H₄ CMe:CH₁ N=C.SE₁, which is oily and yields B'HI [240°] and B'2H2PtCl 14aq crystallising in reddish prisms.

Salphydro-methyl-quinoline C.H. C(SH):CH [187°]. Got by heating (Py. 1,8)-oxy-methyl-quinoline with P₂S₄ at 150° (Roos, B. 21, 629). Yellow prisms (from water). Eti and NaOEt yield C₁dH, EtNS [56°].—B'HCl. [205°-210°] (Conrad a. Limpach, B. 21, 1972). SULPHYDRO.METHYL.THIAZOLE.

hydride CH₂—N>C.SH. [82°]. Formed from 8-bromo-propyl-amine hydrobromide, NaOHAq, and CM, (Hirsch, B. 28, 968). White needles, v. sol. hot water. Yields C.H. MeNS(SMe)

(217°), C.H.,MeNS(SEt) (229°), and the propyl ether C.H.,MeNS(SC.H.) (247°).

ψ-SULPHYDRO-(a)-NAPHTHYL-METHYLBIAZOLE O CMe:N
CS-NC₁₆H. [86°]. Formed

from acetyl (a)-naphthyl-hydrazine and CSCl2 in CHCl, (Preund, B. 24, 4184). Yellow needles, v. e. sol. alcohol. The isomeride from (3). naphthyl-hydrazine melts at 109°.

SULPHYDRO-PENTHIAZOLE. Dihydrids $CH_2 < \stackrel{CH_2.S}{CH_2.N} > C.SH.$ [132°]. Formed by shaking γ-bromo-ethylamine hydrobromide with NaOHAq 7-Diomo-Ediplantine yardololinic with radio and CS₂ in the cold (Gabriel a. Lauer, B. 23, 92). Crystals, v. sol. hot water and alcohol, insol. acids, sol. NaOHAq. Bromine-water at 100° produces CH₂(NH₂).CH₂.CO₂H.

ψ - SULPHYDRO - PHENYL - AMIDO - (α)

NAPHTHYL-THIOBIAZOLE C18H12N3S2 i.e. SC(NHPh):N . [255°]. Formed by mixing NHPh.CS.NH.NHC₁₆H, with CSCl₂ in benzene (Preund, B. 24, 4192). Colourless crystals, v. sol. acetone, sl. sol. alcohol.

ψ - SULPHYDRO - PHENYL - MENHYL - BI -AZOLE OCS. NPh. [72°]. Formed from dichloro-phenyl-methyl-biazole dihydride and alcoholic ammonium sulphide (Freund a. Kuh, B. 23, 2837). Formed also from NHAc.NHPh and CSCl. (Freund a. Goldschmidt, B. 21, 2456). Prisms (from alcohol). Yields phenyl thio-carbimide on distilling with P₂S₂. SULPHYDRO-PHENYL-GLYOXALINE

C₉H₈N₂S i.e. CH:CH NPh. [181°]. Formed boiling NHPh.CS.NH.CH2.CH(OEt)2 with dilute H.SO. (Wohl a. Marckwald, B. 22, 569, 1353). Needles (from hot water), v. sol. B'2H2PtCl.: deep-red crystals.—B'MeI. [152°].

Methyl derivative N=C(SMe) NPh. [54°]. Formed by treatment with alcoholic NaOH and MeI. White needles (from alcohol), insol. water.—B'C,H,N,O,.—B'HNO,. Needles, v. c. sol. water.—B'MeI. [177°]. Crystalline rosettes (from water). Oxidised by dilute HNO, to a nitro- compound (116°).

ψ - SULPHYDRO - PHENYL - DI - METHYL-

PYRIDINE DICARBOXYLIC ETHER

CMe:C(CO_Et) NPh. [245°]. Formed by heating CS CMe:C(CO_Et) O with aniline control of the contro and HOAc (Guthzeit a. Epstein, B. 20, 2112). Sulphur-yellow crystals (from alcohol).

. SÚLPHYDŘO - PHENYL - NAPHTHYL -BIAZOLE O CS . NC 10H7. [164°]. Formed from NHBz.NHC, H, and CSCl, in CHCl, (Preund, B. 24, 4186). Needles, v. sol. alcohol. SULPHYDRO - PHENYL - QUINAZOLIME.

Dihydride C.H. CH., NPh. [1970]. Formed by warming ω-oxy-tolyl-phenyl-thio-urea with conc. HClAq (Söderbaum a. Widman, B. 22, Needles. - B',H,PtCl, [219°]. -1671). B'HAuCl. [197°]. Needles.

Reference.—Oxy - SULPHYDBO - PHENYL - QUIM-

DI-SULPHYDRO-DI-PHENYL-THIO-UREA. Di-mathyl derivative CS(NH.C.H.SMe)2. [162°]. Formed by boiling [1:2] NH2.C.H4.SMe with CS₂ and solid KOH (Hofmann, B. 20, 1794). Prisms, v. sl. sol. alcohol. Forms, when heated, SCN.C.H.SMe (c. 270°).

B-SULPHYDRO-PROPIONIC ACID

CH₂(SH).CH₂.CO₂H. Formed from β-iodopropionic acid and KSH. Got also by reducing sulphido-dipropionio acid (Lovén, J. pr. [2] 29, 376). Liquid, miscible with water, alcohol, and ether. Easily oxidised by air. CuSO, gives a pale-violet pp., but if not in excess it forms a yellow pp. of CH₂(SCu).CH₂.CO₂H while S(C₂H₄.CO₂H)₂ remains dissolved. -Hg(S.C2H1,CO2H)2. Scales.

-Bi(S.C₂H₄.CO₂H)₃.

Isomeride. - Thiomactic acid.

SULPHYDRO - PROPYL - PHTHALIMIDE C.H.O.:N.OH., CH., CH., SH. [48°]. Formed by beating \(\gamma\)-bromo-propyl-phthalimide with KSHAq at 100° (Gabriel a. Inter, B. 23, 88). Needles (from hot ligroin). Fuming HClAq at 180° forms phthalic acid and γ-amido-propyl mercantan.

(Py. 3)-SULPHYDRO-QUINOLINE

C.H. CH:CH N:C.SH [174°]. Formed by heating (Py. 3)-oxy-quinoline with P₂S, at 140° (Roos, B. 21, 620). Yellow plates (from dilute alcohol), insol. cold water, sol. acids and alkalis. Oxidised by H.O. to C., H., N., S. [137]. Eti and alcohol at 100° 3 rm C., H. (SEt) NHI [154°], which yields (C., H. (SEt) N)_H. PtCl. aq, melting, when anhydrous, at 190°

SULPHYDRO - THIAZOLE. Dihydride CH_rS CH_rN>C.SH. [107°]. Formed from bromoethyl-amine, NaOH, CS2, and alcohol (Gabriel, B. 22, 1152). Needles, sol. alcohol and hot water. Sol. alkalis. Bromine-water yields Alcohol, KOH and MeI form oily taurine. $C_2H_4 < S > C.SMe$ (217°), insol. alkalis but sol.

Reference. - OXY-SULPHYDRO-THIAZOLE.

SULPHYDRO-ACETONE. The compound CH, C(SEt), CH, SEt (170°) is formed by passing gaseous HCl into CH, CO, CH, SEt mixed with mercaptan (Autenrieth, B. 24, 167).

w-SULPHYDRO-o-TOLUIC ACID. Methyl ringting CH.(SMe).CaH..CO2H. [138°]. derivative CH₂(SMe),C₆H₁,CO₂H. [138⁵]. Formed by the action of conc. HClAq at 100° on the nitrile CH₂(SMe),C₆H₄CN (278⁵), which is got by dissolving thio phthalimidine in alcoholic KOH and adding Me¹ (Day a. Gabriel, B. 23, 2484). Light oil.

SULPHYDRO-ISOVALERIC ACID

CHPr(SH).CO.H. Formed from a-bromo-isovaleric acid and alcoholic KSH (Duvillier, Bl. [2] 80, 507).

SUPER. Use of this prefix applied to inor-ganic compounds. The prefix super is sometimes employed to denote the presence in compounds of relatively more of the characteristic negative element, or elements, than is found in the normal compounds of the same form. The prefix per is, however, much oftener used than super. It has been proposed by Mendeléeff to designate the oxides that belong to the same type as H.O.

superoxides, to distinguish them from other peroxides (v. Oxides, vol. iii. p. 660).

M. M. P. M. SUPERBIN. A poisonous substance contained in the root of Gloriosa superba (Warden, Ph. [3] 11, 495).

SYCOCERYL ALCOHOL C.H.O. Occurs as acetyl derivative in the resin of Ficus rubiginosa (De la Rue a. Müller, C. J. 5, 62; Rennie a. Goyder, C. J. 61, 916). Thin crystals (from alcohol), insol. water and alkalis. BzCl yields a crystalline benzoyl derivative.

Acetyl derivative C34H36O2. [121°]. Flat six-sided tablets, v. sol. hot alcohol, ether, and chloroform.

SYLVANE C.H.O. (63°). S.G. 887. Got by distilling pine-wood (Atterberg, B. 13, 879). Liquid, readily resinified. Oxidised by KMnO, to acetic acid. Not attacked by Na, alkalis, or Ac.O. HCl passed into its ethereal solution forms a small quantity of C15H22O, a liquid boiling at 240°

SYLVANE-ACETIC ACID v. METHYL-FUR-FURYL-ACETIC ACID.

SYLVANE - CARBOXY-ACETIC ACID METHYL-CARBOXY-FURFURYL-ACETIC ACID and ME-THRONIC ACID.

SYLVESTRENE v. TERPENES.

H=9.7 p.c. SYLVIC ACID C = 78.7 p.c. [c. 162°]. $[\alpha]_{D} = -53^{\circ}$. This acid is obtained from colophony by repeated crystallisation from dilute alcohol, and is perhaps identical with abietic acid (Liebermann, B. 17, 1884; Haller, B. 18, 2166). By heating with HI and P it is converted into a terpone $C_{10}H_{10}$. Sylvic acid appears also to be formed by the action of gaseous HCl on an othereal solution of dextropimaric acid (Vesterberg, B. 19, 2173). A sylvic acid C₂₀H₂₀O₂ is described by Maly (Sitz. W. 44, 121) as formed by adding dilute H₂SO₄ or gaseous HCl to a solution of abietic acid. Duvernoy (A. 148, 147) obtained a sylvic acid [129°] by distilling pimaric acid in vacuo.

Isosylvic anhydride C40H58O3. 30 mm.). $a_p = +63^\circ$. Got by distilling rosin in vacuo (Bischoff, B. 23, 1921). Colourless, brittle, microcrystalline substance, insol. water, v. sol. alcohol and ether. Isosylvic acid [62°] is ppd. on adding dilute HOAc to its solution in

potash. SYLVINOLIC ACID C₂₅H₃₆O₄? [130°]. Formed, together with sylvic acid, by saturating an alcoholic solution of abietic acid with HCl (Maly, Sitz. W. [2] 44, 121). Amorphous powder, y. sol. alcohol and ether.—CaA".—Ag₂A": pulverulent pp., insol. NH,Aq.

SYMBOLS. Symbols are employed to ex-

press the composition, and, as far as possible, the interactions, of compounds; v. Equations,

the interactions, or compounds; v. Equations, CHEMICAL (vol. ii. p. 433), FORMULE (vol. ii. p. 572), ISOMERISM (vol. iii. p. 79), and cf. OFTICAL METHODS (this vol. p. 253). M. M. P. M. SYNANTHRENE C_{1.}H_{1e}. Phosene. Occurs in crude anthracene (Zeidler, A. 191, 298; cf. Barbier, A. Ch. [5] /, 526). Yellowish-white plates. Yields a di-bromo-derivative C_{1.}H₂Br₁ (1752) argetallising in minute yellow needles. [175°], crystallising in minute yellow needles, sol. alcohol (difference from di-bromo-anthracene). Di-bromo-synanthrene is oxidised by CrO, and HOAc to a quinone (?) [240°-250°].

SYNTHESIS. The building up of compounds from their elements, or from groups of elements.

SYNTONIN v. PROTEIDS.

SYNTONIN v. PROTEIDS.

SYRINGIN C₁,H₂O₂, [191^o]. Dimethoxyconiferin. Occurs in the bark of the lilia (Syringa vulgaris) and of the privet (Ligastrum vulgare) (Bernays, J. pr. 25, 121; Kromayer, Ar. Ph. [2] 108, 7; 109, 18, 216; 113, 19; Kroner, G. 18, 215). White needles (containing aq), v. sl. sol. cold water, v. sol. alcohol, insol. ether. Its aqueous solution is slightly bitter, is laworotatory, and does not ppt. metallic salts. Conc. HNO₂ gives a blood-red solution. Conc. HClAq forms a colourless solution, turning blue, and finally giving a blue pp. Conc. II₂SO, gives a yellowish green colour, changing to violethrown and, on pouring into water, giving a bright-blue solution, which soon deposits an azure powder. Does not reduce Fehling's solution. Decomposed by emulsin into glucose and syringenin. KMnO₄ yields glucosyringic acid. CrO₂ forms glucosyringic aldehyde.

Syringenin C, H, O, i.e. [5:3:4:1]? C,H,(OMe),(OH).C,H,OH. Formed as above. Resembles coniferyl alcohol. Glucosyringis acid $\mathbf{C}_{li}\mathbf{H}_{si}\mathbf{O}_{ls}$. [208°]. Formed as above. Needles or prisms (containing 2aq), sl. sol. cold water. Decomposed by dilute $\mathbf{H}_s\mathbf{SO}_s$ into syringic acid and glucose.

Syringic acid C.H.(OH)(OMe), CO.H. Dimethyl derivative of gallic acid. [202°]. Decomposes at 230° into Co, and the di-methyl derivative of pyrogallol.—BaA', 3aq: four-sided tables.—McA'aq. [83-5°]. Crystals, sol. Aq.

Methyl derivative C_nH₁(OMe), CO₁H₂ [168°]. Needles. Yields C_nH₂(OMe), when distilled with lime. Identical with the tri-methyl derivative of gullic acid.—MeA'. [82·5°]. Needles. Glycosyringic aldehyde C₁₃H₂₀O₂. [162°]. Colourless, silky needles. Decomposed by emulsin or dilute H₂SO₄ into glucose and syringic aldehyde. Yields a phenyl-hydrazide [156°] and a crystalline oxim.

Syringic aldehyde C_uH₁₀O₄ i.e. C_uH₁(OH)(OMe)_CHO. [111·5°]. Small needles, smell²..g like vanillin. Turns brown in air. Reacts with phenyl-hydrazine, and combines with NaHSO₄.

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TAIGUIC ACID v. LAPACHIC ACID.

TALOMUCIC ACID $C_cH_{10}O_a$. [158°]. [a]_D = +29·4° at 20°. Formed from talonic acid and HNO₃ (S.G. 1·15) (Fischer, B. 24, 3625). Minute plates, v. e. sol. cold water and warm alcohol; v. sl. sol. ether. Converted by HCl and HBr at 150° into dehydromucic acid. Yields a phenyl-hydrazide [185°-190°]. Pyridine at 150° forms mucic acid.—CaA": crystalline powder.

TALONIC ACID C₄H_{1,O}. Formed by heating galactonic acid with pyridine at 150° (Fischer, E. 24, 3622). Purified by means of its brucine salt. Syrup, very soluble hot alcohol. Levorotatory. Yields a phenyl-hydrazide C₄H_{1,O4}(N,H₂Ph) [c. 155°].—CaA', aq. Needles (from alcohol), v. e. sol. water.—Brucine salt. [130°-133°]. Crystals, v. sol. water.

TAMPICIN C₃,H₃,O₁, [130°]. A neutral substance resembling convolvulin, occurring in Tampica Jalan (Spirgatis, N. R. P. 19, 452). Resin, v. sol. alcohol and ether. Converted by hot baryta-water into amorphous tampicic acid C₃,H₉₀O₁, Boiling dilute acids resolve tampicin into glucose (3 mols.) and tampicolic acid C_{1e}H₃₂O₅, which crystallises from dilute alcohol in minute needles and forms NaA' and EtA', both being crystalline.

TANACETIN $G_{11}H_{16}O_{4}$. A bitter substance obtained from the leaves and flowers of the tansy (*Tanacetum vulgare*) (Leroy, *J. Chim. Med.* 21, 357; Leppig, *J.* 1882, 1175). Amorphous, sol. water and algohol.

TANACETOGENIC ACID C₃H₁₄O₂. (114° at 15 mm.). Formed by the action of Br and (4 p.c.) NaOHAq on tanacetone (Semmler, B. 25, 3346). Oil, solidified below 0°.—AgA'.

TANACETONE $C_{10}H_{16}O$. (84.5° at 13 mm.). Occurs in oil of absinthe, thuja, and sage, con-

stituting the chief part of absinthol, salviol, and (\$\beta\$)-thujol (Semmler, \$B. 25, 3843, 3850). Got from ethereal oil of Tanacetum vulgare by shating with NaHSO₃, decomposing the crystalline product with Na₂CO₃, and distilling with steam. Oil, v. sol. alcohol and ether. Poos not reduce armoniacal AgNO₃. Dextrorotatory; \$a = 38\frac{1}{2}^{\text{a}}\$ in a 20 c.m. tube. S.G. \$\frac{2}{2}\$ 913. \$\mu_{D} = 1.450\$. Reactions.—1. Br and KOHAq yield bromo-

Reactions.—1. Br and KOHAq yield bromoform, hence it probably contains CO.OH,—2. Reduced in alcoholic solution by Na to tanacetyl alcohol C₁₀H₁₀O, (93° at 13 mm.), S.G. 2° '925, µ₀= 1·4635. This body does not combine with Br. With PCl, it yields tanacetyl chloride (72° at 10 mm.).—3. Oxidised by KMnO, to Tanacetketo carboxylic acid C₁₀H₁₀O, Needles (78°) (from ligroin) or plates [74·5°] (from water). Yields AgA'. Hydroxylamine yields C₁₀H₁₀O, (NOII) [103] when prepared from the needles and [169°] when got from the plates. The ketonic acid is oxidised by Br and NaOH to tanacetogen dicarboxylic acid C,H₁₀O, (142°3). Plates (from water). This acid yields Ag,A" while Ao,O yields the anhydride C,H₁₀O, [55°], which gives jsopropyl succinic acid [114°] when fused with potash.

Neduced in alcoholic solution by Na to tanacetyla mine C₁₀H_{1,8}:NOH. [52°]. (186° at 20 mm.). Reduced in alcoholic solution by Na to tanacetyla mine C₁₀H_{1,1}NH₂ (80·5 at 14 mm.), S.G. ²²·874, μ₀ 1·462, which yields B'HCl, which when heated gives tanacetene C₁H_{1,8} (63° at 14 mm.), S.G. ²²·841, μ₀ 1·476. Tanacetone oxim may be converted by warming with alcohol and dilute sulphuric acid into the cymidine C₈H₄(C₈H₁)(NH₂)Me [1:3:4], whence nitrous acid forms carvacrol.

TANACETOPHORONE $C_1H_{12}O$. (90° at 18 mm.). S.G. 22° 938. μ_D 1'482. Got by distilling tanacetogen dicarboxylic soid with soda-lime

(Semmler, B. 25, 3350). An oil, smelling like samphor-phorone. Reacts with hydroxyl-amine.

TANGHININ C₂₇H₄₀O₂2aq. [182°]. [a]₂₀ — 67°. Obtained from the kernels of Tanghinia venenifera of Madagascar (Arnaud, C. B. 108, 1255; 109, 70!). Crystals (from alcohol), v. sl. sol. water, sl. sol. ether. Cardiac poison. Resinified by dilute acids. Barytawater at 180° forms C₂₇H₁₁O₁₀.

TANNIN. TANNIO ACIDS. Under the

Under the above names are included a large series of compounds, occurring in the vegetable kingdom, of different constitutions, many of which have been very imperfectly studied. Their chief characteristics are their astringent taste and property of giving a dark-blue or green colouration with iron salts and a precipitate with a solution of gelatin. They all reduce solutions of the noble metals, and absorb oxygen in presence of alkalis. They are all aromatic derivatives, and yield on fusion with potash either pyrogallol or pyrocatechin. In some cases they have been synthetically prepared from these phonols and their derivatives, but in many cases the tannin appears to exist in the plant as a glucoside and attempts at a synthetical production have proved futile. Schiff. (B. 15, 2590) prepared some of the tannins synthetically, and concluded that they were anhydro- compounds of gallic and protocatechuic acids respectively. Etti (A. 186, 332) and others have also, for example, synthetically prepared catechutannic acid by heating pyrosatechin with water or alkalis. Gallotannic acid was formerly believed to be a glucoside, but subsequent investigation showed that the amount of sugar present was variable, and Schiff (A. 170, 43) finally proved that, although existing in the plant as a very unstable glucoside, when it was isolated it had the constitution of an anhydro- acid formed by the removal of one molecule of water from two molecules of a trioxy-benzoic acid. He considered that in gallotannic acid the anhydride was formed thus :-C,H2(OH)3CO.O.C,H2(OH)2COOH, whilst C. Etti, who has similarly investigated the tannins of the formulæ $C_{12}H_{18}O_{20}$ and $C_{20}H_{20}O_{20}$ has proved that they also are not glucosides, and regards them as derivatives of a ketonic acid of the formula $C_0H_2(OH)_3.CO.C_0H(OH)_3.COOH$. It would appear, then, possible to define the tannic acids as mono-carboxyl acids formed by condensation from two molecules of poly-oxy-benzoic acids and which exist as unstable glucosides in plants. The ease with which gallotannic acid is hydrolysed renders it probable that the difference in constitution between Schiff's and Etti's formulæ does actually exist, and renders it possible to subdivide the tannins into these two groups so soon as the different tannins have been re-examined from this point of view. ketonic character of the tannins was established by Etti through noting that they reacted with phenyl-hydrazine and hydroxylamine.

The origin of tannin in plants has given rise to much debate. According to Waage (Ph. 1890; Phar. Centr. 1891, 247) its formation is similar to that of the conversion of glucose into starch. The plant removes one molecule H.O from glucose for reserve purposes, and it under favourable circumstances three molecules H.O can be removed, a body having the composition

of a triketohexamethylene would be produced

CH₂COCH₂COCH₂CO. This constitution corresponds to the secondary form of phloroglucin. It is probable that the phloroglucin combines with the CO₂ in the nascent state produced by the respiration of the plant, and is thus converted into a carboxylic acid (gallic acid); two molecules of this acid by the removal of another molecule of water would then form tannin. Light and chlorophyll are necessary for the production of tannin.

Westermaier (B. B. 1887, 127-143) showed that with experiments made with Quercus pedunculata the tannin migrates downwards through the bark and the pith. Starch is always present, and it is probable that the starch only migrates in the form of tannin. The leaves of Rumex patentia and Rheum rhaponticum give both the starch and the tannin reactions. Schultze (A. a. 14, 525-526; B. C. 18, 137), by microchemical observations, also supports the view of Sachs and Heberland that the leaves of evergreens contain tannin as a winter reserve material. Tannin and starch only rarely occur When the simultaneously in the same cells. cells are rich in starch they contain a smaller amount of tannin, and vice versa.

In the case of leaves containing fatty oils and tannin, the cells which contain the oil are free from tannin, and cells containing no oil are free from starch. Kraus (B. C. 330-334) also notes that the formation of tannin in leaves depends on the presence of light and CO2, but believes that it acts more as a protecting agent either to prevent the plant from being eaten or rotting than as a reserve material. He points out that as fallen leaves contain as much tannin as they did during their best time of growth, the leaf tannin is of no value to the plant. Heckel a. Schlagdenhauffen (Ph. July 1892) note that the protecting leaf buds of certain species of gardenia contain a resinous substance which on analysis gives figures resembling cinchotannic acid. Both the gardenias and the cinchonas belong to the same order of plants (cf. Cross a. Bevan, C. J. 41, 106; Gardiner, Ph. [3] 14, 588; Braemer, Les Tannoïdes, Toulouse, 1890; Büsgen, C. C. 1890, 397).

Classification.—No satisfactory classification of these bodies exists. Wagner (Fr. 5, 1) divides them into pathological and physiological tannins. The former are chiefly glucosides, and precipitate gelatin, yield gallic acid when hydrolysed with dense sulphuric acid, and when heated alone form pyrogallol. The physiological tannins, on the other hand, form leather, and on distillation yield pyrocatechin. The old classification into iron-blueing and iron-greening tannins is found now to be untenable, as the presence of acids and salts modifies the colour which the tannins produce with FeCl₂, and the purity of many of the tannins examined by the earlier investigators cannot be guaranteed.

gators cannot be guaranteed.

Reactions.—The oxidation of gallic and tannin acids by nitric acid of moderate dilution yields oxalic acid and two acids, probably tricxy-glutaric and trioxy-butyric. The acetyl oquercitannic acid yields the same acids on oxidation (Böttinger, A. 257, 248-252). Metallic Nadoes not reduce gallic acid in absolute alcohol,

but tannic acid similarly treated undergoes simple hydrolysis, the yield of gallic acid amounting to 60 p.c. of the weight of tannin. No reduction products could be prepared (Bottinger, A. 258, 252-260). Ammonia and zinc-dust at 60° convert both acids into benzoic acid. Dilute H₂SO₄ and Zn also form benzoic from gallic acid (Guignet, C. R. 113, 200-201).

The action of heat. Most tannins begin to blacken at 120°, and at 160° decomposition into metagallic acid, and either pyrogallol or pyrocatechin, takes place. Those which yield pyrogallol usually also form a 'bloom' on leather, and give a blue colour with FeCl₂. This class includes galls, sumac, chestnut, and oak bark. The pyrocatechin-yielding tannins do not form a 'bloom' on leather, give green compounds with FeCl, and include hemlock, catechu, rhatany, and mangrove (Trimble, The Tannins, 1892).

The products of the action of heat on the tannins are best obtained by allowing the heating to take place on the material suspended in glycerin (1 g. in 5 c.c. glycerin). After heating to 200° for 80 minutes, dilute with water, and extract with ether. The ethereal extract contains either pyrogallol or pyrocatechin. The tannin must be freed from gallic acid and catechin before subjecting it to this test by previous ether

extraction of the aqueous solution.

The action of dilute acids. 2 p.c. absolute HCl at 100° in sealed tubes decomposes the tannios; insoluble ellagic acid, anhydrides, or phlobaphenes separate, and the filtrate contains gallic acid, glucosc, and unaltered tannin. Glucose should be removed from the tannin by repeated lead acetate precipitation before this treatment, or the amount of glucose before and

atter hydrolysis may be determined by Fehling's solution (Wehmer a. Tollens, A. 213, 327).

The action of alkalis. The pyrocatechinyielding tannins on heating with alkali yield protocatechuic acid, and either phloroglucin or acetic acid. The pyrogallol-yielding tannins form gallic and ellagic acids (20 g. with 150 c.c. of KHO solution, sp.gr. 1.2 for 3 hours are convenient quantities (Trimble, The Tannius).

The tannins in the bark of oak chestnut, horsechestnut, fir, &c., are precipitated in brominated condition by bromine water; tannin, sumach tannin, and oak wood tannin are not so precipitated (Böttinger, A. 240, 330). oak tannin, Böttinger, by treating with acetic anhydride, has formed an acetyl-o-compound of the formula C_{1.}H₁Ac₂O₃, and from it two bromo-derivatives C_{1.}H₁BrAcO₃ and C_{1.}H₁Br₁AcO₃ (B. 20, 761-766). A benzoyl-o-derivative has also been obtained from tannin by treatment with conc. NaOHAq and benzoyl chloride (Böttinger, A. 254, 370). The same author has attempted A. 254, 370). to prepare cyanhydrins, but without success. Well-dried tannic acid heated with anhydrous HON in sealed tubes yielded only an amide of gallic acid. Treated with hydroxylamine no oxim was formed, but only gallic acid (4. 259, 182-136). With pure tannin phenyl-hydrazine, however, forms derivatives which do not however, forms derivatives which do not crystallise, CO₂ and N being evolved at the same time. The tannins experimented upon water extracts of sumach, divi divi, oak wood, oak bark and pine bark; the dry precipitates con-tained phenyl-hydrazine derivatives of tannic

and gallic acids, osazones of dextrose and lavulose, and caramel (A. 259, 125-132; A. 256, 342).

Tannin solutions are very unstable, undergoing hydrolysis into gallic acid on standing. The hydrolysis into gallic acid is almost quantitative when the acid is dissolved in conc. H.SO. and then water added (Böttinger, A. 254, 878). When heated with KHSO, and glycerin to 119°-200° and the melt extracted with water, a residue is left soluble in absolute alcohol which contains two new acids of the composition C₁₄H₁₄O₇Aq and called hydrotannic and isotannic soids respectively. The former, which is the less soluble in alcohol, forms with Ac₂O a tetra-acetyl-compound while the iso-acid forms a brown tri-acetyl-compound (C. J. 1892, 181).

Preparation of tannic acid for pharmaceu-tical purposes. Pelouze in 1834 first suggested the extraction of tannic acid from galls by per-colation with ether, and this method is still in use. The pardered galls are placed in a closed percolator with commercial ether containing alcohol and water. The ethereal layer contains gallic and ellagic acids, together with resins and fats and a small portion of the tampic acid; the lower aqueous solution contains nearly pure tannic acid. The percolation is stopped when the lower layer ceases to increase in volume. The B. P. method consists in taking the damp galls, macerating with commercial ether, and expressing through muslin (Leconnet a Dominé). The purest acid is obtained when 10 pts. powdered galls are allowed to stand two days covered in a percolator with a mixture of 12 pts. ether and 3 pts. alcohol. At the end of this time the percolation is commenced until 10 pts. are obtained. One-third its volume of vater is then added, and the mixture well agitated. The aqueous layer contains nearly pure tannic acid, and is evaporated rapidly in vacuo. The commercial acid is known under the names of ether-tannin, alcohol-tannin, or water-tannin, according to the method of extraction adopted on a large scale.

Purification.—Petroleum ether percolation removes fat, wax, and some of the colouring matter. Solution in water removes resin, and, after decantation, sodium chloride precipitates the acid. Trimble adds lead acetate to the aqueous solution to precipitate colouring matter, filters, and extracts with acetic ether. The acid is re-dissolved in water, and extracted with ether to remove the last traces of gallic acid, and the aqueous solution finally dried in vacuo.

Detection.—1. Dilute H. SO. or HCl precipitates

conc. solutions.—2. FeCl,, a blue or green precipitate destroyed by long boiling, sol. weak mineral acids.-3. Lime-water precipitates the Ca salt. 4. Cinchonine sulphate precipitates white cinchonine tannate.—5. Gelatin forms leather and albumen also gives a precipitate. Alum and NH₄Cl render the precipitation more complete. An alcoholic solution of thymol, followed by conc. H.SO, yields a cose-coloured turbid solution (pyrogallol violet; gallic acid gives no colour: Saul, Ph. [3] 17, 387).—7. Iodine in presence of neutral salts gives a purple colouration (Nasser). 8. Acetate of lead acidulated with acetic acid ppis. tannic and not gallic acid (Guyard, Bl. 2, 41, 336).—9. NH₄Ol and NH₄ give a white precipitate rapidly becoming red, gallic acid a red colourstion only.-10. Cl water and NH, give a red colouration both with gallic and tannic acids. 11. K.FeCy, gives a similar reaction (Rawson, C. N. 59, 52-53).—12. In plants, Moll (A. a. 12, 496) detects tannins micro-chemically by treatment with 7 p.c. copper acetate for some days, then cuts sections, treats with a drop of 0.05 p.c. ferricacetate, washes with water and then alcohol to remove chlorophyll, and mounts in glycerin and looks for blue or green stain .-13. KCN gives a green colouration with tannin and none with gallic acid.—14. K_Cr₂O, gives a brown pp. with most tannins.—15. Saturated solutions of NaCl, CaCl, KOAc, and a number of other salts ppt. tannins from solution. -16. Conc. H₂SO₄ dissolves the dry tannins with a yellow colour, and on heating forms dark-red rufigallic acid and then black metagallic acid.-17. HNO, forms a yellow colour, and finally oxidises them to oxalic acid.—18. As Os heated with the dry tannins converts most into ellagic acid.—19. Most tannins are ppd. by the alkaloids.

Estimation of tannic acid. The methods devised for the estimation of tannic acid in vegetable extracts are very numerous, and may be grouped under the following heads:

- Gelatin or hide-powder absorption.
- 2. Titration with permanganate.
- 8. Precipitation with metallic salts.
- 4. Methods not included in the above.

For details of these various processes, vide Proctor, Textbook of Tanning; Trimble, The Tannins; Thorpe's Dictionary of Applied CHEMISTRY, and Rideal, Chemical Notes on Modern Tanning; The Assay of Tanning Materials; Industries, vol. xi. pp. 19, 139, 451. The two methods most generally employed are the hidepowder method and Löwenthal's permanganato

The hide-powder method is conducted as follows. A weighed quantity of the material is extracted with water and made up to a known volume. 100 c.c. of this solution is then evaporated, dried, and weighed to give the total solids present in the extract. Another portion of the same solution is agitated with, aspirated, or filtered through hide powder, and the total solids left in 100 c.c. of the solution again determined. The difference gives the quantity of tannic acid or matter which combines with gelatin per 100 c.c. of the solution (Fr. 24, 271).

The modified Löwenthal's process, which is now official in Germany, requires a standard solution of permanganate whose indigo value is known. A measured volume of the tannin solu-tion, together with a known volume of indigo solution, is then titrated with the permanganate solution. Another equal volume of the tannin solution is then agitated with hide powder or shaken with a gelatin and alum solution and filtered, and the filtrate, after indigo solution of known amount has been added, is titrated with the permanganate solution. The difference in the quantity of permanganate consumed is a measure of the tannic acid present. The various measure of teamine and present. The various tannins of commerce have different permanganate values; it is, therefore, necessary to standardise the permanganate for different tannin materials (Löwenthal, Fr. 16, 33; Kathreiner, Fr. 18, 118; Simaud, Fr. 22, 595; Saberdia, Fr. 51, 51) Schroeder, Fr. 25, 121).

Gallotannic acid C.H.O. Occurs in gall nuts and sumach.

Constitution. Constitution.—Co.O.C.,H.(OH), COOH (Schiff, A. 170, 43; Paul a. Kingzett, C. J. 33, 217).

Solubility.—Sol. acetone, glycerin, and oils;

insol. CS₂, CHCl₃, petroleum, and C₃H₃.

Compounds.—With gelatin contains 16.5 p.c. nitrogen = 34 p.c. tannin (Böttinger, A. 244, 227). (For other nitrogen values of gelatin-tannin compounds in leather, v. Rideal a. Trotter, S. C. I. 1891.) Penta - acetyl - compound C_pH₂(OAcO)₂CO.O.C_pH₂(OAcO)₂COOH [137°]. (Böttinger, B. 17, 1504).

Action of heat .- At 215° it forms pyrogallol, CO₂, and a trace of metagallic acid C₆H₄O₂. Strong heating at 240°-250° forms chiefly metagallic acid (Pelouze, A. 10, 159). Cold HNO, forms oxalie, trioxyglutarie, and trioxybutyrie acids (Böttinger, A. 257, 248). Boiling with KHO forms tannomelanic acid C₀H₁O₃; cold KHO and air form tannoxylic acid C₁H₂O₃ (Büchner, A. 53, 373). Hydrolysed by dil. H.SO, to gallic acid. Ferments also form gallic acid (van Tieghem, C. R. 65, 1992).

Oak bark. Tannic acid C, H, Oa.

Preparation .- The bark is extracted with alcohol, and the extract agitated with acetic ether and ether. Evaporate off ether, separate the precipitate of ellagic acid, and from residue separate gallic acid from the tannic acid by acetic ether and ether.

Properties .- Reddish-white powder. Sol. alcohol and acetic ether. Sl. col. ether and water. Heated to 130°-140°C. it forms an anhydride C₃₄H₃₀O₁, which is sl. sol. water; sol. alcohol and alkalis, and with conc. H₂SO₄ gives a second anhydride C₂₄H₂₂O₁₆. Heated with cone. HCl it evolves CH₂Cl, gives also the iodoform reaction. On dry distillation it forms pyrocatechin. Fused with KOH yields protocatechuic acid, pyrocatechol, and traces of phloroglucin (Etti, M. 1880, 262-278). When boiled with ether the The solution of the state of th

Etti and Löwe (l.c.).

Derivatives. Oak-red C14H10O62aq (Grabowbervatures.—Oak-red $C_{11}H_{10}O_{2}^{\circ}$ ad (Grabow-ski, A.145, 2); $C_{31}H_{32}O_{1}$, (Böttinger, A.240, 341). Böttinger has prepared various bromo-, acetyl, and benzoyl-derivatives (*Le.*) (Rochleder, A.63, 205; Böttinger, A.202, 270; B.14, 1598; Löwe, Fr.20, 210; Etti, M.4, 514; Garbowell, A.152Grabowski, A. 115, 2).

Fraxitannic acid C26H22O14. In ash-leaves. Forms an anhydride $C_{2n}^{-1}H_{2n}^{-1}O_{1n}$, a henzoyl-compound $C_{2n}H_{2n}O_{1n}(OB_3)$, a promaetyl-compound $C_{2n}H_{2n}(OAc)_1O_{1n}$, a bromaetyl-compound $C_{2n}H_{2n}(OAc)_1O_{1n}$, and a similar nitrocompound. On heating with $Ba(OH)_2$ it forms protocatechuic acid and other products. On heating to 100° it loses * mol. H.O, forming an anhydride C24H20O12 (Gintl a. Reinitzer, M. 3,

745 et seq.).

The following table gives the source of the principal tannins which have been investigated, and references to the papers in which a descrip-

tion will be found.

	• • '					T	A NN	IN.	TA	NNI	C.	A OI	DS.							635
References	Rochleder, Sitz. B. 53 [2] 478;	Bochleder, Z. 1867, 84 Godeffroy, C. N. 40, 144;	Löwe, Fr. 14, 35; Zolnel, Ar. Ph. 229, 123; Hurst,	D. P. J. 262, 288; Eitner, D. P. J. 244, 80	Dreykorn a. Reichard, D. P.J.	Buchner, J. 1861, 771 Schwartz, Sitz. B. 6, 446	Malin, A. Ch. 63, 276 Zeyer, J. 1861, 769	Wagner, Fr. 5, 10 Hofstetter, A. 51, 78; Etti, K.	Rochleder, A. 59, 300; A. 66,	wetz, Sitz. B. 9, 286 Villon C. N. 56, 175		Rochleder, A. 84, 354; Sitz. B. 9, 286	D. P. J. July 1893		Trimble, C. N. Jan. 6, 1898	Guignet, C. R. 113, 200	Rochleder, Sitz. B. 59, 819	Rocmeder, A. 04, 304; Suz. B. 9, 286	Schwartz, Sitz. B. 7, 250; Rembold, A. 143, 270; Ber-	Pelletier a. Caventou, A. Ch. 15, 837
Per cent.	١	68:38			ı	11	11	0:61	t	i	l	ł	ı		i	ŀ	11	i	1	•
Formula	C ₂₆ H ₂₄ O ₁₂	C ₂₆ H ₁₄ O ₁₃ .H ₂ O C ₁₄ H ₁₄ O ₁₃ .i.e.	С.Н. (ОН), СО.О.О.С.Н. (ОН), СООН?	,	$\mathbf{O}_{\mathbf{z}^{\mathbf{H}}\mathbf{z}^{\mathbf{h}}}O_{\mathbf{n}}$	0.H.0	С. Н. С.	C.,H.,O.	C, H, O	•	l	C,E,O.	C 58·10 per cent.	(seme group as mangrose farmin)	C,Hi,O,?	C1.H1.O.2/10.0.1	C ₁ ,H ₁₈ O ₂ C ₂ H ₂₃ O ₁₉ + ½H ₂ O	C ₁₅ H ₁₈ O.	C,H,O,	
Name	Horsechestnut tannin	Rhamnotannic acid Ellagotannic acid			Alder tannin	A snortonnio ocid	Filitannic acid	Beech tannin	Caffetannic acid		Fracticornitannin	without Callutannic acid	Canaigre tannin		Chestnut bark tannin or	gailotannic acid	Ipecacuanhic acid Cherry bark tannin	Caffetannic acid	Quinotannic or cinchona- tannic acid	
Part	Nearly all parts	Juice of berries			Wood	Wood and bark	Root Bark	Fruit Bark	Вету		1	Plant without	Bark	,	Bark	1	Root Bark	Root	Bark	
Plant	Esculus Hippocastanum	Esculus Hippocastanum	Algaronna		Alnus glutinosa	Anacahuita	Aspidium Filix-mas	Bablak (acacia) Retula rubra	Caffes arabica		Calandra granaria (corn	weevu) Calluna vulgaris	Oanaigre		Castanea vesos	- Actor	Cephalis Ipecacuanha	Chirococca racemosa	Cinchons	

TANNIN, TANNIC ACIDS.

Plant	Part	Name	Formula	Per cent.	References
Cinchons novs	Bark	Quinovatannic acid	C14H18O	1	Hlasiwetz, A. 79, 129; Bem-
Divi-di v i	1	Ellagotannic soid	C,H,(OH),CO.O.C,H,(OE),COOH?	i	Zölffel, Ar. Ph. 229, 218; Löwe, Fr. 14, 35; Hurst, D. P. J.
Elm Erythroxylon Coes	Leaves in autumn Leaves	Leaves in autumn Xanthotannic acid Leaves Cocatannic acid	$G_{2a}^{*}H_{2a}O_{4a}$ 3 $H_{2}O$? $G_{1}^{*}H_{2a}^{*}O_{1a} + 2H_{2}O$?	11	Ferrian, J. 1858, 463 Niemann, J. 1860, 368; Warden, Dr. 19, 928
Euphrasia officinalis	Green parts	ı	G ₂₂ H ₂₆ O ₂₈	1	Enz, Vierteljahrsch. Ph. 8,
Filix-mas Frazinus excelsior	Leaves	Filitannic acid Fraxitannic acid	- C ₂ H ₂₀ D ₁₁	1 1	Girtl and Reinitzer, M. 8, 745
Galum verum Hemlook Hops	Bark . Bark –	Galitannic acid Hemlock tannin Hop tannin	, O'H + H'O''H''C CaHI''O'' CaHI''CO''	111	Schwartz, A. 84, 5/1 Böttinger, B. 17, 1041 Bissell, C. J. 34, 328; Ph. [3]
Hex paraguayensis	ı	Caffetannic acid?	G ₁₃ H ₁₃ O ₆ ?	ı	Bochleder, A. 66, 39; J. 1856,
Krameria triandra	Bark of root	Rhatany tannin	C ₂₀ H ₂₀ O ₆	ı	
Laurus caustica	Bark	Larch tannin	G,7H,1,0,?	11	Stenhouse, P. M. 23, 336 Stenhouse, P. M. 23, 336 C. J. 34, 986; G. J. 40, 602; April 47, 800; Cimit 4200;
Mangrove	Bark	1	$G_{\infty}\mathrm{H}_{21}\mathrm{O}_{19}$	ı	10, 193 Trimble, Ph. Feb. 4, 1893; S. C. I. 1893, 364; Sten.
Myrobalans	ı	Ellagotannic acid	C,H,O,o	l	
Nux vomica Pinus sylvestrie	Bark -	Igasuric acid Cortepinitannic or pinicor-		11	Fn. 229, 125 Ludwig, Ar. Ph. [3] ii. 187 Kwalier, Sitz. B. 11, 363
Pinus sylvestris	Needles	tannic acid Tannopinic acid Pinitannic acid	$\zeta = ZC_{15}H_{11}O_{7} + 5H_{2}O_{7}$ $C_{25}H_{25}O_{18}$ $C_{11}H_{25}O_{18}$	1	Kwalier, Sits. B. 11, 356
Potentilla Tormentilla	Root	Oxypinitannic acid	, 0, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	1	Rembold, A. 145, 5
Cuebracho Colorado	Gum or wood	Fomegranate tannin Quebrachitannic acid	C ₂₀ H ₁₀ U ₁₃ C 52:52 per cent. H 5:11 O 49:37	11	Kembold, A. 143, 285 Jean, Arata, An. Soc. Cient. Argent. Feb. 1879; Bl. 28.

			1	ANNIN. T	ANN	IC ACIDS.		637
Etti, M. 10, 650; M. 1, 264; Stenhouse, P. M. 22, 425; Factinger, A. 202, 270;	Berzelius, Lehrb. 8 Auft. 6, 213; Löwe, Fr. 11, 378;	Wagner, Fr. 5, 10; Stenhouse,	F. M. 22, 423 Etti, B. 17, 1823; M. 1, 262 Etti, B. 17, 1823; M. 1, 263 Gautier, Bl. 27, 496 Schwartz, Sitz. B. 9, 298 Kubly, Z. 1869, 308 Beredius, Leirb. B *Auff. 6.	218; Schiff, A. 170, 48 Lidoff, J. R. 29, 607 Lidoff, J. R. 20, 607 Willigt, A. 82, 340 Lodwig, Ar. Ph. [3] ii. 137 Johnseon, Ar. Ph. [3] 138;	Stenhouse, Pr. 11, 403 Vincent a. Delachanal, BL	4', 492 Bottinger, B. 17, 1127 Physson, C. N. 38, 135 Stenhouse, P. M. 23, 532; Rochleder, A. 63, 205; Etti, B. 17, 1823; M. 1, 263; Hasiwetz a. Malin, J. Ph.	101, 109 Rochleder, Sitz. B. 29, 20 Bottinger, B. 17, 1129 Phipson, C. N. 20, 116	ක් සේ
1	1	19-26.7	111111	3:4 13:26	ı	101	111	
C ₁₅ H ₁₅ O ₅ + 2H ₂ O (from wood) C ₁₅ H ₁₆ O ₁₆ C ₁ ,H ₁₅ O ₁₆	C,H,(OH),COOC,H,(OH),COOH	1	C. H. O. + 3H.O. C. H.O. + 3H.O. C. H.O. + 3H.O. C. H.O. O. H.	2C,H ₂ O ₁ +H ₂ O		C,H,O,	C,H,O, Besembles spruce bark tannin	
Bark, wood, and Quercitannic acid	Bark and gall- Gallotannic acid	1	Quercitannic acid Quercitannic acid Chotsanin Rhodotannic acid Ebeotannic acid Gallotannic acid	Rubitannic acid	Sorbitannic acid	Spruce bark tannin Fragarianin Queroitannio scid	Pinitannic acid Micitannic acid	
Bark, wood, and leaves	Bark and gall- nuts	ı		Leaves Leaves and stalks Leaves Beans Leaf, stems, and	green twigs Juice of ripe	Bark Boot	Green parts Leaves Episperm	
Querens	Querons	Quereus Ægilops	Quercus pubescens Quercus robur Red wine Rhododendron ferrugineum Rhubsrb	Rhus Coriaria Rhus Cotinus Bubis tinctoria St. Ignatius beens Salix triandra and S. un-	dulata Sorbus aucuparia	Spruce Strawberry Thea	Thuja occidentalis Unacaria Gambier Walnut	•

TANSY OIL. The essential oil, obtained by distillation of the tansy (Tanacetum vulgare) contains 1 p.c. of a terpene C_0H_{10} (155°-160°), 26 p.c. of an alcohol $C_{10}H_{10}$ (155°-160°), 26 p.c. of an alcohol $C_{10}H_{10}$ (Bruylants, J. Ph. [4] 26, 393; B. 11, 449; cf. Persoz, C. R. 8, 33). Tanacetyl hydride $C_{10}H_{10}$ (195°-196°), 8.G. 4.918, V.D. 5·1, is converted by H.SO, into cymene. It reduces ammoniacal AgNO_s, forming a mirror. NaHSO_s forms crystalline CioHisNaSO. Split up by water into the parent substances

TANTALATES v. TANTALUM, ACIDS OF, AND

TANTALUM. Ta. At. w. c. 182 (exact value not known). Mol. w. not known. Ta has not been isolated.

Occurrence .- Tantalates occur in a few rare minerals, generally associated with niobates; tantalite contains from 35 to 75 p.c. Ta₂O₅, columbite from 13 to 36 p.c., yttrotantalite from 6 to 47 p.c., and a mineral com Western Australia, recently analysed and called stibiotantalite, c. 52 p.c., Ta,O, (Goyder, C. J. 63,

1076).

History. - A short account of the researches that led to the identification of two distinct oxides in tantalite is given in the article Nicobium (vol. iii. p. 505). Marignac (C. R. 60, 234, 1355) gave the formula Ta₂O, to oxide of Ta, which had been represented by Rose as TaO₂. Deville determined the V.D. of the chloride, and deduced the molecular formula TaCl, (C. R. 56, 891). By heating Na, TaF, with Na, H. Rose (P. 99, 69) obtained a black powder, probably a mixture of Ta and oxides of Ta. Berzelius (P. 4, 6) also obtained very impure Ta; Marignac (Ar. Sc. 1868) failed to isolate approximately pure metal.

Preparation of impure Ta.—Very finely-powdered tantalite is fused with three times its weight of KHSO,, in an iron or platinum crucible, until completely dissolved. After cooling, the fused substance is powdered and treated with boiling water, whereby sulphates of K, Fe, and Mn are dissolved out; the insoluble portion is washed, and then digested with yellow ammonium graphila machine allegated. nium sulphide, whereby sulphides of Sn and W are dissolved, and FeS remains mixed with Ta, 0, and Nb, 0. The residue is washed thoroughly, and digested with HClAq to remove FeS, and the portion insoluble in HClAq is thoroughly washed with boiling water until it is white. The mixture of Ta₂O₃ and Nb₂O₅ thus obtained is dissolved in HFAq in a platinum dish, the solution is heated to boiling, and a quantity of KHF, is added equal to one-fourth of the weight of mixed Ta₂O₅ and Nb₂O₅ used; the liquid is evaporated until 1 g. of the mixed oxides is present in about 7 c.c. and allowed to cool; the prismatic crystals of K.TaF, that separate are washed with cold water until the washings give a yellow pp., without any shade of red, after standing for two hours with tincture of galls. The K,TaF, thus obtained is heated, in a platinum dish, with rather more than its m a pastnum cisu, with rather more than its weight of pure cone. H₂SO₄, whereby KHSO₄, HF, and Ta₄O₄ are formed; the HF is removed by heat, and the KHSO₄ by repeated washing with water (Berzelius, P, 4, 6; of H. Rose, P. 144, 64, 70) 144, 64, 72).

Lawrence Smith (Am. 5, 44) recommends to warm 5 g. of very finely powdered tantalite, dried at 150°, in a platinum basin with a little water and 8 to 10 c.c. very conc. HFAq, to filter when reaction is completed, add a little water to the filtrate and evaporate nearly to dryness, to warm with excess of conc. pure H₂SO₄, and after the acid has been almost wholly removed by heating, to place the residue in c. 500 c.c. dilute HNO₂Aq (L. M., C. N. 51, 289, 304), and boil until Ta,O, and Nb,O, are ppd. By dissolving in HFAq, adding KHF, and proceeding as described above, Ta,O, is obtained free from

Nb₂O₃.

The pure Ta₂O₃ obtained by one of the preceding methods is dissolved in HFAq, in a platinum vessel, the solution is heated to boiling, and 708 pts. by weight of KHF₂ are added for 100 pts. Ta₂O₅ used. The solution is evaporated and allowed to cool; the crystals of K₂TaF, are washed with a little cold water, dried, mixed with c. half their weight of potassium, and heated in an iron crucible, the mixture of K, TaF, and K being covered with KCl. The contents of the crucible, after cooling, are added, little by little, to water; the black powder that separates is washed with water, and then with dilute alcohol and dried (Berzelius, P. 4, 6). The black powder is probably a mixture of Ta and oxides of the metal. Berzelius found that 100 pts. took up 17 pts. O when heated in air, 100 pts. pure Ta require 22 pts. O to form Ta,O. H. Rose (P. 99, 69) obtained a black powder-probably Ta mixed with oxides-by reducing Na2TaF, by heating with sodium.

Properties and Reactions .- The black powder obtained by Rose was a good conductor of electricity; it glowed when heated in the air, and slowly formed Ta,O,; it was insoluble in acids, scowed; heated in a stream of Cl it burnt to TaCl. Oxidation was effected by molten alkalis or alkali carbonates. The S.G. of a specimen containing c. 40 p.c. acid sodium tantalate was

The at. w. of Ta was determined by Marignac The at. w. of Ta was determined by Marignac (A. 140, 153; Suppl. 4, 351 [1865]) by decomposing K.TaF, and (NH₄),TaF, by H₅SO₄ and determining the quantities of Ta₂O₅ and K₂SO₄ produced. The values obtained varied from 180·1 to 185·2. H. Rose in 1856 (P. 99, 80) analysed TaCl₅ by decomposing by water, ppg. Ta₂O₅xH₂O by NH₂Aq, and estimating Cl in the filtrate. His results showed marked discrenancies pancies.

Ta is metallic in its physical properties, so far as may be judged from the impure specimens that have been prepared. Ta₂O₅ dissolves in HFAq, probably forming TaF. No salts are known to be formed by replacing the H of an oxyacid by Ta. In all the salts of Ta that have been isolated, other than the haloid compounds, Ta forms part of the negative radicle. the fifth member of the even-series family of Group V.; it is closely related to Nb, and less closely to N, P, V, As, Sb, Di, Er, and Bi. The only compound of Ta whose V.D. has been determined is TaCl,; in this molecule the atom of Ta is pentavalent (v. Nitrogen group of Eigments, vol. iii. p. 571).

Detection and Estimation,-Tantalum com-

pounds form potassium tantalate when fused ! with KOH, and the fused mass dissolves in water. The product obtained by fusion with NaOH dissolves in water to a clear liquid only after NaOH has been removed by washing, as sodium tantalate is insoluble in much NaOllAq. Addition of acid to an aqueous solution of an alkali tantalate, followed by boiling, ppts.
Ta.O. xH.O more or less completely. By adding HClAq to a solution of an alkali tantalate, and placing zinc in the solution, no blue colour is produced (cf. Niosium, detection of, vol. iii. p. 506). According to Levy (C. R. 103, 1074), an amethyst colour is produced by adding a very small quantity of Ta₂O₂, to a solution of resorcin in H CO 4. To 2. to in H₂SO₄Aq. Ta is estimated as Ta₂O₅; the process is sufficiently indicated under Prepara-

Action was to

Tantalum, acids of, and their Salts. TagO, reacts with molten alkalis, and alkali carbonates, from salts which may be regarded as derived from various hydrates of Ta₁O₂. Two hydrates are obtained, Ta₂O₂2H₂O and 2Ta₂O₂3H₂O, by decomposing TaCl, by a little water, and by fusing Ta₂O₂ with KHSO₄ and washing with water (v. Tantalum, oxides and hydrated oxides of, p. 640). The first of these H₄Ta₄O₁, corresponding with H₄Pa₄O₁, and the second may be formulated H₄Ta₄O₁₂. The tantalates that have been examined do not seem to be derived from either of these compounds, but from the hypothetical acids HTaO₃, corresponding with HPO₃ and HNO₃, and H₈Ta₆O₁₉ (=3Ta_O₃4H₂O₃. Tantalates are not produced by neutralising Ta₂O₃...H₂O₃ but by fusing Ta₂O₃ with alkalis, or by double decomposition from alkali salta.

TANTALATES. The tantalates belong to the form xTa₂O₃yMO, where $M = (NH_4)_2$, Mg, Hg_2 , K_2 , Ag, or Na,; of those that have been fairly fully examined, some correspond with the metaphosphates and meta-niobates M¹XO₂, and others belong to the more complex form M¹₈Ta₈O₁₉. Some of the alkali tantalates dissolve slightly in water, the other tantalates are incomplex. insoluble. Fluotantalates and fluoxytantalates are also known (v. infra). The tantalates have been investigated chiefly by H. Rose (P.

100, 417) and Marignac (Bl. [2] 6, 111, 118).

Annonium tantulate. A pp. is obtained by adding NH Cl to solution of Na Tu O I g. x H O. but the composition of the pp. is not known with certainty.

Magnesium tantalate. By adding MgSO4Aq to solution of Na, Ta,O10.xH2O a crystalline pp. was obtained which, after drying at 100°, had the composition Mg, Ta,O₁₉, 9H₂O. A crystalline Mg tantalate was obtained by Joly (C. R. 81, 266, 1266) by fusing Ta,O, with MgCl₂.

Mercurous tantalate. A brown, amorphous compound, perhaps Hg.Ta.O.p.xH.O. is formed by adding HgNO.Aq to solution in water of Na, Ta, O, xH2O.

Polassium tantalates. (1) K, Ta, O,, 16H, O, this salt is obtained by fusing Ta, O, with KOH, dissolving in water, and crystallising. (2) KTaO,: this salt, potassium metatantalate, is formed by heating the other tantalate, alone or with (NH₄)₂CO₂, and then treating with water. Silver tantalate. The yellowish white pp.

obtained by adding solution of a salt of Ag to solution of Na₂Ta₂O_{1p.2}H₂O, and drying at 100°, has the composition Ag,Ta₂O_{1p.2}H₂O.

Sodium tantalates. The meta-salt

NaTaO₃ is obtained by fusing Ta₂O, with Na₂CO₃, and washing with water. A salt of the composition Na₂Ta₂O_{1p.2}H₂O (x = 25 and 30) is prepared by fusing Ta₂O₃ with NaOH, dissolving in water and areallising. in water, and crystallising.

FLUOTANTALATUS. (Tantalifluorides.) These salts may be regarded as compounds of TaF. with metallic fluorides, or as metallic derivatives of the hypothetical acid H.TaF,; they are prepared by dissolving Ta,O, in HFAq, adding metallic fluorides, and crystallising; some of them are formed by dissolving Ta,O, and a metallic oxide in HIAq (Marignac, A. Ch. [4] 9, 276; Berzelius, P. 4, 6).

Ammonium fluotantalate (NH.) TaF, is obtained by evaporating a solution of NH.F in solution of TaF, in HFAq, and evaporating; the salt is aystalline and easily soluble in

Copper fluotantalate CuTaF, forms blue, deliquescent, rhombic prisms; it is prepared by dissolving CuO and Ta₂O₃ in excess of HFAq, and evaporating.

Potassium fluotantalate K₂TaF, forms white needles by dissolving KHF₂ in solution of Ta₂O₈ in HFAq, evaporating, and crystallising from hot water. The salt is very slightly soluble in cold water, but dissolves easily in hot water. On long boiling, K., Taf-Aq gives a white pp., probably having the composition K., Taf-Q., Fig. (=2Taf-, Ta, Q., 4KF). By dissolving K., Taf-, in warm 4 p.c. H., Q., Aq with a little HfAq and allowing to cool, Piccini (Zcit. für anor . Chemie, 2, 21) obtained crystals of the fluoxytantalate

K. Tao.F., H.O. (-Tao.F., 2KF.H.O).

Solium fluotantalate Na, TaF., H.O; obtained, as white crystals, by dissolving Na, Ta, O,, in HFAq, evaporating, and drying at 100° the salt that separates.

Zinc fluotantalate ZnTaF, 7H2O; a deliquescent salt, obtained by dissolving ZnO and Ta,O, in excess of HFAq and crystallising.

Tantalum, alloys of. By heating K₂TaF, with Al, and washing with HClAq, Marignac (P. 100, 145) obtained a grey power, S.G. 702. By heating to whitness, in a carbon crucible, a mixture of Ta.O., and iron filings, an alloy of Ta and Fe was obtained resembling pig iron (Gahn, Berzelius a. Eggertz, S. 16, 437)

Tantalum, bromide of, TaBr,. A yellowish, crystalline compound, obtained by heating a mixture of dry Ta₂O₅ and C in vapour of Br, and removing excess of Br by a long-continued stream of dry CO₂; decomposed by water to HBrAq and Ta₂O₅xH₂O (H. Rose, P. 90, 456; 99, 75). The conditions of preparation are similar to those in making TaCl, (q. v.).

Tantalum, carbide of. By heating TaN (v. TANTALUM NIFTUE) with C to the melting-point of steel, N is given off and the nitride in partly converted into brass-yellow coloured TaC₂ (Joly, Bl. [2] 25, 206).

Tantalum, carbonitride of. Joly (Bl. [2] 25. 206) obtained a substance, to which he gave the formula 10TaC.TaN, by very strongly heating a mixture of Ta₂O₄ with C and soda.

Tantalum, chloride of, TaCl,. Mol. w. c. 859 (not determined with great accuracy, as at. w. of Ta is doubtful). V.D. 185 at 360° (Deville a. Troost, C. R. 64, 294). Melts at 211°, and boils at 242° at 753 mm. pressure (D. a. T., l.c.). Only one chloride of Ta has been isolated.

Preparation .- About 5 g. pure dry Ta,O, is mixed with a considerable excess of dry sugar or starch, and the mixture is completely charred by heating in a closed crucible; the charred mass is broken into small pieces, which are heated to redness and placed, while red hot, in a rather wide tube of hard glass that is quickly heated to redness while a stream of thoroughly dried CO₂ is passed through it as long as any trace of moisture is given off from the contents of the tube; the tube is then allowed to cool, the current of dry CO, being maintained; when the tube is cold a stream of dry Cl is passed through it, and when every part of the apparatus is filled with Cl (but not until then) the contents of the tube are heated. TaCl, forms immediately behind the carbonaceous matter, as a pale-yellow solid; when the reaction has entirely ceased and CO is no longer evolved, the TaCl, may be sublimed into another part of the tube, a plentiful stream of dry Cl being maintained during the process. If sublimation is attempted before the whole of the Ta,O, has been chlorinated, before the whole of the La₁U₃ has been chlorinated, a part of the TaCl, is decomposed by the CO, with re-formation of Ta₂O₃. If there should be any air in the tube during the process a white sublimate is formed which is probably an oxychloride (H. Rose, P. 90, 456; 99, 75). Should the Ta₂O₃ used contain any WO₃, the sublimate obtained is reddish; by gently heating, the greater part of the red WOCl, may be removed, as it is rown redshift by D. as it is more volatile than TaCl.

Demarcay obtained TaCl, by passing vapour of CCl, over Ta₂O, heated to redness (C. R. 104,

Properties and Reactions. - Pale-yellow prismatic needles, melting at 211°, and boiling at 242° under the pressure of 753 mm.; begins to vaporise at 144°; V.D. 185 at 860° (Deville a. Troost, C. R. 64, 294). Decomposes in ordinary air, giving off HCl and becoming covered with a are, giving on its and comming covered wan acrust of crystalline Ta,O_s. Decomposed entirely by water to HClAq and Ta,O_s.xH₂O. Conc. H₂SO₄ causes evolution of HCl, and forms a somewhat turbid solution from which Ta,O_s.xH₄O separates on boiling; by adding the solution of the solution of the whole water to this solution, and boiling, the whole of the Ta is precipitated as Ta₂O₅ "H₂O. Conc. HClAq reacts similarly to H₂SO₀, but only a portion of the Ta₂O₀, xH₂O is ppd. on adding water and boiling. TaCl, is partly dissolved by heating with KOHAq. TaCl, is stiluble in absolute alcohol; H₂SO₂Aq does not ppt. Ta₂O₂, xH₂O from this solution.

No double compounds of TaCl, with KCl or NaCl-similar to those of TaF,-have been ob-

Tantalum, fluoride of. Ta,O,.xH,O dissolves in HFAq; neither boiling, nor adding H₂SO,Aq to the solution, ppts. Ta₂O₂. The solution in HFAq gives off vapours on evaporation that pro-bably contain TaF₁; by evaporating at a low 99, 75). By evaporating in vacuo a solution of Ta₂O₄.xH₂O in HFAq, Marignae obtained a white amorphous mass—probably an oxyfluoride—and then small crystals that were likely

TaF, combines with some metallic fluorides, forming fluotantalates (q.v., p. 639).

Tantalum, haloid compounds of. The only haloid compounds of Ta that have been isolated are TaCl, and TaBr. The former has been gasified, and the formula is molecular. also probably exists in solution of Ta2O, xH2O in HFAq. There is no reaction between I and TaO, mixed with C even at a very high temperature. TaCl, and TaBr, are readily decomposed by water, with formation of TaO, xHO and HXAq. Double compounds of TaF, with some metallic fluorides are known; they belong to the form M12TaF, (v. FLUOTANTALATES). Oxyhaloid compounds probably exist, but none has been iso-lated with certainty.

Tantalum, nitrides of. TaCl, absorbs NH, at the ordinary temperature; by heating the product in NH₃, Joly (Bl. [2] 25, 206) obtained an amorphous, yellow solid, to which he gave the formula Ta,N. By heating this yellow solid to redness in very dry NH₃, a black solid was obtained which, after washing with water and drying, had the composition TaN. This black solid conducts electricity; 'heated in air it burns to Ta₂O₃; NH₃ is given off by the action of molten KOH; it is insoluble in acids, except in a mixture of HFAq and HNO₃Aq (Joly, *l.c.*; cf. H. Rose, P. 100, 166).

Tantalum, nitrocarbide of; v. TANTALUM CARBONITRIDE, p. 639.

Tantalum, oxides and hydrated oxides of. The oxide Ta₂O₅ has been isolated, and also a hydrate of this oxide Ta₂O₂.2H₂O, and probably also another hydrate 2Ta₂O₃.3H₂O. The existence of another oxide, TaO2, is doubtful.

TANTALUM PENTOXIDE Ta,O,. (Tantalic anhydride. Tantalic oxide.) The preparation of this compound from tantalite is described at the the beginning of this article under Preparation of tantalum (p.638). Ta₂O₅ is also obtained by decomposing TaCl₅ by water, or by adding H₂SO₄Aq to solution of a tantalate and boiling, and then heating the Ta₂O₃.xH₂O thus ppd Ta₂O₃ is a white powder; it has not been fused; by heating with boric acid or microcosmic salt in a porcelain oven it is obtained in rhombic prisms (Ebelmen, A. Oh. [3] 33, 34; Nordenskjold a. Chydenius, J. 1860. 145). S.G. o. 7-6 (Marignac, Ar. Sc. 1868; Deville, C. R. 56, 894). Ta₂O, is insoluble in acids except HFAq; after being very strongly heated, it is insoluble in HFAq. Ta₂O₅ dissolves in molten alkalis, also in molten KHSO₄ (v. Tantalates, p. 639).

HYDRATES OF TANTALUM PENTOXIDE. By de-composing TaCl, by water, Ta₂O₄xH₂O is obtained, which, after very thorough washing with water, then with NH, Aq to remove adhering HCl, and finally with water, and drying at 100° gives off from 6 to 7.8 p.c. water when heated to redness. The formula 2Ta₂O₂.3H₂O requires 5.7 p.c. H₂O, and the formula Ta₂O₄.H₄O requires 7.5 p.c. H₂O. It is doubtful whether one or more temperature, Rose obtained crystals that dis-solved easily in water, and were partly vaporised when heated, leaving some Ta₂O₄ (P. 90, 456; a pp. of Ta₂O₄xH₂O is obtained, which, when

thoroughly washed and dried at 100°, is said | inoroughly washed and dried as 100, is said to be Ta₂O₂.2H₁O = H₄Ta₂O₄ (H. Rose, P. 100, 417). Strong acids, such as H₂SO₄, HNO₃, and HCl, ppt. Ta₂O₂.xH₂O apparently in combination with the acid used as precipitant from solutions of alkali tantalates; weak acids ppt. insoluble alkali tantalates.

TANTALUM DIOXIDE TaO. (Tantalum tetroxide [Ta_O]) The isolation of this oxide is doubtful. Berzelius obtained a brown powder by heating Ta₂O₃ to redness in a carbon crucible; it was not dissolved by any acids, not even by a mixture of HNO, Aq and HFAq; when strongly heated in air it gave Ta,O, (P. 4, 20).

Tantalum, oxyfluoride of. The white powder formed by decomposing K.TaF, by boiling water may be an oxyfluoride, according to Marignac (A. Ch. [4] 9, 276).

Tantalum, salts of. No salt has been isolated

by replacing the H of acids, except HCl and HF, by Ta. When alkali tantalates are decomposed by strong acids such as HCl, HNO, or H,SO, the ppd. Ta,O,xH,O retains some of the acid used as precipitant; compounds of Ta,O, with

these acids are perhaps formed.

Tantalum, sulphide of. By strongly heating Ta.O, in CS, vapour, also by heating to redness a mixture of vapour of TaCl, and H.S, a yellowish black solid is obtained, which has the composition TaS. according to Berzelius (P. 4, 6; v. also II. Rose, P. 99, 575). Roasted in air, this solid gives Ta, 23; heated in Cl it produces TaCl, and S.Cl.; conc. IINO, Aq oxidises it to Ta, O, xH, O and H, SO, Aq. TaS, does not combine with alkali H.SO, Aq. TaS, does not combine with alkan sulphides (R., l.c.); fused with KOH, it forms K.S and potassium tantalates. M. M. P. M.

TARCHONYL ALCOHOL Con H102O (?). Obtained from the leaves of Tarchonanthus camphoratus by extracting with alcohol (Canzoneri a. Spica, O. 12, 227). Silvery scales, insol. water and ether. Converted by PCl, into a chloride [70°] crystallising in small plates (from

alcohol)

TARCONINE v. vol. iii. p. 496. TARNINE v. vol. iii. p. 497. TARTARIC ACID C4H, O, i.e.

CO.H.CH(OII).CH(OH).CO.H. Dextro-tartaric acid. Di-oxy-succinic acid. [135]. S.G. 1764 acid. Di-oxy-succinic acid. [135]. S.G. 1-764 (Schiff, A. 113, 189); 1-74 (Buignet, J. 1861, 15); 1-7594 (Perkin). S. 115 at 0°; 132 at 15°; 343 at 100° (Leidie, Fr. 22, 269; G. R. 95, 87; cf. Schiff, J. 1859, 41; Maisch, J. 1865, 392). S. (alcohol) 25-6 at 15°. S. (ether) 4 at 15° (Bourgoin, Bl. [2] 29, 214; A. Ch. [5] 13, 400). [a]_p = 15.06 - 131p in a p per cent. solution (Landolt, B. 6, 1075; Lippmann, B. 24, 3300). H.F. 372,000 (Von Rechenberg). Heat of solu-tion: -3454 at 9° (Pickering, C. J. 51, 376).

Occurs free or as K or Ca salt in grape-juice, tamarinds, unripe mountain-ash berries, madderroot, potatoes, Jerusalem artichokes, sorrel, gherkins, mulberries, pine-apples, black pepper, the leaves of Chelidonium majus, the bulbs of Scilla maritima, in beet-juice, and in many other

Formation .- 1. Mostly together with racemic acid, by oxidation of saccharic acid, dextrose, cane-sugar, milk-sugar, starch, gum arabic, and sorbin by nitric acid (Dessaignes, A. Suppl. 2, 242; Hornemann, J. 1863, 381; Kiliani, A. 205, 175).—2. By the action of sodium-amalgam on Vol. IV.

an alcoholic solution of oxalic ether (Debus, A. 166, 124; C. J. 24, 376). The product is probably inactive tartaric acid.

Preparation .- Powdered chalk is added to a boiling solution of cream of tartar; the filtrate is ppd. by calcium chloride, and both pps. decomposed by the proper quantity of boiling dilute H₂SO₄. The filtrate from CaSO₄ is evaporated to crystallisation. It may be purified by saturating with CaCO₃, digesting with ZnCl, and decomposing the zine salt by H.S (Ficinus, Ar.

Ph. [3] 14, 310).

Properties .- Monoclinic prisms, with hemihedral facets; a:b:c = 785:1:805; $\beta = 79^{\circ}$ 43'. Dextrorotatory, the rotation being dependent on the concentration of the solution, and being also greatly affected by the presence of alcohols, acids, and other substances in the solution (Landolt, B. 13, 2329; Biot, J. 1850, 169; Pribram, M. 9, 25. 15, 2522; BIOL, J. 1800, 105; I Horam, A. 6, 485; B. 22, 6; Long, Am. S. 86, 351; Thomson, J. pr. [2] 35, 146). Sodium molybdate in the proportion of Nu MoO, to 2C, H₂O₆ increases the rotation 37 times, while ammonium molybdate (1) and the rotation of trybaric solid (1 mol.) increases the rotation of tartaric acid (3 mols.) 56 times (Gernez, C. R. 104, 783; 105, 803). Lithium and magnesium molybdate also increase the rotation. Sodium tungstate also increases the rotation, the maximum effect being 22 times (Gernez, O. R. 106, 1527; 108, 942). Crystals of tartaric acid are strongly pyro-electric. An aqueous solution of tartario acid is ppd. by baryta, lime, and lead acctate. Potassium salts, when the solution is not too dilute, form a crystalline pp. of KC, H,O,; the formation of the pp. being promoted by rubbing the sides of the vessel with a glass rod and by the addition of alcohol. CaCl, ppts. CaA', from neutral solutions of tartrates; the ppn. is hindered by ammonium salts. Calcium tartrate dissolves in KOHAq and is re-ppd. in gelatinous form on boiling. Reduces ammoniacal AgNO, forming a mirror; the solution then contains oxalic acid (Claus, B. 8, 950). Tartaric acid prevents the ppn. by alkalis of the oxides of Al, Bi, Ni, Co, Cr, Cu, Fe, Pb, Pt, and Zn, even on boiling (Aubel a. Ramdohr, A. 103, 33; Grotho, J. pr. 92, 175). 1 mol. acid prevents the ppn. of 1 mol. Cu(OII). A solution of tartaric acid, coloured by a drop of K2CrO4, gradually becomes colourless (difference from citric acid) (Salzer, B. 21, 1910). A saturated solution of potassium bichromate is slowly turned coffee-brown by tartaric (but not by citric) acid (Cailletet, C. C. 1879, 14). Boiling alkaline KMnO, is turned green, and finally brown, by tartaric acid, but only green by citric acid. Decolourises KMnO, in acid solution. When H,SO is present, twice as much KMnO, must be added to produce a permanent red colour as when it is absent, for in the latter case MnC, H,O, is formed (Fleischer, B. 5, 350). Tartaric acid gives an odour of burnt sugar when heated till carbonised. A crystal added to conc. H₂SO₄ containing 1 p.c. resorcin gives a red colour on warming (difference from citric and maleic acids) (Mohler, Bl. [3] 4, 728). To detect small quantities of tartaric soid in

presence of citric acid. Add about 1 g. citric acid to a 20 p.c. solution of molybdate of amacid to a 20 p.c. solution of more drops of a dilute solution of H₂O₂, and heat for three minutes on the water-bath. If the citric acid is pure the solution remains yellow. If 0-1 p.c. or more of tartaric acid is present, the liquid become blue (Crismer, Bl. [8] 6, 23).

Redctions.—1. Melts at 185°, changing to the isomeric metatartaric acid. The metatar.

taric soid may be reconverted into tartaric scid by boiling with water (Grosjean, C. J. 43, 334).— 2. At 140°-150° water is eliminated and ditar, 2. At 140°-150° water is eliminated and ditar-trylic acid C_aH₁₀O₁₁ is formed. On further heating soluble tartaric anhydride (tartrelic acid), and then insoluble tartaric anhydride, are formed. On further heating the products of distillation (from 250 g.) are pyruvic acid (9 g.), pyrotartaric soid (2 g.), formic acid (4 g.), resins, aldehydes and volatile acids (2 g.), and tarry bodies (3 g.) (P. Liebermann, B. 15, 428). 'Dipyrotartracetone' C₆H₁₂O₂ (230°), a colourless liquid, with aromatic odour, is among the products of the distillation of tartaric acid. It combines with bromine (Bourgoin, C. R. 86, 674).-8. By heating tartaric acid (10 pts.) with water (1 pt.) at 175° it is convexted into racemic acid and inactive tartaric acid. At 165° there acid and inactive tartaric acid. At 105 there is a greater yield of the inactive acid (Jungfleisch, J. 1872, 515). Heated with more water at 150° it yields CO₂ and pyrotartaric acid (Wedard, C. C. 1888, 889).—4. Potash-fusion vields acetic and oxalic acids. -5. Oxidation by CrO₂, KMnO₄, PbO₂ or MnO₂, and H₂SO₄ yields CO₂ and formic acid. The rate of oxidation has been studied by Krutwig (Z. P. C. 2, 787). By slow oxidation by HNO, tartronic acid may be obtained.—6. Reduced by HI and P to malic and succenic acids.—7. PCl, forms chloro-fumario and successions acids. —7. PCl, forms chloro-fumatic chloride.—8. FeSO₄ at 100° yields iso-arabic acid $C_bH_1O_3$, a thick dextrorotatory syrup, $[a]_b = 20^{\circ}$, yielding the salts CaA'_2 9aq, $Ca_2OA'_2$ 8aq, PbA'_{22} and $Pb_2A'_2O_2$ (Ballo, B.22,750).—9. Chloral forms $C_bH_1Cl_2O_3$ [124°], crystallising from chloroform in small needles, insol. water, sol. warm alcohol and ether (Wallach, A. 193, 46).—10. On submitting tartaric acid to electrolysis and treating the syrupy mass with phenyl-hydrazine, glyoxal-osazone [160°] and glyoxal-carboxylic osazone [218°] are obtained (Friedel a. Combes, Bl. [8] 8, 770).—11. On adding powdered tartaric acid to fused glucose tartaric glucoside is obtained (Guyard, Bl. [2] 41, 291; cf. Berthelot, A. Ch. [3] 54, 78).—12. m-Anido-benzoic acid at 160° forms 'tartylo-dibenzamio' acid C_{1n}H₁₀N₂O₂
i.e. (CO₂H.C₆H₁NH.CO)₂C₂H₂(OH)₂, a colourless powder, insol. water, sol. hot alcohol. Its alkaline salts form yellow solutions in which Cu(OAo)₂ ppts. C_{1n}H₁₄(CuOH)₂N₂O₂. On heating to 190° it yields the anhydride C_{1n}H₁₄N₂O₂, a greenish-yellow powder, converted by an alcoholic solution of aniline into tartranil dibenzamic

CO₂H.C₆H₄.N<CO⁽⁾CH.CH(OH).CONHPh [200°] (Schiff, A. 232, 156; G. 16, 28). Another product of the action of tartaric acid on mamido-benzoic acid is 'tartryl-benzamic' acid

CO.H.CH(OH).CH(OH).CO.NHC.H,.CO.H, which crystallises from water in pale-yellow aggregates, yields an acetyl derivative and an anhydride 'tartranbenzamic' acid C11H,NO. orystallising from water in green plates, forming C₁₁H,BaNO₄ and C₁₁H,CuNO₅, and converted at 210° in 'benzamtartridic' acid by dehydration. A warm alcoholic solution of aniline converts 'tartranbenzamic' acid into 'tartranilbenzamic'

acid [245°], which yields an acetyl derivative [198°]. 'Tartryl-benzamic' acid heated with dry amido-benzamide at 140° forms the compound amido-benzamide at 140° forms the compound $C_LH_2(OH)_4(OC)$. MLC₄H₂OONH₂)₂ a white powder, insol. water, sl. sol. alcohol, and yielding $C_{11}H_{11}$ CuN₂O, aq.—18. Glycerin at 100° yields the compounds $C_3H_3(OH)_2$.O.C. $_4H_2O_3$ and $C_4H_4(OH)(OC,H_2O_3)_2$ (Desplats, J. 1859, 500). Glycerin at 140° gives $C_{11}H_{11}O_{12}$ and $C_{13}H_{12}O_{18}$ —14. Erythrite at 100° forms $C_{12}H_{12}O_{11}$, which gives $C_{13}(C_{12}H_{13}O_{11})_2$ 3aq (Berthelot, A. Ch. [3] 54, 84). 15. Quercite at 120° forms $C_2H_{12}O_{12}$, which gives $C_{13}C_2H_{12}O_2$ 2aq.—16. Pinite at 120° forms $C_{23}H_{23}O_{13}$, which gives $C_{13}H_{23}O_{13}$, which gives $C_{13}H_{23}O_{13}$, which gives $C_{13}H_{23}O_{13}$, which gives $C_{13}H_{23}O_{13}$, which gives $C_{23}O_{23}H_{23}O_{33}$, which gives $C_{23}O_{23}H_{23}O_{33}$.—17. Mannita crystallising from alcohol in plates.

Estimation.—Methods for estimating tartaric acid have been described by Scheurer-Kestner, C. R. 86, 1024; Berthelot, Fr. 3, 216; Vogel a. Braun, Fr. 7, 149; Kissel, Fr. 8, 409; Fleischer, Braun, Fr. 7, 149; Kissel, Fr. 8, 409; Fleischer, Fr. 12, 328; Oliveri, G. 14, 453; Piccard, Fr. 21, 424; C. Schmitt a. Hiepe, Fr. 21, 539; Amthor, Fr. 21, 195; Nessler a. Barth, Fr. 21, 60; 22, 159; Kayser, Fr. 22, 123; 23, 29; Musset, Fr. 24, 279; Ferrari, Fr. 24, 279; Varington, C. J. 28, 25; Grosjean, C. J. 35, 341; Klein, Fr. 24, 379; Bornträger, Fr. 25, 327; 26, 699; Gantter, Fr. 26, 714; Von Lorenz, Fr. 27, 8; Philips. Fr. 29, 577; Goldenberg. Fr. 27, 28; Fr. 27, 8; Philips, Fr. 29, 577; Goldenberg, Fr. 22, 270; Heidenhain, Fr. 27, 681; Weigert, Fr. 23, 357; Haas, C. C. 1888, 1045; Ward, Ph.

[3] 19, 380.

Salts (Berzelius, P. 19, 305; 36, 4; A. Ch. [2] 67, 303; Werther, J. pr. 32, 383; Dumas a. Piria, A. Ch. [3] 5, 353; De la Provostaye, A. Ch. [3] 3, 129).—(NH₁).A''. [a]_D = 33.7° in a 1.2 p.c. solution (Sonnenthal, M. 12, 603). Efflorescent monoclinio prisms, v. sol. water; $a.bc. = .868:1:1\cdot244a = 88^\circ9'$. Givcoff NH₃ in air. Yield succinic acid on fermentation (Koenig, G.11.189). $-(NH_4)HA''$. $[a]_D = 25.7^{\circ}$ (Landolt). Minute lamine, sl. sol. cold water. Forms with ammonium Monoclinio crystals; $a:b:c=.402:1:1\cdot109$; $a=75^{\circ}12'$.—KHA". Cream of tartar. [a]_n=22° in a 4 p.c. solution. 100 g. solution contain :369 + 000569f grammes at f (Blarez, C. R. 112, 434, 808). S. 25 at 0°; 4 at 10°; 55 at 20°; 1·13 at 40° (Chancel, C. R. 60, 408; of Alluard, 1.13 at 40° (Chancel, C. R. 60, 408; cf. Alluard, C. R. 59, 500). Obtained by crystallisation of argol, which is deposited during vinous fermentation. Trimetric crystals; a:b:o='712:1:'787. Insol. alcohol.—Na,A''2aq. [a]_p=31° in a 1 p.e. solution (Sonnenthal; cf. Thomsen, J. pr. [3] 34, 80; 35, 145). S. 29 at 6°; 44 at 24°; 66 at 42:5° (Osann). Trimetric prisms; a:b:o='770:1:'387. V. sol. Hot water, insol. alcohol.—NaHA'', [a]_p=24·3° in a 1·8 p.e. solution (81). -NaHA". $[a]_D = 24.3^{\circ}$ in a 1.3 p.c. solution (8.). -NaHA"aq (Dumas a. Piria, A. 44, 80). S. 11 in the cold; 55 at 100°. Minute crystals, with hemihedral facets. Insol. alcohol.—Li, A". $[a]_D = 87.5^\circ$ in a .7 p.e. solution (S.). Deliques.

eent.—LiHA" 1½aq. Small crystals, v. sol. water (Dulk, Schw. J. 64, 180, 193; A. 2, 47).—LiHA"aq.—Li,HA",TeO 2aq. Needles (Klein, A. Ch. [6] 10, 118; C. R. 102, 47).—Hydroxylamine salt (NH,O),A". Very thin plates (Lossen, A. Suppl. 6, 233).—NH,NaA" 4aq. Trimetric crystals, with hemihedral facets, isomorphous with KNAA" 4aq; a:bic= \$23:1: 420. [a]_1=28°. [a]_0=32.7° (Landolt). S. 26 at 0° (Pasteur, J. 1849, 309).—LiNAA" 2aq.—Na,A",TeO 2aq.—K_A"TeO aq.—(NH,)KA". Monoclinic crystals, isomorphous with K,A". Give off NH, in air. V. sol. water. [a]_0=31° (L.).—KLiA"aq.—KNAA" 4aq. Rochelle salt. S. 30 at 3°, 66 at 26° (Osann). Heat of solution -6290 at 15°. The heat of solution of KNAA" is -2989 (Pickering, C. J. 51, 351). Large -6290 at 16°. The heat of solution of kNaA" is -2989 (Pickering, C. J. 51, 351). Large trimetric prisms, with hemihedral facets. Melts at 70°-80° in its water of crystallisation, and becomes anhydrous at 215° (Fresenius, A. 53, 234). [a]_D = 20°7° (L). Molecular rotation: Long, Am. S. 36, 351.—K₂A"₂TeO (dried at 100°).—RbHA". Trimetric prisms, isomorphous with the prisms of the prisms o with the eastium salt; a:b:c= 726:1: 695 (J. P. Cooke, Am. S. [2] 37, 70). S. 1·18 at 25°; 11·7 at 100° (Allen, Am. S. [2] 34, 367).—NaRbA" 4aq. Isomorphous with Rochelle salt (Piccard, J. 1862. Tablifornious with Acchemics at the tearth, J.1802, At 20° (a) = 0° in a f p.c. solution and 6.5° in a 20 p.c. solution.—"ILIA"aq. [a] = 9.5° in a p.c. solution at 20°.—TIKA". [a] = 10° in a p.c. solution at 20°.—TIKA". [a] = 10° in a p.c. solution at 20°.—TI(NH), A". [a] = 10° in a p.c. solution at 20°.—BaA". White amorphous pp., becoming crystalline. S.G. 21-4 2-973 (Clarke, Am. 2, 174).—BaA''aq (Dulk). S. (amorphous) 1-2; (crystalline; 077 (Vogel a. Reischauer, J. 1859, 288). K.BaA'', 2aq. Powder, sl. sol. water.—Na,BaA'', 2aq. Needles, sl. sol. water, more soluble in a solution of Rochelle salt. Ppd. on mixing a solution of Rochelle salt with BaCl₂.—BaA"TeO (dried at 100°).— SrA" 4aq. Monoclinic prisms. S. 7 at 16°. S.G. 198 1.966 (Clarke).—SrA" 3aq (Marignac, Ann. M. [5] 15, 280).—(NH₄)₂SrA"₂12aq. Thin plates.— K₂SrA" 2aq.—Na₃SrA" 2aq.—CaH₄A"₂. S. 71 at 15 6°. Trimetric crystals.—CaA" 4aq. Occurs in grapes. Ppd. as white crystalline powder on adding CaCl, to a solution of KA". Small trimetric prisms. a:b:c = 872:1: 908 (Anschütz, A. 226, 191). S. -016 at 15°: 3 at 100° (Mohr, J. 226, 191). S. 016 at 15°: 3 at 10° (Mohr, J. 1865, 393). Forms, with calcium malate, the double sait CaA'CaC,H,O, 6aq, orystallising in needles, S. 1·25 at 17° (Ordonneau, Bl. [3] 6, 262).—MgA"4aq. S. 8 at 16°. [a]_b = 36°.—Mg,C,H,O, 3aq. S. 024. Ppd. by adding NH, to a solution of MgA" (Mayer, A. 101, 166).—MgNa,A", 10aq.—MgKa,A"8aq.—MgHA", S. 2 at 16°.—BeA"3aq (Atterberg, Bl. [3] 21, 162).—BeK,O,H,O, 3aq. Prism® (Toczynski, Z. 1871, 277).—KS,DO)A"4aq. Tartire results. Prepared at 10.—Den only fastering or a state of the part of th comes K(SbO)C,H,O,. S. 5 at 8°; 8 at 21°; 52

at 100°. '05 to '1g. produce vomiting. Its solution reddens litmus, and gives a crystalline pp. of K(SbO)A" with alcohol. Its solution is ppd. by mineral acids, by alkalis, and by H₂S. HgCl₂ is reduced by it to calomel. Heat of formation: Guntz, C. R. 104, 699. Volumetric estimation of Sb in tartar emetic (Dunstan a. Boole, Ph. 8]
19, 385). — K(SbO)A"H₂A" 2₃aq. Efflorescent prisms. Alcohol added to its aqueous solution ppts. tartar-emetic, leaving tartaric acid in solution (Knapp, A. 32, 76).—K(SbO)A"3KHA". Mammellated groups of needles, v. sol. water.— Mammenated groups of needles, v. sol. waser. (K(SbO)A", NaNO, (Martenson, J. 1869, 539).—
Na(SbO)A" ½aq. Trimetric, hygroscopic prisms;
a:b:c=922:1:108. — (Na,A"),2Sb(OH), 3aq.
Amorphous, v. sol. water (Clarke a. Evans, B. 16,
2385). — NH₄(SbO)A" ½aq. — NH₄(SbO)A" ½aq.
(Berlin, A. 64, 359).—Rb(SbO)A" ½aq. Isomory phous with tartar-emetic (Grandeau, A. Ch. [3] phous with tartar-emetic (Grandeau, A. Ch. [3] 67, 155).—Tl(SbO)C,H,O_a aq. [a] = 100° in a 2 p.o. solution 4,20° (Long, Am. S. [3] 38, 264).
—Ag(SbO)A''A; Crystals (J. P. Cooke, Am. S. [3] 19,393).—Ba(SbOA''),2\[2\] aq.—Cd(SbOA''),6 (SbOA''),2\[4\] (A, 104, 328).— (Ca(SbOA''),2\],\[4\] (A, 104, 328).— (Ca(SbOA''),2\],\[4\] (A, 104, 328).— in the calcium of tartar-emetic converted at 200° mixed with calcium nitrate in trimetric forms mixed with calcium nitrate in trimetric forms (Marignae, Ann. M. [6] 15, 280).—Sr(SbOA"), Iloxagonal crystals. — Sr₂(SbOA"), [NO₃), 12aq. Very soluble crystals (Kessler, P. 75, 410).— Pb(SbOA"), 4aq. — Bo,Sb₂(C,II,O_a), — Sb(HA"), 4aq. Needles, v. sol. water (C. a. E.).—Sb₂A", 6aq.—(SbO)HA" aq (Clarke a. Stalle, B. 13, 1788).—(SbO)HA" (Guntz, C. R. 104, 850).—O,II,O,Sb₂O,aq. White granular pp., formed by adding alcohol to a solution of Sb₂O, and the stalled of the stal in aqueous tartaric acid (Berzelius). Converted in aqueous tartaric acid (Borzelius). Converted by heat into SbOC₁H_O.—(C₁H₂O₁), Sb₂O₂Gaq (P'cligot, A. Ch. [3] 20, 289).—(O,H₂O₁), Sb₂O₂Gaq (P'cligot, A. Ch. [3] 20, 289).—(O,H₂O₄), Sb₂O₂Gaq (dried) (P.).—(C₁H₁O₂), Sb₂O₂H₂O. Crystals (Guntz, A. Ch. [6] 13, 399).—Herberine salt (G₂H₁₈NO₄(SbO)A" (Sterhouse, J. 1863, 452).—Bruoine salt C₂H₂N₂O₂(SbO)A" (Clarke, B. 15, 1540).—Atropine salt C₂H₂N₂O₂(SbO)A" (Large A. Ii-line salt C₂H₂N₂O₃(SbO)A" (Large Gillorescent trimetric crystals; a:b:c.=876:1:694. Got by dissolving As₂O₃ in NH₂HA" (Mitsoher-Got by dissolving As O₃ in NH, IIA" (Mitscherlich; Werther, J. pr. 32, 409).—K(AsO₃)A" 2 aq. Got by dissolving arsonic acid in a solution of cream of tartar (Pelouze, A. Ch. [3] 6, 68).—
(Sr(AsOA"), NH, NO, 12aq. Large trimetric crystals (Marignae).—Bi, A", 6aq. Small crystals, decomposed by water (Schneider, P. 88, 555. K(BO)CHO (Schwarzeberg 4, 61, 244). tals, accomposed by water (scineliter, 7. 86, 55).—K(BiO)C,H,O, (Schwarzenberg, A. 61, 244).
—Bi₂K(BiO)(C,H,C₀)₂ (Frisch, J. 1866, 401).—
K(BO)A" (dried at 100°). Potassium borotar K(BO)A" (Gried at 100"). Foldsstim borotar-trate. Amorphous mass, v. sol. water, insol. alcohol. At 100° it becomes K(BO),H,O, Purgative. [a] = 58° in a 20 p.c. solution at 20°. — K₂(BO)C,H,O, — K₂(BO),C,H,O, — Na(BO)A". — Na,(BO),C,H,O, (Duve, J. 1869, 540). — K₂(BO)₂C,H₂O,Na(BO)A". — Ba(BO),C,H₂O, —PbA". S.G. 17-2 4.012 (Clarke, Am. 2, 174). White crystalline pp., v. sol. HNO₃.—Pb₂C₄H₂O₄ aq (Erdmann, A. 21, 14). Insol. water, v. sol. KOHAq. — Pb₂(C₄H₂O₄)₂. — Ce₄A''₂ 9aq (?). — Th₂K₂A''₃. — CuA'' 3aq. S. 06 in the cold; S at 100°. Light-

green powder.- CuA"4NH, (Schiff, A. 123, 46). green powder.— CuA"ANI, (Schiff, A. 123, 46).
—(H(NH,JA"),(HgO),3H,0 (Harff, Brandes'
Arch. 5, 259; Burckhardt, ibid. '(2) 11, 257).—
(KHA"),HgCl, 6aq.— K,2NiA", (dried at 110°).
Efflorescent, apple-green crystalline powder
(Fabian, A. 103, 248).—CoOl(HA"),5NH,22aq
(Jörgensen, J. pr. [2] 18, 239).— ZnA"2aq
(Schiff, A. 125, 146).—Zn,2C,H,O, 3aq. Powder,
insol. water.—Cr(OH)A". Violet flakes, turning
derk blue over H. 50, (Schiff, A. 195, 145). insol. water.—Cr(OH)A". Violet flakes, turning dark-blue over H₂SO₄ (Schiff, A. 125, 145). At 220° it yields CrC, H₂O₆.—K(CrO)A" 3 aq (Malaguti, C. R. 16, 457).—(UrO₂)A" 3 aq (Péligot, A. 56, 231).—K₂(UrO₂)A"₂ (dried at 200°).—(SbO)₂(UrO₂)A"₂ 3 aq.—SnA". Minute crystals.—K(FeO)A"4 or 5 aq. Propared by digesting cream of tartar with water and Fe(OH)₃. Brown scales well by transmitted light, Acids part from scales, red by transmitted light. Acids ppt. from its solutions a basic salt, sol. excess. — NH₄(FeO)A"4 (or 5) aq. — Fe₂A"₅. — FeA". Formed by boiling tartaric acid with water and iron wire (Méhu, N. J. P. 40, 257). Minute crystalline powder. S. 877 at 45.6° (Dulk, A. 2, 62).—K(MnO)A" 4aq (Descamps, Z. 1870, 317). Ag.A'. Amorphous curdy pp. got by adding AgNO, to a cold solution of Rochelle salt. Crystallises from a warm solution in white scales. Nearly insol. water. Its ammoniacal solution deposits Ag on warming (Liebig a. Redtenbacher, A. 38, 132; Erdmann, J. pr. 25, 504).

—AgHA" (Perkin, C. J. 51, 369). Monoclinic

Ethylene-diamine salt C,H,O,(N,2H,C,H,). Dextrorotatory. Leaflets, v. sol. Water. The acid salt is sl. sol. water, S. 3 at 15°, and the solution is dextrorotatory (Colson, Bl. [3] 7, 808).

Mono-methyl ether MeHA". Formed by boiling tartaric acid with McOII (Guérin, A. 22,

boiling tartaric acid with McOII (Guérin, A. 22, 248). Prisms.—KMeA".—BaMe_A"_aq (Dumas a. Péligot, A. Ch. [2] 61, 200; [3] 5, 373).

Di-methyl ether Me_A". [48°]. (280° i.V.). S.G. (liquid) ½ 1°340. [a]_D = 2°454 at 18° (Anschütz a. Pictot, B. 13, 1176; 18, 1399); = 2°14 (Phillips a. Guye, C. R. 110, 714). Yields an acetyl derivative [103°] [a]_D = -14° and a dihenzoyl derivative [11]. = -88°8°.

benzoyl derivative $[a]_D = -88.8^\circ$.

benzoyl derivative [a]_D = -88°8°.

Mono-ethyl ether EtHA". [90°].
Formed by dissolving tartaric acid in boiling alcohol (G.; Marian, N. J. T. 13, 2, 43; Trommsdorff, N. J. T. 24, 1, 11; Guérin, A. Ch. [2] 62, 57]. Very deliquescent prisms.—NaEtA". Powder, sl. sol. alcohol (Mulder, B. 8, 370).—KETA". S. 106° at 23·5°. Colourless trimetric prisms; a:b:c=288:1: 417.—Cu(EtA'), 5aq.—Ba(EtA''), 2aq. S. 38 at 23°; 128 at 100°.—Pb(EtA''), —Cu(EtA''), 6aq. Blue silky efflorescent needles.—AgHA". Prisms.

Di-ethyl ether Et_Ah". (280° iV.); (233° cor. at 197 mm.). S.G. ½ 1:2097; ½ 1:2019. [a]_D = 9 at 18° (Anschütz a. Pictet, B. 13, 1176); 7:22 at 12°; 8:02 at 20° (Perkin, O. J. 51, 363). M.M. 8.766 at 14.8°. Liquid miscible with water (Demondesir, A. 80, 301). Sodium forms CO_Et.CH(ONa).CH(OH).CO_Et. the latter being converted by EtCl into a deposit and a

CO_Et.CH(ONa).CH(ONa).CO_Et, the latter being converted by EtCl into a deposit and a liquid, part of which is soluble in alcohol and which and part insoluble in alcohol and ether (Mulder, R. T. C. 8, 375; 9, 238; 10, 171; cf. Cohn, B. 20, 2003). The soluble product mixed with alcoholic CuCl₂ and poured into water forms a pp. crystallising in light-green needles, sol. alcohol and ether, insol. water and CuCisH2,O11. Tartaric ether is converted by treatment with gaseous HCyO into allophanyl-tartario ether NH₂,CO.NH.CO.O(C₄H₃Et₂O₅) [188°], which is m. sol. hot water and alcohol.

A cetyl derivative of the ether CO_Et.CH(OAc).CH(OH).CO_Et. Formed from the ether and AcCl, the mixture becoming hot (Perkin, C. J. 20, 145). Heavy oil, sl. sol. water, insol. saline solutions. Neutral to litmus.

Di-acetyl derivative of the ether CO_Et.CH(OAc).CH(OAc).CO_Et. [67°]. (292°) (Pictet, B. 14, 2790); (230° at 100 mm.). Formed by heating tartaric other with AcCl at 100° (Perkin;

by heating tarturation with Accitation (Ferali; Wislicenus, A. 129, 187). Prisms (from water), v. sl. sol. water. Slowly saponified by KOHAq. Acetyl-benzoyl derivative of the ether CO_Et.CH(OAc).CH(OBz).CO_Et. Formed by heating the mono-benzoyl derivative of the

Mono-benzoyl derivative of the ether CO_Et.CH(OH).CH(OBz).CO_Et. [647]. Formed by heating the ether with BzCl at 100°. Prisms, sl. sol. hot Aq. Saponified by alcoholic potash yielding C₂H₂(OII)(OBz)(CO₂Et).CO₂K, C₂H₂(OH)(OBz)(CO₂Et).CO₂K, and finally, potassium tartrate. C₂H₂(OH)(OBz)(CO₂Et).CO₂H forms tufts of needles, sl. sol. water.

Di-benzoyl derivative of the ether

[a]_D = -60° (Phillips a. Guye, C. R. 110, 716).

Di-n-propyl ether Pr₂A'. (303° i.V.),

S.G. 17 1·1392. [a]_D = 13·77 at 18° (A. a. P.);

= 12·44 (P. a. G.).

Di-isopropyl ether Pr₂A". (275°). S.G. 2º 1·130. [a]_D = 14·89 at 20° (Pictet, J. 1882,

20 1·130. $[a]_D = 1.00$. 856). Liquid. Di-isobutyl ether (Pr.CH₂)₂A". [68°]. (324°). S.G. 102 1·015. $[a]_D = 19\cdot9^\circ$ (P.).

(324°). S.G. 192 1-015. $[a]_D = 19.9^\circ$ (P.). Yields a dibenzoyl derivative $[a]_D = -42^\circ$. Isoamyl ether $(C_sH_{11})HA''$. Formed by digesting tartaric acid (150 pts.) with isoamyl alcohol (88 pts.) at 130° (Balard, A. Ch. [3] 12, 309; Breunlin, A. 91, 314). Nodular mass, with very bitter taste.— $KC_sH_{11}A''$ aq. Crystalline.—NaC_sH₁₁A''. Nodules. — Ba $(C_sH_{11}A'')_2$ 2aq: pearly plates (from water).—Pb $(C_sH_{11}A'')_2$ —Ca $(C_sH_{11}A'')_2$ —Ag $C_sH_{11}A''$. Tufts of needles. Di-acetul derivative $C_sH_{11}O_s$. 4.e.

Di-acetyl derivative $C_{H_10}O_g$ i.e. $CO_2H.CH(OAc).CH(OAc).CO_2H.$ [$a_{1p}=-23\cdot14$ (Phillips a. Guye, C. R. 110, 716). Formed slowly from the anhydride by the action of water. Hard deliquescent crystals (containing Saq), melting at 58°. V. sol. water, alcohol, and ether, sl. sol. benzene. Lævorotatory. Its salts form lævorotatory solutions (Colson, Bl. [3] 7, 806; C. R. 114, 417). Converted into tartario acid by hot KOHAq.—KHA": crystalline powder.— BaA": slender deliquescent needles.—CaA".—CuA".—Ag₂A": white crystalline mass.— Ethylene-diamine salt C,H,O,(N,H,C,H,).

Laworotatory. V. sol. water.

Anhydride of the di-acetyl derivative C₃H₃O₂, [127°]. Formed by heating tartaric acid with AcCl (Ballik, Sits. W. 29, 26; Pilz, Sits. W. 44 [2] 7; Perkin, C. J. 20, 149). Slender needles (from benzene). Dextrorota-

Benzoyl derivative C₁₁H₁₀O₇ i.e. CO₂H.CH(OH).CH(OBz).CO₂H. Formed UO2H.CH(OH).CH(OBz).CO2H. Formed by heating tartaric acid with benzoic acid at 150°

(Dessaignes, J. Ph. [3] 82, 47). Minute crystals, V. sol. water, sl. sol. alcohol.—Ag,A": white pp.
Di-benzoyl derivative C, H, O, i.e.
CO,H.CH(OBz).CH(OBz).CO,H. [90°].

[a] = -116° in alcohol. Formed by dissolving

its anhydride in hot water. Needles (containing aq). Converted by heat into a crystalline substance melting at 132°.

Anhydride C₁₈H₁₂O₇. [174°]. [a]_D = 143° in acctone at 18°. Formed by heating tartaric acid with BzCl. Small needles, insol. cold water, sol. alcohol, benzene, and alkalis. Dextro-

Di-nitroxyl-derivative

CO.H.CH(NO.).CH(NO.).CO.H. Nitrotartaric acid. Formed by dissolving tartaric acid (1 pt.) Nitrotartaric olume of H₂SO, (Dessaignes, A. 82, 362; 89, 339). The crystals are dried and crystallised from ether (Kekulé, A. 221, 245). Silky prisms, decomposed by hot water, forming oxalic and tartronic acids, CO., and NO. Alcohol containing IINO, forms di-oxy-tartaric acid. Ammonium sulphide reduces it to tartaric acid.— (NH.)HA''.—Ag A'' aq. V. sol. water.—Et₂A''. [46°]. S.G. ¹⁵ 1-278. Formed by dissolving tartaric ether in a mixture of HNO, and H.SO, and ppg. with water.

Amide C.H.O. (CC NH2). Formed by passing NH, into an alcoholic solution of the other, or of its di-acetyl derivative (Demondesir, A. 80, 303; Pasteur, C. R. 35, 176; Grote, A. 130, 202; Ruhemann, B. 20, 3366). Trimetric crystals (from water), v. c. sol. water. Dextrorota-

Amic acid C.H.NO. i.e. CO.H.CH(OH).CH(OH).CO.NH... Formed by passing NH3 over tartaric anhydride moistened with alcohol (Laurent, Compt. Chim. 1845, 153). with alcohol (Laurent, Compt. Ordin. 1843, 1845). Formed also, together with tartaric acid, by heating tartaric ether with NH, Aq at 100′ (Grote). Syrup. -CaN₂ 6aq: tetrahedra, v. sol. water.—Pb₁(C₄H, NO₂)...—BaN₂ 8aq.—EtA'.

Anilide C₂H₁O₂(CO.NHPh)... [250°].

Formed by boiling aniline with tartaric acid (Polikier, B. 24, 2959). Pearly scales, insol. water, sl. sol. other solvents. Yields mono-, di-, and tri-acetyl derivatives, melting at 227°, 216°,

and 137° respectively.

Phenyl-amic acid C₁₀H₁₁NO₅ i.e. CO₂H.CH(OH).CH(OH).CO.NHPh. Formed by boiling the phenylimide with NII3Aq (Arppe, A. 93, 352). Plates, v. sol. water and alcohol.—BaA'2: spangles, m. sol. hot water .-Agh': white powder, v. sl. sol. water.

Phenylimide C₁₀H₂NO₄ i.e.

CH(OH).CO NPh. [230°]. Formed, together

with the anilide, by heating tartaric acid with aniline at 150°. Pearly plates, v. sol. water. Di-o-toluide C₂H₁O₂(CO.NH.C.H.Me)... [183°]. White plates, insol. water (Bischoff, B. 23, 2049). Ac₂O at 140° yields a di-acetyl compound [222°].

Di-p-toluide C₂H₁O₂(CO.NH.C₄H₁Me)... [264*]. Got by heating p-toluidine with tartaric acid at 185°. Silky needles (from alcohol). Converted by Ac₂O into a di-acetyl derivative

Hydraside C₂H₂(OH)₂(CO.NH.NH₂)₃.

zine hydrate (Von Rothenburg, B. 26, 2057). Needles, sl. sol. alcohol. Converted by benzoic aldehyde into C.H. (OH) (CO.N.H:CHPh), [225°], crystallising in yellowish plates (from alcohol).

Lævo- tartario acid СО_Н.СН(ОН).СН(ОН).СО.Н. acid. [170°]. When a solution of racemic acid is divided into two equal parts and one is neutralised by animonia and the other by soda, and the solutions mixed and allowed to evaporate, hemihedral crystals of Na(NII,)C,H,O, are obtained. Half of these crystals have the hemihedral faces oppositely situated to those of the other half; and on carefully selecting the two kinds of crystals (the solutions of which exhibit equal and opposite action on polarised light), ppg. their solutions by lead nitrate, and decomposing the lead salts by H2S or H2SO40 solutions are obtained which on evaporation yield crystals, the one of dextro- and the other of lavo-tartaric acid (Pasteur, A. Ch. [3] 28, 56), If in a solutien of sodium ammonium racemate of S.G. 1.26 a crystal of the dextro- salt be put on one side and one of the lavo- salt be put on the other side of the vessel, the two salts will crystallise separately (Jungtleisch, J. 1h. [5] 5, 346). The separation of sodium ammonium racemate into the dextro- and lavo- tartrates does not take place if the solution is heated to 118° in a scaled tube and allowed to crystallise without access of air (Bichat, Bl. [2] 46, 54). According to Wyrouboff (C. R. 102, 627), the splitting up of the sodium ammonium racemate depends upon strength of solution and temperature only.

Laevo-tartaric acid is exactly like dextro tartaric acid in solubility and S.G. Its crystals are like the reflection of those of the dextroacid. The two acids are oppositely pyro-electric. Solutions of the layer acid exhibit an effect on light equal and opposite to that produced by solutions of the dextro- acid of like strength. When conc. solutions of equal quantities of the dextro- and levo- acids are mixed, heat is given out and racemic acid separates. The saits of the lavo-tartaric acid have the same amount of water of crystallisation, and the same crystalline form as the salts of dextro-tartaric acid. They exhibit opposite hemihedry, opposite rotation, and are oppositely pyro-electric. Differences are observed between the compounds of the two seids with optically active substances. Acid ammonium (active) malate combines with acid ammoniam dextro- (but not levo-) tartrate. Cinchonine levo- tartrate C, H2, N2OC, H2O, con-

tains aq, while the dextro-tartrate contains 4aq. Di-methyl-ether Me₂A''. [48°]. (160° at 16 mm.). Laworotatory (Anschütz, B. 18, 1398; A. 247, 112).

the di-Di-acetyl derivative of methyl ether CO2Me.CH(OAc).CH(OAc).CO,Me. $[a]_D = -1.3$ (in a 3.6 p.c. solution in alcohol of S.G. 826). Formed by heating Me₂A" with AcCl. Monoclinic plates (from benzene); a;b:c=1.052:1:1.007; $\beta=87^{\circ}$ 54'. On mixing with the corresponding dextro-compound it forms the isomeric racemic compound [86°].

Amide C₄H₄O₄(NH₂)₂. Combines with the amide of active malic acid, forming needles, S.

more than 33.

Racemie acid C.H.O. Paratartaric acid.

[2067] (Bischoff, B. 22, 1812). S.G. (of H₂A")

1 1.778; (of H₂A" aq) 1.687 (Perkin, C. J.

51, 366]. S. (of H₂A") 8.16 at 0°; 18 at 20°;

187-8 at 100°. S. (of H₂A" aq) 9.23 at 0°; 20·6

at 20°; 1849 at 100° (Liedie, C. R. 95, 87).

Heat of solution at 9°: −5675 (for H₂A");

−7065 (for H₂A" aq) (Pickering, C. J. 51, 367).

H.C. (for H₂A" aq) 278,400. Acid potassium racemate either occurs sometimes in crude argol, or is produced therefrom in the purification processes (Kestner; Jungfleisch, C. R. 85, 805). On crystallisation of cream of tartar, acid potassium racemate remains in the mother-liquor.

Constitution.—Assuming racemic acid to be a compound of the dextro- and levo-tarraric acids, its formula must be at least $(C_4\Pi_aO_a)_2$.

Formation.—1. By mixing solutions of dextro- and lawo- tartario acids.—2. By heating tartaric acid (30 g.) with wate (4 c.) for 30 hours at 175° (Jungfleisch, Bl. [2] 18, 203).—3. By heating the dextro- or lawo- tartrate of quinine or cinchonine at 170° (Pasteur, A. 72, 164; 84, 154; 88, 211).—4. By heating tartaric ether.—5. By heating inactive tartaric acid at 200° or by boiling it with HClAq (Dessaignes, Bl. 1865, i. 34).—6. By oxidation of fumaric acid by aqueous KMnO₄ (Kekulé a. Anschütz, B. 18, 2150; A. 226, 191; cf. Tanatar, B. 12, 2293).
7. By the action of HNO₄ on lawulose, mucic acid, and inulin; and, together with tartaric acid, by the action of HNO₄ on milk sugar, cans sugar, saccharic acid, dulcite, and mannite (Carlet, Rep. Chim. pure, 2, 345; 4, 17; Hornemann, J. pr. 89, 283).—8. Together with inactive tartaric acid by boiling silver di-bromo-succinate with water (Perkin a. Duppa, C. J. 13, 102; Pasteur, A. Suppl. 2, 242; Jungfleisch, Bl. [2] 19, 198).—9. By boiling silver iso-di-bromo-succinate with water (Demuth a. Meyer, B. 21, 268).
10. By boiling glyoxal with dilute HCy and HCl (Schöyen, A. 132, 168; Strecker, Z. [2] 4, 216).—11. By the action of zinc-dust (2 mols.) and dilute HOAc (3 mols.) on glyoxylic acid (1 mol.) at 100° (Genviesse, Bl. [3] 7, 225; C. R. 114, 555).—12. From piperic acid, sorbic acid, and CHO.CH.CH.CH.CH.CO₂H by careful oxidation with dilute KMnO₄ below 4° (Doebner, B. 23, 2374).—13. By heating a solution of desoxalic acid (Lowig, J. 1861, 605; Klein, J. pr. [2] 20,

Preparation.—Sodium ammonium racemate, got from the mother-liquor from which cream of tartar has separated, is treated exactly in the same way as cream of tartar in the preparation of tartaric acid. The small opaque needles of racemic acid can be separated by handpicking from the large, transparent crystals of tartaric acid.

Properties. — Triclinic crystals (containing aq); a:b:c=*484:1:806; $a=120^\circ$; $\beta=96^\circ$ 15'; $\gamma=76^\circ$ 5' (De la Provostaye, A. Ch. [3] 3, 131). Slightly efflorescent. Gives off aq at 100°. Less soluble than tartaric acid. In dilute solutions of racemic acid the lowering of the freezing-point is the same as with an equal weight of tartaric acid (Racult, Z. Ph. 2, 186). Absorption of a solution of racemic acid by filter paper does not separate the dextro- and lawo- acids (March-

lewski, B. 26, 988). A solution of gracemic acid is ppd. by CaSO₄ (unlike tartaric acid). Calcium racemate is insol. acetic acid (unlike calcium tartrate). NH₄Ol does not hinder the ppn. of calcium racemate. When heated above 200° racemic acid yields the same products as tartaric acid. By various ferments (e.g. Penicillium glaucum) racemic acid, when fres or as acid ammonium salt, is converted into tartaric acid (Pasteur; cf. E. Mulder, R. T. C. 1, 231). A solution in HNO₂ (S.G. 1-52) poured into half its volume of H.SO₄ deposits the crystalline C₂H₂(O.NO₂)₂(CO₂H)₂ (Dessaignes, J. Ph. [3] 32, 46). AcCl converts racemic acid into di-acetyl-racemic anhydride C₂H₂(OAO₂)₂C₂O₃ [123°]. Racemic acid and its salts are inactive to light.

Salts (Fresenius, A. 41, 1; 53, 230).—
(NH₄),A". Trimetric prisms; a:b:c=509:1::847.
V. sol. water, nearly insol. alcohol. Give off NH₄ in air.—(NH₄)HA". S. 1 at 20°; less sol. boiling water. Monoclinic prisms. Reddens litmus.—K₄A" 2aq. Six-sided tables. S. 103 at 25°. Nearly insol. alcohol.—KHA". S. 55 at 19°; '7 at 100°. Insol. alcohol.—K(NH₄)A". Striated prisms.—Na₂A". S. 38 at 25°. Trimetric prisms. Insol. alcohol.—NaHA" aq. S. 9 at 19°. Monoclinic prisms (from water). Ppd. from aqueous solution by addition of alcohol.—Na(NH₄)A". A. Ch. [6] 9, 229).—NaKA" 4aq. S. 47 at 6° (Fresenius, A. 53, 230).—NaKA" 3aq. Monoclinic crystals (Wyruboff, A. Ch. [6] 9, 232).—RbA".—CaA" 4aq. Acicular prisms (Anschütz, A. 226, 191).—BaA" 2½aq. S. '05. Crystallino pp.—SrA" 4aq. —TIA" (De la Provostaye, A. 126, 79).—LiTIA" 2aq (Wyruboff).—NaTlA" 2aq. S. 25 at 25°.—MgA" 5aq. S. '35 at 19°.—CdA" (Schiff, A. 104, 326).—PbA" (dried at 100°).—Pb,C,H,O, (Krug, J. 1861, 367).—CuA" 2aq. Pale-blue needles, sol. alkalis and solution of Na₂CO₃.—NA₂CuC,H,O, 4aq. — MA" aq. — NiA" 5aq. NH₄(AsO)A" ½aq. S. 94 at 15°. Efflorescent crystals.—K(AsO)A" ½aq. S. 94 at 15°. Efflorescent crystals.—K(AsO)A" ½aq. S. 7at 19°. Non-efflorescent white crystals (Werther, J. pr. 32, 385).—K(SbO)A" ¾aq. S. 7at 19°. Non-efflorescent white crystals (Werther, J. pr. 32, 385).—K(SbO)A" ¾aq. Monoclinic prisms. — Ag,A". Shining scales, less sol. Aq than silver tartrate. Mono-methyl ether MeHA". Formed by exporating racemic acid with MeOH (Guérin-

Mono-methyl ether MeHA". Formed by evaporating racemic acid with MeOH (Guérin-Varry, A. Ch. [2] 62, 77; A. 22, 252). Rectangular prisms, v. e. sol. cold water. Decomposed by hot water into the parent substances.

—KMeA" aq. Prisms.—Ba(MeA") 24aq. Mono-

—nmen 3aq. Fisins.—Datatek 1,2 and. Monoclinic prisms.—AgMeA". Pp.

Di-methyl ether Me,A". [85°]. (282°
i.V.). Formed by methylation of racemic acid, and also by mixing equal weights of the dimethyl ethers of the lawo. and dextro-tartaric acids (Anschütz a. Pictet, B. 13, 1178; 18, 1397; A. 247, 116). Monoclinic crystals; optically inactive. Yields a di-acetyl derivative C,H₂(OAc)₂(CO₂Me)₂ [86°] in trimetric crystals; abc = 8095:1: 6728. This compound, examined by Racult's method, has the same molecular weight as the di-acetyl derivative of di-methyl tartrate.

Mono-ethyl ether EtHA". Deliquescent prisms, v. sol. alcohol. Inactive to light.—KEtA" aq.—Ba(EtA"), 2aq.—AgEtA". Prisms.

Di-Bihyl ether Et.A". (238° cor. at 197 mm.) S.G. 15 1 2098; 35 1 2021. M.M. 8 759 at 15 5° (Perkin, C. J. 51, 364). Yields an oily acetyl derivative and a di-acetyl derivative C₂H₂(OAc)₂(CO₂Et)₂, [51°] (230° at 100 mm.). BzCl forms C₂H₂(OH)(OBz)(CO₂Et)₂, [57°]. The compound C₂H₂(OEt)₂(O₂Et)₂ (147° at 15 mm.) is formed from differential terms are considerable. [58°] and is formed from di-bromo-succinic ether [58°] and NaOEt (Michael, J. pr. [2] 46, 234). $\Lambda g_* \Lambda''$. AgHA". Monoclinic, a:b:c = 721:1: 869; β = 70°

Inactive tartaric acid GO,H.CH(OH).CH(OH).CO.H. Mesotartaric acid. [140°-143°]. S. 125 at 15°. Formation.—1.By heating cinchonine tartrate

or racemate for several hours at 170° (Pasteur, A. 88, 212). The product is mixed with CaCl., which ppts. calcium racemate, and the filtrate slowly deposits calcium inactive tartrate.—2. By boiling tartaric or racemic acid for 400 hours with HClAq (Dessaignes; Pasteur, Bl. 1862, 107).—3. By heating tartaric acid (30 g.) or racemic acid with water (4 c.c.) for 2 days at acid K salt Jungteisch, Bl. [2] 19, 101).—4. A product of the action of HNO, on sorbin (Dessaignes, C. R. 55, 769), erythrite (Przybytek, B. 17, 1412; Bl. [2] 43, 126) and glycerin.—5. By oxidation of levulose (Kiliani, B. 14, 2530).— 6. By oxidation of phenol by alkaline KMnO, at 0° (Doebner, B. 24, 1755).—7. A product of the action of moist Ag₂O on di-bromo-succinic acid. 8. By the action of nitrous acid on di-amidosuccinic acid (Lehrfeld, B. 14, 1819) .- 9. By oxidation of maleio acid by alkaline KMnO₄ (Kekulé a. Anschütz, B. 14, 713).

Properties.—Prisms (containing aq). Loses its aq at 100°; at 200° it yields pyrotartaric and racemic acids. Prolonged boiling with HClaq converts it into racemic acid (Dessaignes). The conversion is also effected by heating the acid with a little water at 175°. The ether is converted by AcCl into C₂H₂(OA₂)₂(CO₂Et)₂ [48°], crystallising in silky readles

needles.

needles.

Salts KHA". Needles. S. 12·5 at 19°.—

RbHA" ½aq. — RbA"aq. — RbNaA" 2½aq. —

CaA" 3aq. S. ·17 at 100°. S. (IIOAc) ·028

at 18°; ·085 at 100°.—PbA" aq: amorphous

pp. — ZnA" 2aq (dried at 110°).—TlHA".—

TlA".—NaTlA" 2¼aq.—Ag,A" aq: white pp.

Metatartaric acid (O,H₂O₃), A deliquescent,
glassy mass, v. sol. water, obtained by melting

tartaric acid (Braconnot, A. Ch. [2] 68, 299;

Erdmann, A. 21, 9; Laurent a. Gerhardt, A.

70, 848). It is sometimes formed when a

70, 848). It is sometimes formed when a solution of tartaric acid is evaporated over a water-bath (Grosjean, C. J. 43, 334). Converted by boiling water into tartaric acid.

Salts.—(NH,)HA". Minute needles. More

soluble than the acid ammonium tartrate. Its solution is ppd. by CaCl, and NH,Aq only when highly concentrated. CaA" 4aq. Minute lonticular grains, sol. dil. HClAq, converted by boiling water into calcium tartrate.

Ditartaric acid C.H.,O., An anhydride of tartaric acid, got by heating tartaric acid at 170° sariaric and, got by nearing saturation and still it is no longer ppd. by lime-water (Fremy, A. 19, 197; 29, 142; 78, 297). Amorphous and very deliquescent. Sol. alcohol, insol. ether. Its saits are amorphous, v. sol. water, and ppd.

by alcohol. They are converted into metaby accord. They are converted into meta-tartrates, and finally into tartrates, by boiling water.—CaA'.—BaA''.—PbA''.—OuA''.—Ag₂A''. V. sol. water (Schiff, A. 125, 129).

Ethyl ether Et.A". Fat-like solid.

Tartrelic acid QHO. Soluble tartaric anhydride. Formed by quickly heating small quantities of tartaric acid till the fused mass swellsup. Yellowish deliquescent mass, sol. water, forming an acid solution, from which CaCl. ppts. CaA'₂ as an amorphous mass, which becomes crystalline on adding alcohol. Tartrelic acid is converted into tartaric acid by boiling water.

Insoluble tartaric anhydride C.H.O. Formed by heating tartaric acid for some time at 150° and exhausting the product with cold water. Powder, insol. water, alcohol, and ether. Converted by hot water into tartaric acid.

TARTRONIC ACID Callio, i.e.

CH(OH)(CO,H),. Oxy-malonic acid. Mol. w. 120. [187°]. Neat of solution -4331 (Gal a. Werner, Bl. 12] 46, 803).

Formation. -1. By spontaneous decomposition of nitro-tartaric acid in aqueous solution (Dessaignes, C. R. 34, 731; 38, 442.—2. By the reduction of mesoxalic acid by sodium-amalgam (Raeyer, J. 1864, 641).—3. By the action of Ag,O on bromo-malonic acid (Petrieff, B. 11, 414).—4. By boiling chloro-malonic ether with KOHAq, the yield being 25 p.c. of the theoretical amount (Conrad a. Bischoff, A. 209, 222).— 5. From di-bromo-pyruvic acid and baryta-water at 40° (Grimaux, B. 10, 903).—6. From glyoxylic acid by treatment with KCy, the resulting nitrile being saponified (Böttinger, B. 14, 729) .- 7. A product of the action of alkaline cupric solution on glucose (Claus, Z. [2] 5, 152; A. 147, 114).—8. By slow oxidation of glycerin (Sadtler, B. 8, 1456; Campani a. Bizzari, G. 12, 1).--9. By heating sodium carboxy-tartronate • (Gruber, B. 12, 514).

Preparation.--1. By boiling the di-nitrate of

tartaric acid (20g.) with alcohol (60g. of S.G. 925) (Demole, B. 10, 1778).—2. By warming tri-chloro-lactic ether CCl₃.CH(OH).CO₂Et with a 10 p.c. solution of NaOHAq (5 mols.), neutralising with HOAc and ppg. with BaCl₂ (Pinner

B. 18, 752, 2852).

Properties.—Prisms (containing laq), v. sol. water and alcohol, sl. sol. other. After drying at 100° it loses its water of crystallisation and becomes v. sol. ether. Massol (C. R. 114, 422) obtained anhylrous crystals [155]. Decomposed by fusion, yielding CO2 and glycolide C2H2O2.

by fusion, yielding CO₂ and glycolide C₁H₂O₂. Reduced by HIAq to malonic acid.

Salts.—Na₂A" (dried at 100°). V. sol. water. — K₂A" a₄, — (NH₄)A". Needles. — *(NH₄)HA". Yields glycollic amide on heating.—BaA" 2aq. Micro-crystalline powder, v. sl. sol. water (Pinner).—BaA" aq (G.).—CaA" 2aq (C. a. B.).—CdA".—PbA" (dried at 120°).—MnA".—Ag₂A". Needles (from hot Aq). Ethyl ether Et,A". (c. 224°). Heavy oil (Freund, B. 17, 786; Pinner).

The acetyl derivative CH(OAc)(OCEt).

The acetyl derivative CH(OAc)(CO,Et)₂ (c. 161° at 60 mm.), S.G. $\frac{12.6}{16}$ 1·131, is formed from bromo-malonic ether and KOAc in EtOH at 50° (Conrad a. Brückner, B. 24, 2997). Br converts it into mesoxalic ether C(OH)₂(CO₂Et)₂

Amide CH(OH)(CO.NH2)r. [196°]. Six-

sided plates, m. sol. hot water.

Amic acid CO.H.CH(OH).CO.NH, [160°]. Formed by boiling sodium dialurate with water Menschutkin, A. 182, 82). Needles, sl. sol. cold water. Converted by nitrous acid into glycollic acid.—KA'aq.—BaA', aq.—PbA', ½aq. Needles, v. sol. hot water.—AgA'. Needles.

Phenyl derivative CH(OPh)(CO₂H).

Formed by saponification of its ether CH(OPh)(CO₂Et)₂ (230°-240° at 60 mm.), which is got from bromo-malonic ether, phenol, and NaOEt (C. a. B.). At 196° it forms NaOEt (C. a. B.). CH₂(OPh).CO.H.

TARTRONYL-UREA v. DIALURIO ACID.

TAURINE C.H, NSO, i.c.

CH,(NH,).CH,SO,H. Amido-ethane sulphonic acid. Mol. w. 125. S. 6.5 at 12°. H.F. 185,700 (Berthelot a. Matignon, A. Ch. [6] 22, 182). Obtained by the action of acids and alkalis on taurocholic acid (Gmelin, Ticdemann a. Gmelin's Die Verdauung, 1, 43; Domarcay, A. 27, 286; Dumas a. Polouze, A. 27, 292; Redtenbacher, A. 57, 170; Strecker, A. 65, 132; 67, 34; 91, 101). Occurs in the free state in putrid bile and in the muscles of the oyster, in shark's blood, in the liver, spleen, and kidneys of the ray, and in the lungs of oxen (Valenciennes a. Fremy, C. R. 41, 735; Städeler a. Frerichs; Clöetta, A. 99, 289). Formed also by heating B-chloro-ethane sulphonic acid with NH, Aq at 100° (Kolbe, A. 122, 33), and by the action of SO₂ on yinylamine (Gabriel, B. 21, 2667). Prepared by evaporating ox bile with dilute HCl at 100°, decanting from a resin, allowing to crystallise, and re-crystallising from water. It may be purified by means of the lead sait.

Properties. -Transparent crystals, m. sol. water, insol. alcohol. Neutral to litmus. Not melted below 240°. Converted by nitrous acid into isethionic acid (Gibbs, Am. S. [2] 25, 30).

Decomposed by potash-fusion.

Salts.—NaA'. Very deliquescent (Lang, Bl. [2] 25, 180).—CaA'₂. Slender noedles, v. o. sol. water.—PbA'₄. Needles, v. c. sol. water.—PbA'₄(OH)₂—CdA'₂.—HgA'₂—HgA'₂O (Engel, Bl. 190) 25 529). AGA'₂. Pb,A',(OH), -CdA', -11 Bl. [2] 23, 532).—AgA'.

Benzoyl derivative NHBz.C.H.SO,H. Formed by heating μ -phenyl-thiazole tetrahy-dride with HCl and bromine-water (Gabriel a. Heymann, B. 23, 159). Syrup.-AgA'. Spherical groups of plates.

Phthalyl derivative
(C₈H₄O₂):N.CH₂.CH₂.SO₃H.

Got by oxidising di-phthalimido-di-ethyl-disulphide with IINO, (S.G. 1·25) (Gabriel, B. 24, 1116). Crystals (containing 1] aq.), sol. EtOAo₁. Tastes bitter.

Imide C₂H (NH SO.) [45°-50°]. Prepared 8 - chloro - ethane - sulphonic chloride CH, Cl. CH, SO Cl by treatment with ammonia (James, C. J. 49, 491). Solid, resembling gum arabic; bitter in taste. V. sl. sol. cold, v. sol. hot, water, insol. alcohol and ether. Ppd. HgO appears to form the compound (C₂H₄SO₂N)₂Hg.

Ethyl-taurine v. ETHYL-AMIDO-ETHANE SUL-PHONIC ACID.

Methyl-taurine v. METHYL-AMIDO-ETHANE AULPHONIC ACID.

TAUROCHENOCHOLIC ACID C, H, NSO, Occurs as K and Na salts in goose-bile (Heintz

a. Wislicenus, P. 108, 547; Otto, A. 149, 192). Amorphous, sol. water and alcohol. Decomposed by boiling with baryta or potash into taurine and chenocholic acid.—NaA'aq (dried at 110°). Small tables. Its aqueous solution gives pps. with CaCl₂, AgNO₃, and lead subacetate, but not with lead acetate.

TAUROCHOLIC ACID C., H, NSO, Occurs as Na salt in the bile of most animals (Strecker, A. 67, 30; 70, 169; Hüfner, J. pr. [2] 19, 302; Copeman a. Winston, J. Physiol. 10, 213). Obtained by ppg. with lead acetate, filtering from lead glycocholate, and ppg. lead taurocholate by lead subacetate. Deliquescent silky needles, v. sol. water and alcohol, m. sol. ether. Dextrorotatory, [a]_b = 25° (Hoppe-Seyler, Arch. Path. Anat. 15, 126). Boiling water splits it up into taurine and cholic acid. Antiseptic, and ppts. albumen completely from its solutions (Maly, M. 4, 89). Salts.—NaA' (dried at 120°). Ppd. by alco-

hol in an amorphous state, rendered crystalline by ether. -- KA'. Needles, resembling wavellite. TAUROCYAMINE C,H,N,SO, i.c. NH:C(NH,),NH.CH,.CH,.SO,H. [226°]. S. 4 at 21°. Formed by heating taurine with cyan-

amide (1 mol.) and water at 110° (Engel, B. 8, 1597; Dittrich, J. pr. [2] 18, 63). Small white prisms, v. sol. water, insol. alcohol and ether. From cold water it crystallises with aq.

TAXINE C_a, H₂NO₁₀. [82°]. Obtained from the leaves, twigs, and fruit of the yew (Taxus baccata) by extracting with ether (Lucas, Ar. Ph. [2] 85, 145; Van der Harst, R. T. C. 3, 279; Marmé, Bl. [2] 26, 417; Hilger a. Brande, B. 23, 464). The ethereal solution is quickly shaken with acidulated water, and the solution ppd. by NH,Aq. Crystalline. Gives off aromatic fumes on melting. V. sl. sol. water, v. sol. alcohol and ether, insol, benzene. Conc. H.SO, gives a deep purple : Fröhde's reagent a reddish-violet colour. Gives yellow pps. with sodium phosphomolyb-date, I in KI, and potassium bismuth iodide. Insol. alkalis. The salts crystallise with difficulty.—Salts: B'HCl.—B',HLSO,—B',HLPtCl. -B'HAuCl,.-B'EtI.

TECTOQUINONE. [171°]. Obtained from teak resin or by the distillation of teak wood (Romanis, C. J. Proc. 4, 116). Amber-yellow crystals, sol. alcohol. Reduced by zinc-dust and HOAc to C₁₈H₂₂. Yields a nitro-derivative and

a bromo-derivative [165°].

Salts of telluric acid, TELLURATES. TELLURIES.
Salts of telluric sold,
H_TeO_4(q.v., p. 649). The normal tellurates of
monovalent metals have the composition
M_TeO_4xH_O; there are also acid tellurates
MHTeO_4xH_O; and two classes of tetratellurates, (1) M_Te_O_1xH_O, which are soluble in
water when M is an alkali metal, and (2) M.Te,O13, which are insoluble in water. The hydrated tetratellurates may be represented as acid ditellurates derived from the hypothetical acid H.Te.O.; thus K.Te.O.; 4H.O. = 2KHTe.O., 3H.O. Some acid salts may be represented as derived from hypothetical ditelluric acid, e.g.

PbTe₁O₂ (= PbTeO₂.TeO₃).
The normal alkali tellurates are obtained by saturating H.TeO, with MOHAq or M2CO3Aq and crystallising. Alkali acid tellurates, and hydrated tetratellurates, are obtained by interactions of acids with the normal tellurates; anhydrous (insoluble) tetratellurates of the alkali

metals are formed by heating the acid tellurates: thus 6KHTeO₄ = K₂Te₄O₁₅ + 2K₂TeO₄ + 3H₂O.

Most of the other tellurates are obtained from the alkali salts by double decomposition.

The alkali tellurates, other than those of the form M.Te,O₁₃, are soluble in water; most of the other tellurates are insoluble or sparingly soluble in water. Tellurates generally dissolve easily in HClAq: the solutions are not ppd. by water, but on boiling the solutions become yellow, give out on boning the solutions become yellow, give off Cl, and then yield a pp. of H,TeO, on addition of water. Acidulated solutions of tellurates are slowly decomposed by H,S, probably with ppn. of ToS, (c. Tellurates are slowly reduced by SO, lutions of tellurates are slowly reduced by SO, more quickly on heating, with separation of Te. When tellurates are heated to redness they give off O and form tellurites; heated with K₂CO₃ and charcoal, they give K₂Te.

The tellurates have been examined chiefly

The tellurates have been examined chiefly by Berzelius (P. 32, 577); and some of them also by Oppenheim (J. pr. 71, 267).

Potassium tellurates. The normal salt K,TeO, 5aq is obtained by dissolving H,TeO, and K,CO, in the ratio H,TeO, K,CO, in hot water and crystallising; also by dissolving H.TeO, in excess of KOHAq, heating, and al lowing to cool slowly. Crystallises in rhombic prisms, isomorphous with K.SO, (Handl, J. 1861. 266). The crystals become moist in air and form K1HTeO, 2aq and K2CO. The acid salt 2KHTeO, 3aq separates on adding to K2TeO, Aq sufficient H2SO, Aq, or other strong acid, to remove half the potassium; the salt is crystallised from hot water. This salt is slightly soluble in cold water, but much more soluble in hot water; when heated it is converted into K₂TeO₄ and K₁Te₁O₁₃. The tetrat-flurate K₂Te₂O₁₃ is obtained, as a yellow powder, by heating 2KHTeO₄. Baq below redness and washing out K₂TeO₁ in water. K₁Te₂O₁₃ is insoluble in water, also in HClAq or HNO₃Aq except after prolonged boiling. The hydrated tetratellurate K₂Te₄O₁₃4H₂O--which may also be regarded as an acid ditellurate 2KHTe₂O₁3H₂O - isformed by adding H2SO, Aq, or another strong formed by adding Π_2 : G_1 : Aq in quantity to remove 6K from $4K_1$: TeO_1 , Aq in quantity to remove 6K from $4K_2$: TeO_1 , $4K_2$: TeO_1 , $Aq + 3H_2$: SO_1 , Aq = K_2 : Te_1O_1 , $Aq + 3H_2$: O_1 : Aq + $3H_2$: O_1 : O_1 : O_1 : O_1 : O_2 : O_2 : O_2 : O_3 is partly decomposed to KHTeO, and H.TeO, Aq by repeatedly crystallising in aqueous solution.

The following tellurates have been described (Berzelius, l.c.; Oppenheim, l.c.): Animonium salts (NH₁)₂Te₀, (NH₄)₂Te₂O₁, obtained by ppg. solutions of the corresponding salts of K or Na with NH.Cl. Barium salts ppn. Calcium salt CaTeO, obtained by ppn. Calcium salt CaTeO, obtained by ppn. Calcium salt CaTeO, obtained by ppn. Lead salts PbTeO, PbTeO, PbTeO, pbTeO, bp ppn; a basic salt is also said to exist. Silver salts Ag.TeO., and several basic salts xAg.O.yTeO., Sodium salts Na.TeO.xaq, NaHTeO.xaq, NaHTeO.xaq, NaHTeO.xaq, and Na.Te.O., to obtained similarly to the potassium salts. Tellurates of Al. larly to the potassium salts. Tellurates of Al, Cr, Co, Cu, Fe, Li, Mg, Mn, Hg, Ni, and Sr have also been described, but only very superficially. M. M. P. M.

TELLURHYDRIC ACID H.Te; v. Hydrogen TELLURIDE, vol. ii. p. 727.

TELLURIC ACID H.TeO.; crystallises from

Formation.—1. By oxidising Te by aqua regia.—2. K.TeO, is formed by the interaction of Cl with K.TeO, Aq, also by fusing TeO, with K.TeO, and the control of Cl with K.TeO, and the control of Cl with K.TeO, Aq, also by fusing TeO, with K.TeO, and K.TeO, Aq, also by fusing TeO, with K.TeO, and K.TeO, Aq, also by fusing TeO, with K.TeO, and K.TeO, Aq, also by fusing TeO, with K.TeO, Aq, also by fusing TeO, also by fus KNO, or KClO.

Preparation.—1. A mixture of TeO, KClO, and KOH, in the ratio TeO, 2KClO, 2KOH is thoroughly fused; the fused mass is dissolved in water and BaCl Aq is added; the pp. of BaTeO. is purified by recrystallisation from hot water, and is then dried at 100°; the dry BaTeO, is mixed with its own weight of water and one-fourth its weight of cone. H SO, and heated till decomposition is complete, when BaSO, is removed by filtration, and the filtrate is evaporated at 100° to the crystallising point; the crystals that separate are dried, powdered, washed repeatedly with alcohol to remove H.SO, and recrystallised from water (Oppenhein, J. pr. 71, 267). Berzelius (P. 28, 392; 32, 1) fused TeO₂ with an equal weight of KaCO₃ or Na CO₂, dissolved in water, added KOH equal to the weight of TeO₂ used, passed in Cl until the liquid smelt strongly thereof, ppd. by BaCl_Aq, and proceeded as described above.—2. TeO₂ is dissolved in HNO₃Aq, the solution is boiled with PbO₂ and filtered, Pb is ppd. from the filtrate by H.SO,Aq, the filtrate from PbSO, is evaporated to dryness at 100', the residue is digested with alcohol and ether to remove H.SO₄, and is then crystallised from hot water in vacuo (Becker, A. 180.

Properties and Reactions. - H, TeO, 2H,O is obtained by slow crystallisation in white, monoobtained by slow crystallisation in white, monocinic crystals, resembling gypsum, S G. 2-9999 at 25.5° (Clarke, Am. S. [3] 16,401). When obtained by rapid evaporation H. TeO, 2H. O appears as a glassy solid. Heated to c. 130° H. TeO, is obtained; decomposition begins at a little above 160° to TeO, and H.O, and at c. 180° TeO, begins to decompose to TeO, and O, this decomposition being complete at c. 350° (Wills. decomposition being complete at c. 350° (Wills, C. J. 35, 704). H.TeO, has S.G. 3·425 at 18·8° (Clarke, l.c.). H.TeO, 2H.O is slightly soluble cold water; it is dissolved fairly easily by boiling water; soluble in acid and alkali solutions; almost, if not quite, insoluble in alcohol. H.TeO, dissolves very slowly in boiling water. Aqueous solutions of H.TeO, have a metallic, Aqueous solutions of H₁TO₄, have a metallo, not a sour, taste; they very slightly redden litmus. Thomsen (Th. 2, 277) gives the following H.F.: [Te,O',Aq] = 98,380; [TeO'4Q,O] = 21,200. H.TeO₄ dissolves gradually in hot, fairly conc. HClAq, with evolution of Ol and formation of H₂TeO₄Aq. H₂TeO₄Aq is not reduced by passing H.S. into it, but if the solution is saturated with HS and kept in a warm tion is saturated with H.S and kept in a warm place, in a closed flask, for some time, the liquid becomes brown, and flakes, probably of TeS, (v.

TELLURIDES. Any compound of Te with a

single element more positive than itself is called a telluride. Tellurides of the heavier metals are generally formed by melting the metals with Te, also by passing H.Te into solutions of salts of the metals; tellurides of K and Na are formed

by heating TeO, with K2CO, or Na2CO, and charcoal; many tellurites and tellurates give tellurides when heated in a current of H. ppts. tellurides of Cu, Ag, and some other metals, by boiling solutions of salts of these metals with Te (Parkmann, C. C. 1862, 814). Tellurides of K and Na dissolve in water with a red colour; this colour is due either to polytellurides or to the presence of traces of oxides according to Demarçay (Bl. [2] 40, 99). Berthelot a. Fabre (C. R. 105, 92) obtained colourless solutions of (C. R. 105, 92) obtained colourless solutions of alkali tellurides by passing pure H₂Te into solutions of alkalis; a trace of O produced a red colour and separated Te. Tellurides react with HClAq giving off H₂Te; they are oxidised to tellurites by HNO₂Aq, and to tellurites and tellurates by agua regia. Warmed in Cl tellurides give metallic chlorides and TeCl₁.

Tellurides of Sb, As, Bi, Au, Fe, K, Ag, and Na are mentioned under these metals (cf. Brauner, C. J. 55, 388).

M. M. P. M.

Brauner, C. J. 55, 388). M. M. P. M. TELLURITES. Salts of tellurous acid

H₂TeO₃ (q. v., p. 656). The normal and acid tellurites of monovalent metals belong to the forms M, TeO, and MHTeO,. Some salts are also known containing relatively more of the acidic radicle; these may be formulated as $M_2O.x$ TeO₂ where x is 2 and 4; or they may be regarded as M.TeO₂.xTeO₂, where x is 1 and 3; or finally these hyperacid salts may be looked on as M₂Te₂O₅ and M₂Te₄O₉—that is, as derivatives of the hypothetical acids H₂Te₂O₅

Tellufrites are generally formed by heating together basic oxides and TeO, in the proper proportions; some tellurites of the heavier metals are obtained by ppn. from solutions of alkali tellurites. Tellurites of the alkali metals dis-solve readily in water; those of the alkaline earth metals are less soluble; the others are insoluble in water. Most tellurites dissolve in HClAq, forming yellow solutions which do not give off Cl on heating; this reaction distinguishes them from tellurates (v. p. 649). Solutions of tellurites in a little HClAq deposit H₂TeO₃ on dilution. Most tellurites are fusible, and crystallise on cooling; the hyperacid alkali tellurites form colourless glass-like solids after fusion. By strongly heating with charcoal and K₂CO₃ most tellurites give K₂Te.

Tellurites of potassium. The normal salt K,TeO, and the acid salt K,TeO, TeO. R_1eO₃, and the acta sate R₂1eO₃.1eO₂ (= K_TO₂O₃ or K_0.2TeO₂) are prepared by fusing TeO₄ with K₂CO₃ in the propex proportions. K₂TeO₃ melts at a red heat; dissolves slowly in cold water, more quickly in boiling water; the aqueous solution has an alkaline taste and reaction, and is decomposed by the CO_2 in the air. $K_2O.2TeO_3$ melts below redness, and solidifies again to a transparent, colourless, crystalline mass; dissolved by boiling water, and the solumass; dissolved by boiling water, and the solution on cooling deposits K_0.4TeO... The tetratellurite or hyperacid tellurite K_0.4TeO._4H_0 (= K_TeO_8TeO_4H_0 or K_Te_O_4H_0) is prepared by boiling H_sTeO_4A with K_CO. and filtering at 100°; the salt is deposited on cooling in microscopic six-sided prisms and tablets. This salt reacts with cold water to give a solution of K_TeO_4 and K_TeO_4 and a gelatinous pp. of H_TeO_5; when heated 4H_0 is given off, and K_0.4TeO_5 remains as a salt which melts at a

moderate red heat and solidifies on cooling to a colourless glass.

The tellurites have been examined chiefly by Berzelius (P. 32, 577; v. also Oppenheim, J. pr. 71, 267). Salts of the following metals have been isolated, but many have been studied in a very superficial way: Al, NH, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, Ag, Na, Sr, and Zn. M. M. P. M.

TELLURIUM. Te. At. w. c. 125 (v. infra). Mol. w. c. 250 (v. infra). Melts at c. 455° (Carnelley a. Williams, C. J. 37, 125). Boils at c. 1390° (Deville a. Troost, C. R. 91, 83). S.G. 6.2549 at 0° (after compression); 6.2322 at 0° organ at o' (after compression); 0'2522 at o' (uncompressed) (Spring, B. B. 5, 854); 6'2549 at 18'20' (after melting in H) (Přiwoznik, C. C. 1892. ii. 962; for further data v. Clarke's Table of Specific Gravities [2nd ed.] 10). V.D. at c. 1390' to c. 1440° = 130 (Deville a. Troost, C. R. 56, 891). to 6. 1440 = 130 (Devine a. 11008.) (1450, 50.) S.H. (21° to 51°, crystalline) '0475 (Kopp, T. 1865. 71); (at 98°, crystalline) '0483; (at 98°, after distillation in SO.) '0518 (Fabre, A. Ch. [6]) 14, 101). C.E. (linear, at 0°) 00001675 (Fizeau, C. R. 68, 1125). E.C. 000777 at 19-6 (Ag at 0° = 100) (Matthiesen, P. 103, 428); conductivity increases slightly when light falls on Te; the increase is very much less than in the case of Se (v. Adams a. Day, Pr. 24, 163; 25, 113). E.C. decreases slightly to o. 100°-140°, and F.G. increases to 200°; on cooling after fusion E.C. decreases regularly and markedly; the following values are given by Exner (P. 158, 625) .0035 at 200°, .00286 at 20° (after fusion), .000435 at 20° (after very slow cooling from fusion). crystallises in rhombohedra; a:c=1:1·3298; it is isomorphous with S and Se (v. Muthmann, Z. P. C. 8, 396). For emission-spectrum v. Plücker a. Hittorf (Pr. 13, 153); Thalen; Salet (A. Ch. [4]28,51); Ditte (C. R. 73, 622); Hartley a. Adency (T. 1884 [1] 117). For absorption-spectrum of vapour of Te v. Gernez (C. R. 74, 1190). H.C. $[Te,O^3,Aq] = 98,380 \ (Th. 2, 278)$.

Historical.—Examining a mineral containing gold from the Seven Mountains in 1782 Müller von Reichenstein suspected the presence of a new metal (Abhand. ciner Privatgesellschaft in Böhmen). He sent a specimen of the mineral to Bergmann, who said that it contained a metal which was not the same as that in blende. In 1798 Klaproth received some of the mineral from M. von R., and isolated the characteristic element, to which he gave the name tellurium (from tellus = the earth) (K., Beiträge zur chem. Kenntniss der Mineralkürper, 3, 1; cf. Crell's Ann. 1798, 91; and G. A. 12, 246). The compounds of Te were more fully examined by Berzelius (S. 6, 311; 34, 78; P. 8, 411; 28, 392; 32, 1,

Occurrence .-- Te is found native, in small quantities, and in a few localities-chiefly in Hungary and Transylvania, and in Virginia, U.S.; it generally accompanies Au and Ag; specimens have been obtained with 97-98 p.c. Te. Tellurides are also found in small quantities in Hungary, Mexico, California, Bolivia, and some other places; in considerable quantities in Colorado; these are generally compounds of Te with Bi, Ag, Pb, Bi and S, Ag and Au, Au, Pb and Sb; tellurite (or tellurium-cohre) containing TeO, is found in small quantities in the Seven Mountains (v. G. Bose, P. 18,64; Rammelsberg, J. M. 1874. 30; Burkart,
 J. M. 1873. 476; Silliman a. Marvine, Am. S. [3] 8, 25; Mathewson, J. M. 1866. 93; Genth.

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Loj o, 20; manewson, J. M. 1866. 98; Genth, J. M. 1875. 188, 314).

Fornation.—1. By passing SO₂ into H. TeO₂Aq;

H. TeO₂Aq + 2SO₂ + H. O = 2H. SO₄Aq + Te. Also by ppg. solution of TeCl. in dilute HClAq, or of a by ppg. solution of TeU, in dilute HClAq, or or a Te compound in H₂SO₄Aq, by an alkali sulphite. 2. By reducing a boiling solution of (NH₄)₂TeO₄Aq by grape sugar (Stolba, J. 1873. 214).—3. By decomposing K₂TeAq by air or oxygen (v. Oppenheim, J. pr. 71, 267; 81, 308; Himly, J. 1877. 213).—4. By ppn., by means of zinc, from solutions of Te compounds in H₂SO₄Aq (v. Löwe, J. pp. 60, 162). J. pr. 60, 163).

Preparation .- There are several methods of preparing crude To from the minerals that contain it. Native bismuth telluride is made into a paste with oil and K₂CO₃, and gradually heated to whiteness in a covered crucible; K₂Te is extracted from the fused mass by boiling water, and the solution deposits Te on standing in air. Or the mineral containing To is powdered and treated with dilute HClAq; the insoluble matter is gradually added to three times its weight of conc. H,SO,, and heating is continued until SO2 ceases to be given off; the solid that forms on cooling is dissolved in water containing a little HCl; the solution is filtered from AgCl, Te is ppd. from the filtrate by zinc, and undissolved zino is removed by digestion with dilute HClAq. For details and other methods v. Berzelius (P. 8,411; 28,392); Löwe (J. pr. 60, 163); Wöhler (A. 84,69); Oppenheim (J. pr. 81,308); Schmitzer (D. P. J. 211, 484, 492); Schwarz (D. P. J. 186,

29).
To prepare pure Te, Brauner (C. J. 55, 382; cf. M. 10, 411) recommends to digest the crude material with HClAq in a large flask, and to oxidise by HNO, Aq added little by little till the solid matter becomes white, to evaporate several times with conc. HClAq (to remove HNO,), and then to dilute cautiously with water, taking care not to add enough water to ppt. H2TeO, along with any PbCl, which may come down. He then adds some saturated SO₂Aq, warms to 60°-70°, and ppts. Te by passing SO₂ into the warm solution. The Te thus obtained generally contains a little copper and lead selenides. The pp. is dried and fused in small portions with KCy; the fused mass, which contains K2Te, is dissolved in water, from which air has been removed, in a stoppered flask; the liquid is allowed to clear (there is generally a small pp. of tellurides of heavy metals mixed with a trace of Te) and is then poured off, and a current of air is passed through it, whereby Te is ppd. The Te is dried, placed in a porcelain boat, which is introduced into a wide tube of hard glass surrounded by wire gauze, and distilled in a current of pure dry H. (For a method of purification based on the ppn of Te from (NH₄)₂TeO₄Aq by grape sugar, v. Stolba, J. 1878. 214.)

Properties.—As prepared by stalline, very H, tellurium is a white, shining, crystalline, white, crystalline, Properties .- As prepared by sublimation in brittle solid, unchanged by exposure to air. During distillation in H, Brauner (l.c.) noticed that some H.Te was formed, and was decomposed with deposition of needle-shaped crystals of Te, some of which were 1 centim. in length. The arystals of Te are hexagonal rhombohedra, iso-

morphous with S and Se (v. Muthmann, Z. P. O. 8, 396). By allowing K. TeAq to decompose in air, H. Rose obtained six-sided prisms with rhombohedral summits (P.21, 443; cf. Fabre a. Berthelot, C. R. 104, 1405). Amorphous Te is obtained as a brown powder by ppg. H. TeO, Aq by SO; on warming, the amorphous variety changes to the crystalline, giving off a large quantity of heat (F. a. B., I.c.). To that has been melted and cooled quickly seems to contain both the crystalline and the amorphous varieties. According to Fabre (A. Ch. [6] 14, 100), both varieties have practically the same S.H. at c. 100°. Te melts at c. 455° and boils at c. 1390°; the vapour is golden yellow. Heated in air it burns with a brilliant blue-green flame to white clouds of TeO2, which are poisonous; the smell, like that of decaying radishes, that is noticed on burning impure Te is due to the oxidation products of So, which is commonly present in specimens of crude Te. Te dissolves in very cone. boiling KOHAq, forming a red liquid that contains K₂TeO₃ and K₂Te; on allowing to cool, or on adding water, the whole of the Te separates. HClAq is without action on Te; cone. hot H₂SO₂ dissolves it slightly, but the Te cone. not H₂SO₄ dissolves it slightly, but the Te separates on dilution; when heated strongly with cone. H₂SO₄ To dissolves to H₂TeO₅ with evolution of SO₂. Te dissolves in SO₅, forming TeSO₅. Cone. HNO₂Ad forms a solution of H₂TeO₄; aqua regia forms H₂TeO₅, and some H₂TeO₅. Molton KNO₂ produces K₂TeO₅.

In its physical properties Te approaches the

In its physical properties Te approaches the metals, and especially resembles S5. In its chemical properties To is, on the whole, non-metallic; but the oxide TeO₂ combines with certain anhydrides of strong acids to form saltlike compounds, and the oxide TeO is said to dissolve in H2SO, Aq, forming Te(SO,)2. Te is closely related to Se, and less closely to S; it shows distinct analogies with Cr, Mo, W, and U (v. Oxygen group of elements, vol. iii. p. 705, and Chromium group of Elements, vol. ii. p. 168). The atom of Te is divalent in the gaseous molecules TeH, and TeCl., and tetravalent in

the gaseous molecule TeCl

Atomic weight of tellurium. The at. w. of Te was determined by Berzelius in 1812, 1818, and 1832 by oxidising Te by HNO₃Aq and weighing the TeO₂ produced; he obtained values varying from 1279 to 1285 (P. 8, 24; 28, 395; 32, 16). In 1857 von Hauer analysed K2TeBr. and obtained values from 126.5 to 128.1 (W. A. B. 25, 135). In 1879 Wills determined the weight of TeO, obtained by oxidising Te by HNO, Aq and by aqua regia, and he also made analyses of K, TeBro; his results varied from 126·1 to 129·3 (C. J. 35, 704). In 1883 Brauner obtained numbers varying from 124 94 to 125 4, by oxidising Te to TeO2, by converting Te and TeO, into (TeO₂), SO₃, and by synthesising Cu, Te (J. R. 1883. [1] 433; abstract in B. 16, 3055). In 1889 Brauner made a very careful revision of the at. w. of Te (C. J. 55, 382):—(i.) by oxidising Te to TeO₂ he obtained values varying from 124.48 to 127.28; (ii.) by converting TeO, into (TeO₂₎₂SO₂, the numbers varied from 124.7 to 129 (one result gave 135-9); (iii.) by conversion of Te into (TeO₂)₂SO₃, the numbers varied from 124-3 to 129-7; (iv.) by syntheses of tellurides of Ag, Cu, and Au, the numbers varied from 125.7

to 129.9; (v.) by analysis of TeO₂ the value 127.2 was obtained, but only one satisfactory analysis was made; (vi.) by analyses of TeBr, the numbers varied from 127.27 to 127.31. The results obtained by analysing TeBr, were more concordant than any obtained by the other methods; but the value 127.3 is almost 75 units greater than the at. w. of iodine; hence it seems as if the at. w. of Te is greater than that of I. But if this is so, Te must be separated from S, Se, and the chromium metals, which are placed in Group VI. in the periodic arrangement of the elements; and Te must be placed either with the halogens in Group VII. (I being put into Group VI.), or this element must find a place in Group VIII. (I remaining in Group VII., and an empty place being left in Group VII., Series 7). The chemical properties of Te show that it belongs to the same group as S and Se; and the chemical properties of I make it impossible to place that element elsewhere than with F, Cl, and Br.

Is tellurium a homogeneous body? Rather than doubt the applicability of the periodic law, Brauner made the hypothesis that tellurium is not a homogeneous body, but that it contains an admixture of foreign substances. He dissolved Te, and ppd. in fractions by SO₂, fused the fractions with KCy, dissolved in water, and ppd. fractionally by a current of air; he then distilled each fraction in II, and converted it into TeBr., and analysed each fraction. The values thus obtained for the at. w. of Te were almost identical, the mean being 127-33. Pure TeO. was then dissolved in HClAq, and the solution was ppd. in eight fractions by ammonia; the filtrate from the eighth fraction was ppd. by SO. in presence of HClAq; after boiling off SO, from the filtrate from the ninth fraction, the liquid was saturated with H2S, and the TeO2 in solution was obtained, converted into Te, and this converted into TeBr₄; the at. w. thus obtained (in three experiments) was 127.32, the three experiments agreeing extremely well. Te was then fused, but not distilled, in a current of H; it was then converted into TeBr,, which was freed from TeBr., by fractional sublimation in vacuo, without converting the TeBr, into vapour, and analysed; the values obtained for the at. w. of Te differed very much, ranging from 128.5 to 137.4. From these results Brauner concluded that 'if tellurium, obtained by any process of fractionation whatever, be subjected to distillation in a current of hydrogen, and the tetrabromide be prepared from this by sublimation in a vacuum, its analysis always gives the same atomic weight for tellurium. . . . If, however, the tellurium be only fused in a current of an indifferent gas, and the tetrabromide be not sublimed, higher numbers will be obtained. . . . It is therefore very probable that on distilling tellurium in a current of hydrogen, and the tetrabromide in a vacuum, one constituent of tellurium escapes partly, the presence of which in the last cases renders the atomic weight higher.' Brauner prepared TeBr. by fusing TeBr, with excess of Te, and subliming either in vacuo or in a current of CO,; the analyses of different specimens of TeBr, showed percentages of Br varying from 54.658 to 55.14; the percentage of Br calculated for Te = 127.32 is 55.6. Brauner concluded that 'tellurium is

not a simple substance.' This conclusion is still held by B. to be correct. In a private communication (January 1894) he says: 'I consider Te to be a mixture of two elements that cannot be separated by ordinary chemical means, not even by fractionation. It cannot, however, be shown that the at. w. of Te is about 125, for all attempts I have made in this direction have failed completely. All atomic weight determinations made by me, and others, giving values higher or lower than 127.3 are due, partly to impurities, but in most cases to some undetected source of error.'

Molecular weight of tellurium. Deville a. Troost (C. R. 56, 891) found the V.D. of Te between c. 1390° and c. 1440° to be 130; this gives the mol. w. of c. 260. As the at. w. of Te is not known with certainty, it is not possible at present to correct the value deduced for the mol. w. from the determinations of V.D. The

gascous molecule of Te is diatomic.

Reactions and Combinations .- 1. Heated in air, or oxygen, Te is burnt to TeO2-2. Heated in excess of chlorine TeCl, is produced; with bromine TeBr, is produced; with iodine the product is TeI₂—3. To and sulphur can be melted together in all proportions; it is doubtful whether definite compounds are formed or not (v. Tellurium sulphides, p. 655). Te and selenion can also be melted together in all proportions; no definite compound has been isolated .- 4. Nitric acid forms H.TeO,; according to Klein a. Morel (Bl. [2] 43, 198), cold HNO, Aq DISTIPLY DISTIPLY OF THE DESIGNATION OF THE DESIGNA hot conc. potash solution, forming a red solution that contains K.Te and K.TeO,; on addition of water Te separates (2K2TeAq + K2TeO3Aq = 3K₂OAq + 3Te).—6. Fusion with potassium nitrate produces K.TeO₄.—7. Fusion with potassium carbonate produces a mixture of K₂Te and K.TeO3.—8. Te dissolves in sulphur trioxide, forming TeSO3 (v. thio-oxide under Tellurium охибея, р. 655).

Detection and Estimation.— Free Te is readily detected by fusing with charred cream of tartar and dissolving in water, whereby a red solution is obtained that deposits Te in darkbrown flakes on standing in air. Tellurous acid and tellurites dissolve in dilute HClAq, and addition of water ppts. white H_TeO₃; SO₂ ppts. Te from solutions of tellurites in dilute HClAq or HNO₂Aq. Solutions of tellurites in acids give no pps. with water; solutions in HClAq give off Cl on boiling, being reduced to tellurites, and are then ppd. by water. For a test for Te based on the formation of red TeSO₂ by passing TeH₂ into H_SO₄Aq r. Divers a. Shimosé, C. J. 43, 329. Te is generally estimated by ppg. the element, from solution of H_TeO₂ or a tellurite, by alkali sulphite, SO₂, or grape sugar (Kastner, abstract in C. J. 29, 440; cf. Donath, abstract in C. J. 60, 242). In C. J. 59, 238, Brauner describes a method for the volumetric estimation of Te by KMnO₄Aqe

Tellurium, acids of; tellurhydric acid H₂Te (vol. ii. p. 727); tellurous acid H₂TeO₂ (this vol., p. 656); telluric acid H₂TeO₃ (this vol., p. 649). The existence of the potassium salt of HCNO is probable (v. Tellurogyanidas,

vol. ii. p. 353).

Tellurium, alloys of. The compounds of Te with metals are sometimes classed with the more definite alloys (v. Tellurides, p. 649).

Tellurium, antimonides of, v. Antimony; Combinations, No. 7, vol. i. p. 283.

Tellurium, arsenides of, v. ARSENIC; Combinations, No. 6, vol. i. p. 303.

Tellurium, bromides of. Two bromides have been isolated, Tellr₂ and Tellr₁; both are formed by the direct combination of Te and Br. The bromides can be sublimed, under reduced pressure, without change. The V.D. of neither has been determined; but, from the analogy of TeCl₂ and TeCl₄, the formulæ are probably molecular.

molecular.

Tellurium dibromide TeBr₂. Formula probably molecular, from analogy of TeCl₂. Prepared by fusing TeBr₁ with excess of powdered Te, and subliming either in racuo or in a current of dry CO₂. A blackish green crystalline mass; obtained in steel-grey needles by slow sublimation (Brauner, C. J. 55, 410). Melts c. 305°, and boils c. 343° (Carnelley, Melting- and Boiling-point Tables, 1, 21). TeBr₁ is very Poiling-point Tables, 1, 21). TeBr, is very hygroscopic; it is decomposed by water to H₂TeO₂Aq and HBrAq. Dissolves in tartaric acid solution, forming TeBr, and Te (Brauner,

Lc.).
TELLURIUM TETRABROMIDE TeBr. (Telluric bromide.) Formula probably molecular, from anatogy of TeCl. Prepared by shaking together powdered Te and Br, in the proportion Te:4Br, warning in a current of dry CO₂, and then subliming in vacuo (for details and description of apparatus, v. Brauner, C. J. 55, 396). Forms a crystalline crust, which is fiery red when hot and orange coloured when cold. S.G. $\frac{150}{40} = 4.31$ (Brauner, I.c., p. 407). Melts at c. 380°, and boils at 414°-427°, according to Carnelley a. Williams (C. J. 35, 563; 37, 125). Dissolves in a little water without change; on dilution a colourless liquid is obtained, containing HBr and H.TeO,; crystals are obtained by evaporating over H. SO, and are said by Berzelius to be TeBr, xH_O. By adding AgNO, Aq to a solution of TeBr, in tartaric acid, Brauner (C. J. 55, 398) obtained AgBr and also crystalline scales probably (C₄H₄O₅), Ag.O.TeO. 2aq; this compound is called by B. tellurium-silver tartar enectic (cf. Klein a. Morel, C. R. 100, 1140). TeBr, forms double salts with alkali bro-The salt TeBr, 2KBr (= K, TeBr,) is mides. prepared by dissolving the proper quantity of KBr in water, adding Te, running in Br, shaking till the Te is dissolved, filtering, and evaporating at 100° (Wills, C. J. 35, 711; cf. von Hauer, W. A. B. 25, 135). Dark-red, opaque, lustrous crystals; orthorhombic, a:b:c=1:1.4901:1.3658 (W., l.c.); cf. Wheeler (Am. S. [3] 45, 267), where some other salts of the form M. Telir, are described.

Tellurium, chlorides of. Two compounds are known, TeCl, and TeCl,; both have been gasified, and the formulæ of both are molecular. The chlorides are formed by the direct combination of their elements.

TELLURIUM DICHLORIDE TeCl2. Mol. w. e. 196. Powdered Te is heated in a distillation-flask in a stream of Cl until the Te is completely converted into TeCl,; Te is added equal

in weight to the original quantity used, the whole is heated for a little time, an inverted condenser being attached to the flask, and the TeCL is then distilled off at 320°-380° (Michaelis, TeCl. is then distilled off at 320°–380° (Michaelis, B. 20, 2488). TeCl, is a black, amorphous solid, melting at 175° (M., l.c.) to a black liquid; Carnelley a. Williams give m.p. as 200° (C. J. 37, 125). Boils at 327° (C. a. W., l.c.). The vapour of TcCl, is reddish, and gives a characteristic absorption-spectrum (M., l.c.). V.D. at 440°, in vapour of N. ~98°2 (M., l.c.). The sapour becomes rellowish in presence of sir or vapour becomes yellowish in presence of air or O; TeO, and TeCl, are formed, and after continued heating these react to produce TeOCl. (M., l.c.). TeCl, absorbs moisture when exposed to the air, but does not fume; on addition of much water H2TeO3 is formed; HClAq forms Te, and TeO, which remains dissolved in the acid

(M., l.c.).
TELLURIUM TETRACHLORIDE TeCl, (Telluric chloride.) Mol. w.c. 269. Powdered To is heated, in a distillation flask, in a stream of dry Cl until the solid becomes pale yellow, when it is distilled in a stream of dry CO, (Michaelis, B. 20, 1780). TeCl, is a colourless, crystalline solid, melting at 214°, and boiling without decomposition at 380° (M. Lc.; Carnelley a. Wiltiams give the m.p. as 221° [C. J. 37, 125], and the b.p. as 414° [C. J. 35, 563]). V.D. 131 at 440°, 125 at 530° (M., l.c.). The vapour of TeCl, shows no absorption-spectrum (M., B. 20, 2488). TeCl, dissolves without change in dilute HClAq. It deliquesces in the air, cold water ppts. an oxychloride, and H. TeO, is also formed; boiling water dissolves TeCl,, and H.TeO, separates on

cooling.

TeCl, combines with alkali chlorides to form salts TeCl, 2MCl = M, TeCl, ; these salts are best obtained by adding MCIAq to a slight excess of Te(1, dissolved in dilute HCIAq and crystallising (v. Wheeler, Am. S. [3] 45, 267). The salts crystallise in regular yellow octahedra, without water. Weber (P. 104, 422) described a compound TeCl₄.3AlCl₈, obtained by melting together TeCl₄ and AlCl₃. TeCl₄ absorbs NH₃, forming a greenish-yellow solid that is unchanged in air and has the composition TeCl, 2NH, (Espen-

schied, A. 113, 101).
Tellurium, fluorides of. Only one fluoride of Te has been isolated. The formula TeF, is

probably molecular, from the analogy of TeCl.

Tellutium tetrastluonide TeF. (Telluric fluoride.) Prepared by dissolving H.TeO. in HFAq, evaporating at 100° to a syrup, allowing to cool, separating the white nodules that are formed, and heating in a Pt basin (Högborn, Bl. [2] 35, 60). If carbonate or hydroxide of an alkali metal, or of Ba, is added to the solution of H.TeO, in HFAq before evaporation, double salts of the forms TeF, MF and 2TeF, MF. are obtained; these salts are decomposed by water (H., l.c.).

Tellurium, haloid compounds of. where X = Cl, Br or I; the only fluoride that has been isolated is TeF. The chlorides TeCl, and TeCl, have been gasified, and the formulae that the complex of the complex are molecular; the formulæ of the other haloid compounds are also probably molecular. An iodide containing more I than TeI4—perhaps TeI4, corresponding with SI4—may exist in the solution of H₂TeO₂ in HIAq. No compound corresponding with S₂Cl₂, Se₂Cl₂, Se₂Br₂, and Se₂I₂ has been isolated. The haloid compounds of Te are more stable towards heat than the corresponding compounds of Se or S. The haloid compounds of Te are decomposed by water, giving H₂TeO₃ and HXAq; cold water is said to ppt. an oxychloride from TeCl₄. The compounds TeX₄ combine with the haloid compounds of the alkali metals to form salts M₂TeX_a; when X=F the salts are said to be of the form MTeF_a.

Tellurium, hydride of, TeH₂ v. Hydrogen Telluride, vol. ii. p. 727.

Tellurium, iodides of. Two iodides have been isolated, TeI₂ and TeI₄; a third—perhaps TeI₄—may exist in the solution of H₂TeO₃ in HIAq. TeI₂ is formed by directly combining Te and I; TeI₄ is obtained by digesting H₂TeO₃ with HIAq.

TELUBIUM DI-IODIDE Tel. Prepared by gently warming a mixture of powered Te and excess of I; may be sublimed as a black, crystalline crust; when strongly heated I is given off. Not changed, by water, hot or cold (Berzelius, Lehrbuch, 5th edit., 3, 1139).

Tellurium tetra-iodide Tel. (Telluric todide.) Obtained by digesting powdered H₂TeO₂ with HIAq in a closed flask, whereby hard black granules are formed. Melts when heated, and gives off I. Boiling water causes decomposition, probably forming an oxyiodide. If a solu-ion of H₂TeO₂ in HIAq is evaporated over H₂SO₄ and CaO₂H₂ in vacuo, lustrous prisms are obtained that are perhaps a compound of Tel. and HI (B., l.c.). By dissolving alkali fodides in Tel. dissolved in dilute HIAq, and crystallising, black salts of the form M₂Tel. are formed in regular octahedra; the potassium salt contains 2H₂O and crystallises in monoclinic forms (Wheeler, Am. S. [3] 45, 267).

Tellurium, oxides of. Three oxides have been isolated, TeO, TeO, and TeO,. TeO is probably slightly basic; TeO, is a the anhydride of the weak acid H.TeO,, but it also shows feebly basic properties; TeO, is a very weak acidio oxide. None of the oxides has been gasified; all are known in the solid state only. An oxide of Te and S, TeSO, is also known.

Tellurium monoxide TeO. This oxide was

Tellurium monoxide TeO. This oxide was prepared in 1883 by Divers a. Shimosé (C. J. 43, 319). It is obtained by long-continued heating TeSO, to 180°-230° in vac 10 until SO, ceases to be given off, powdering the residual solid, digesting it with water containing a little Na₂CO₂, washing with hot water, then with alcohol, and drying in a steam oven. TeO is a black, amorphous solid, with a slight brown shade, showing a graphitic lustre when pressed with a hard body. It is unchanged in air, but when heated it burns to TeO₂; when strongly heated in vacuo TeO₂ and Te are formed. TeO is scarcely affected by cold KOHAq; boiling KOHAq decomposes it, giving Te. SO₃, even it boiling, scarcely acts on TeO. The oxide dissolves in hot H₂SO₂Aq; D. a. S. say that the solution deposits Te(SO₄), on cooling, but no analyses of the crystals that separate are given; Magnus (P. 10, 491) gave this formula to the product of the interaction of Te with hot conc.

H₂SO₄. Heated in HCl gas TeCl₂ is formed. TeO is slowly reduced to Te by SO₂.

Tellurium dioxide TeO, (Tellurous oxide. Tellurous anhydride.)

Occurrence.—As tellurite or tellurium ochre, in the Seven Mountains.

Formation.—1. Te is heated in the air.—2. By decomposing a boiling solution of TeCl, in HClAq by boiling water.—3. By heating H₂TeO₃.

4. By oxidising Te by HNO₂Aq, and heating the solution.—5. According to Hilger (4. 171, 211) by heating Te with H₂SO₃, SO₂ is evolved and TeO₂ separates on cooling.

and TeO, separates on cooling.

Preparation.—Powdered Te is dissolved in warm IINO, Aq. S.G. 1·25, and the solution is heated somewhat above 20°; below 8° H.TeO, separates, between 8° and 20° both TeO, and H.TeO, are formed, and the solid that forms from the solution above 20° is TeO, only (Klein a. Morel, Bl. [2] 43, 198). By allowing the solution of Te in HNO, Aq to stand for some hours, and then adding some alcohol, TeO, is obtained in crystals (Oppenheim, J. pr. 71, 267;

cf. Berzelius, P. 28, 392).

Properties. — A white, crystalline solid; melts at a red heat to a transparent, yellow liquid, which on cooling forms a white crystalline mass, giving off so much heat that the mass, giving on so much mass was solid glows feebly. TeO₂ may be sublimed in a slow stream of air. Clarke (Am. S. [3] 14, 285) gives S.G. as 5.7559 at 12.5°. As obtained from a solution of To in HNO₃Aq, TeO₂ forms quadratic octahedra; S.G. 5.65 to 5.68 at 0° (K.a. M., l.c.). As obtained by heating H₂TeO₃ till all water is removed and the residue melts, TeO₄ forms orthorhombic needles; S.G. 5.88 to 5.91 at 0° (K. a. M., l.c.). Freshly-prepared TeO, has no taste, but after a time it acquires a disagreeable metallic taste (Berzelius, P. 28, 392). It does not redden litmus paper. It is almost insoluble in water; 1 pt. dissolves in 150,000 pts. of water (K. a. M., l.c.). TeO₂ is very slightly soluble in most acids; it is more soluble in HCIAq (v. infra, Reactions, No. 3). Dissolves readily in solutions of caustic alkalis, but in alkali carbonate solutions and in ammonia only after long-continued boiling. TeO2 does not form H2TeO, by reacting with water, but as it is obtained by heating this acid it may be called tellurous anhydride.

Reactions and Combinations.—1. Reduced to Te by heating in hydrogen to the temperature whereat Te vaporises.—2. Easily reduced to Te by heating with carbon.—3. TeO₂ absorbs hydrogen chloride, giving off much heat and forming compounds TeO₂xHCl. At -10°, after saturation with HCl, the compound TeO₂.9HCl is formed; on slightly warming HCl is given off, and TeO₂.2HCl remains, and does not change when heated to 90°; on heating more strongly, TeOCl₂ is formed (Ditte, A. Ch. [5] 10, 82). Hydrogen bromide is also absorbed by TeO₂; by saturating TeO₂ with HBr at -15°, a black solid, resembling I, and having the composition TeO₂.3HBr, is formed; this compound begins to decompose at -40°, above this temperature TeO₂.2HBr is produced, which remains unchanged to c. 800°, at which temperature it decomposes to TeOBr, and H₂O (D₁, L₂). Hydrogen iodide and hydrogen fuoride are also absorbed by TeO₂ but the products have not been ex-

amined.-4. Tellurites (q. v., p. 650) are formed by dissolving TeO, in caustic alkali solutions, or by fusing TeO, with alkali carbonates.—5. A compound of TeO, with sulphuric anhydrids 2TeO_SO_—sometimes called basic tellurium sulphate—is formed by dissolving TeO, in hot H.SO, diluted with 8 to 4 times its weight of water, and evaporating; it crystallises in rhombic tablets, somewhat soluble in cold dilute rhombo tablets, somewhat soluble in contained H₂SO₄Aq (Klein, C. R. 99, 326).—6. A compound with nitric anhydride 2(4TeO₂N₁O₃),3H₂O is described by Klein a. Morel (Bl. [2] 43, 198), as obtained, in rhombic needles, by dissolving TeO, in moderately conc. HNO, Aq, and also by dissolving Te in excess of HNO, Aq, S.G. 1.15 to 1.35, and evaporating at a gentle heat. This compound—which is sometimes described as basic tellurium nitrate—is decomposed at c. 330°, giving off N oxides and decomposed at c. 550°, giving on it oxides and leaving TeO₂; with much hot water it gives a pp. of TeO₂.—7. A compound, probably TeO₂.Ag₂O.(C₄H₁O₃)...2aq, is formed by dissolving TeO₂ in HBrAq, adding tartaric acid, and ppg. by AgNO, Aq (v. Brauner, C. J. 55, 398; cf. Klein a. Morel, C. R. 100, 1140).

Telluric anhydride.) Obtained, as an orangeyellow, crystallino mass, by heating H,TeO₄ (v. Tellurio Acid, p. 649) to somewhat above 160°. If the temperature becomes too high some of the TeO, is decomposed to TeO, and O; it is advisable, therefore, to digest the residue with cold HClAq (to remove any TeO.), to wash out HClby water, and to dry at 100°. TeO, is not changed by cold, nor by boiling, water; nor is it acted on by cold HClAq, by hot or cold HNO, Aq, nor by dilute KOHAq. Very cone. boiling KOHAq slowly dissolves TeO, forming K, TeO, TeO, dissolves in boiling HClAq, Cl is slowly given off, and H₁TeO₃ is formed in the solution (v. Berzelius, P. 28, 392). Clarke (Am. S. [3] 14, 286) gives S.G. of TeO₃ as 5 0704 at 14 5°.

TELLURIUM THIO-OXIDE TeSOs. (Tellurium sulphoxide. Tellurium-sulphur trioxide.) This compound is obtained by dissolving pure Te in pure SO₃, and warming after a time to c. 30°, pouring off SO₃, and drying in vacuo (Weber, J. pr. [2] 25, 218; for description of apparatus, and details, v. Divers a. Shimosé, C. J. 43, 323). TeSO, is a red amorphous solid, melting at 30° When pure it remains unchanged, in a scaled tube, for months (D. a. S., l.c.). The colour gradually changes to brown by heating to 35°; the change is instantaneous at 90°. The product, which is a brown solid, has the composition TeSO₂ (D. a. S., l.c.). At c. 180° SO, is given off and black TeO remains (D. a. S., l.c.). TeSO₂ is not acted on by SO₃; it dissolves in 190° Ac giving a panethyst-red solution, water H.SO.Aq, giving an amethyst-red solution; water decomposes it to H₂TeO_s, TeO, Te, H₂SO_sAq, and H₂SO_sAq (D. a. S., l.c.).

TeSO, may perhaps be regarded as tellurium

sulphite.

Tellurium, oxyacids of, H₂TeO₂, v. Tellurios acid (p. 656); H₂TeO₄, v. Tellurio acid (p.

549).
Tellurium, oxybromide of, TeOBr... A paleyellow solid; obtained by heating TeO. 2HBr (v. Tellurium proxide); Reactions, No. 8, p. 654) above 300°. Melts at red heat, forming a very dark-coloured liquid, which gives off almost black vapour with partial decomposition to TeO_g and TeBr, (Ditte, A. Oh. [5] 10, 82).

Tellurium, oxychloride of, TeOCh. pared by heating TeO, 2HCl (v. TELLURIUM DI. OXIDE; Reactions, No. 8) to above 90°. Very similar to TeOCl. (Ditte, A. Ch. [5] 10, 82). Decomposed at fairly high temperature to TeO. and TeCl.

Tellurium, oxyiodide of. According to Berzelius (Lehrbuch [5th edit.] 3, 1141), a greyishbrown, heavy powder is formed by digesting Tel, with boiling water, and this powder is probably an oxylodide of Te; no analyses are given.

Tellurium, salts of. No compounds have been prepared by directly replacing the H of oxyacids by Te. According to Divers a. Shinosé (C.J.43, 319), $Te(SO_4)_2$ is formed by dissolving TeO in hot H_2SO_4Aq and cooling, but no analyses are given; Magnus (P. 10, 491) gave the formula Te(SO₂), to the product of the interaction of Te and how cone. H₂SO₃. The compounds 2TeO₂.SO₃ and 2(4TeO₂.N₂O₃). Saq are sometimes called basic tellurium sulphate and basic tellurium sulphate. rium nitrate respectively; the commound TeSO, (v. supra, Tellurium Thio-oxide) may perhaps be looked on as tellurium sulphite; and a compound, probably TeO...Ag.2. (C, II. (0))... 2aq. is called tellurium-silver tartar emetic (v. Tellurium dioxide; Reactions, Nos. 5, 6, and 7, supra).

Tellurium silver tartar emetic v. Tellurium DIOXIDE; Reactions, No. 7, supra.

Tellurium, sulphides of. Berzelius (P. 8, 411) described two sulphides, TeS₂ and TeS₃, corresponding with the oxides TeO₂ and TeO₃. According to Becker (A. 180, 257), OS₂ removes almost all the S from these supposed compounds. B. concludes that the substances described by Berzelius are not definite compounds; he thinks that compounds of Te and S are probably formed by passing H.S into TeO.Aq and TeO.Aq. As the substances obtained by Berzelius seem to have very definite properties, they are shortly described here.

TELLURIUM DISULPHIDE TeS,. A dark-brown pp. formed by passing H₂S into H₂TeO₃Aq, or into an acidified solution of an alkali tellurite; softens when heated and cools to a grey, somewhat lustrous mass; gives off S when strongly heated. TeS, reacts as an acidic sulphide, forming compounds &MS.TeS., where M = (NH.), Cd, Li₂, Fe, Mg, Pb, K₂, Na₂, Zn, &c. The thiotellusites of the alkali metals are best obtained by saturating aqueous solutions of the tellurites with H2S, and crystallising in vacuo; the thiotellurites of alkaline earth metals are formed by boiling the sulphides of these metals with TeS₂ and water; the thiotellurites of the heavy metals are obtained by μρn. from solu-

Tellurium trisulphide TeS. A blackish grey, lustrous solid; formed by saturating H.TeO.Aq with H.S. and allowing to stand for some time in a closed vessel in a warm place. Thiotellurates of the alkali metals, xM.S.TeS. anotecurates of the alkali metals, xM,N.TeS,, are formed by saturating M,TeO,Aq with H,S (v. Oppenheim, J. pr. 71, 267).
Tellurium, sulphoxide of, v. Tellurium Thio-

OXIDE, supra.

Tollurium, thio-oxide of, v. supra,

Tellurium, thio-salts of, v. Tellurium disul-PHIDE, p. 655; and TELLURIUM TRISULPHIDE, p. M. M. P. M.

TELEUROCYANIDES v. vol. ii. p. 853. TELLUROUS ACID H.,TeO.

Formation. -1. By dissolving Te in HNO.Aq. S.G. 1.25, and at once ppg. by water; if the solution is left for some time before adding water the pp. is TeO, -2. By decomposing TeCl, by

Preparation.—TcO₂ is fused with an equal weight of K₂CO₃ or Na₂CO₃ as long as CO₂ is given off; the tellurite thus formed is dissolved in water, and HNO, Aq is added until the liquid has a very distinctly acid reaction; the flocculent pp. thus produced is allowed to remain in contact with the liquid for some hours, and is then thoroughly shaken up with the liquid, a little HNO, Aq being added if the acid reaction disappears during this process; the pp. is then washed with ice-cold water, and dried at the ordinary temperature (Berzeliu, P. 28, 392; cf. Oppenheim, J. pr. 71, 267). The sciution of the alkali tellurite in HNO Aq may be decomposed by adding water, but this must be done at once, as after standing water ppts. TeO2.

Properties and Reactions .- A white, light, amorphous solid, with a bitter, metallic taste. Reddens litmus paper. Dissolves slightly in cold water; when the aqueous solution is heated to c. 40° TeO₂ separates. When slightly heated gives TeO₂ and H₂O. H₂TeO₃ disolves in many acids; from the solution in HClAq, water or alkalis Pots. H.TeO.; the solution in HNO Aq gives a pp. of TeO₂ on addition of water after standing for some time. From the solution in H₂SO₄Aq and HNO₃Aq the compounds 2TeO₂SO₂ and 2(4TeO₂N₂O₃), 3aq have been obtained (v. Tellurium Dioxide; Reactions, No. 5 and 6, p. 655). H.TeO, forms tellurites (q. v., p. 650). Thomsen (Th. 2, 278) gives $[Te,O^2,H^2O] = 77,180$. M. M. P. M.

TELLURIUM, Organic Compounds of.

Methyl telluride Me. Po. (82°). Formed by distilling K. To with Ba(SO, Me). (Wöhler a. Dean, A. 93, 233; Heeren, Dissertation, Göttingen, 1861). Pale-yellow, mobile, heavy oil, with persistent alliaccous smell. Oxidised by HNO, to Me, ToOIINO, crystallising in prisms .-Me.TeHOAc. Transparent cubes, v. sol. water. which crystallises in long prisms [97.5°].—
Me,TeBr, [89°]. Prisms.—(Me,Te),H,CO, Difficult to crystallise.—Formate Me,TeCH,O. Deliquescent needles.—Me, Tel₂. Formed by heating Te with McI at 80° (Demarcay, Bl. [2] 40, 100).—(Me, Te), H, C, O, —Me, TeO. Got from Me, TeCl₂ and Ag, O. Deliquescent crystalline mass, alkaline to litmus.—Me, TeOCl₂. Got from the chloride and NH, Aq. Short prisms (from alcohol). — (Me₂Te)₂OBr₂. — (Me₂Te)₂H₂SO₄. Cubes, v. sol. water, insol. alcohol.

Methyl-iodide Me Tel. Crystalline, sl. sol, water. Converted by moist Ag₄O into an alkaline base which yields (Me, TeCl), PtCl,.

Ethyl telluride v. vol. ii. p. 519.

TEMPLIN OIL. An essential oil obtained from fir cones (Flückiger, J. 1855, 642; Berthelot, J. Ph. [8] 29, 38). Colourless, becoming greenish-yellow in air. Boils at 155°–177°. S.G. 18 Yields on rectification a laworotatory

terpene (172°) S.G. 4 ·856. HNO, (1 vol.) and alin the series (172) S.O. 2. 300. INO₃ (§ Vol.) and alcohol ($\frac{1}{3}$ vol.) yield terpin hydrate $C_{10}H_{20}O_{2}$ aq [118°] (250°) S. 9 at 100°. Alcohol and HCl yield crystalline $C_{10}H_{18}$ HCl and $C_{10}H_{18}$ 2HCl

[559].
TERACONIC ACID C.H., O. i.e.
CMe.: C(CO.H). CH., CO.H. Propylidene-succinic [163°]. Formed in small quantity by distilling the isomeric terebic acid (Geisler, A. 208, 50). Na and NaOEt convert terebic ether into sodium ethyl teraconate (W. Roser, B. 15, 293). Formed also by treatment of the ether CO.Et.CBrPr.CH. CO.Et with alcoholic potash (Schleicher, A. 267, 130). Crystals, sol. alcohol and ether, v. sol. cold water. Above 163° it yields H.O and an anhydride. Conc. HBrAq at 0° forms terebic acid.

Salts.—BaA".—CaA". Pp., v. sl. sol. water. Ag, A". Needles, m. sol. water. Mono-ethyl ether ΕtΠΑ". Oil. Decom-

poses Na₂CO₃, forming crystalline NaEtA", a solution of which gives with AgNO₃ a pp. of the unstable AgEtA".

Di-ethyl ether Et.A". (255 i.V.). Oil. TERACRYLIC ACID C,H,2O₂. (218° i.V.). product of the distillation of terpenylic acid (Fittig a. Krafft, B. 10, 521, 1659, 1740; A. 208, 79; Amthor, J. pr. [2] 42, 389). Liquid, smelling like valerie acid, sl. sol. and lighter than water. Yields acctic acid on fusion with potash. Fuming HBr forms C,H,BrO2, which gradually splits up into HBr and heptolactone C,H12O2. CaA'₂5aq. Prisms or needles.—AgA': needles. Ethyl ether EtA'. (191°). Fruity oil.

TERBIUM. Tr. At. w. not determined with certainty; probably c. 162 (v. infra).

The examination of gadolinite, a rare Swedish mineral, by Mosander, Cleve, and others made probable the existence therein of at least seven earths, to one of which the name terbia was given (v. Erbium, vol. ii. p. 456, where the history of these earths is stated more fully, with references to original memoirs). It is still very doubtful whether the substance called terbia is a homogeneous body or a mixture of more than one compound (cf. METALS, RABE, vol. iii. p. 242). Delafontaine (A. Ch. [5] 14, 238) prepared an orange-yellow, earthy compound, which he regarded as pure terbia, from samarskite, by a long process of fractional ppn., first by K₂SO₄Aq, ther by oxalic acid, and finally by formic acid (cf. Marignac, A. Ch. [5] 14, 247; Cleve, Bl. [2] 31, 197).

Terbia Tr₂O₂ is described as an orange-yellow

amorphous solid; when heated in H for some time it becomes white. Tr_iO_3 dissolves in acids, forming salts of the type Tr_iX_3 , where $X = SO_1$, CO_2 , $2NO_3$, &c. The emission spectrum of terbia has been mapped by Roscoe a. Schuster (C. J. 41, 283). The at. w. of Tr—the supposed element has not been isolated—was determined by Delafontaine to be 113.5; Marignae found the value 148.5; Lecoq de Boisbaudran found 163.1, 161.4, and by later work 159.5 (C. R. 102, 395;

111, 474). M. M. P. M. TERÉBENE v. Terpènes.

TEREBENTHENE v. TERPENES DITEREBENTHYL C. H.s. V.D. 4.6. (345°). S.G. 12 '9688. $[a]_D = 59^{\circ}$. A product of distillation of colophony (Renard, C. R. 105, 865; 106, 856). Oil, resinified by air. KMnO₄ oxidises it

to propionic, acetic, and formic acids and CO... to propionic, acetic, and formic acids and CO₂. Cold fuming HNO₂ forms C₂₀H₂₇(NO₂), a yellow powder, sol. alcohol and ether. Br in CS₂ at -10° forms C₂₀H₂₈P₁₇, which on heating yields diterebenthylene C₂₂H₂₈ (347°) S.G. 12° 9821, whence Br forms C₂₀H₂₁Br₁. HNO₂ produces C₂₀H₂₁(NO₂), and HSO₄ forms C₂₀H₂₁SO₄H, all amorphous solids. Reminion water since C_{x2}H_{x2}(NO_x)_x and H_xSO_x forms U_{x2}n_x; SO_xn, an amorphous solids. Bromine-water gives rise to C_{x2}H_xB_x, a brown, amorphous solid. Gaseous HCl passed into the ethereal solution forms C_{x2}H_{x2}HCl. H_xSO_x yields C_{x2}H_{x2}SO_xH, which is sol. water, alcohol, and ether, forming fluorescent solutions. Diterebenthyl passed fluorescent solutions. Diterebenthyl passed through a red-hot tube forms H, C,H,, C,H, pentane, hexane, hexylene, hexinene, heptinene, cymens, and other hydrocarbons.

TEREBENTILIC ACID C,H,OO, [90°]. (250°).

Got by passing the vapour of the hydrate of oil of turpentine C_{in}H_{in}2H_iO over soda-lime at 400° (Personne, A. 100, 253; cf. Hempel, A. 180, 86). Crystalline powder, sol. hot water, v. sol. alcohol and ether. May be sublimed .- AgA'. Crystalline.

TEREBENTIC ACID C₉H₁₄O₅. Got by discesting oil of turpentine with oxide of lead (Weppen, A. 41, 294). Crystals (from alcohol). TEREBIC ACID C,H₁₀O₄ i.e.

 $CMe_2 < CH(CO_2H) > CH_2$. Mol. w. 158. [176°]. H.C.v. 766, 642 (Ossipoff, C. R. 108, 812). S. (ether) 2.856 at 35° (Amthor, J. pr. [2] 42, 385). Formed by the action of nitric acid on oil of turpentine (Bromeis, A. 37, 297; Rabourdin, J. Ph. [3] 6, 185; Cailliot, A. Ch. [3] 21, 27; Svanberg a. Eckmann, J. pr. 66, 220; Mielck, A. 180, 47; Bredt, A. 208, 37; Erdmann, A. 228, 179). Formed also by oxidising pinol (Wallach, A. 253, 256; 259, 317). Terebic acid is perhaps identical with oxyhexic acid (Gorboff, J. R. 1887, 605). Monoclinic crystals (from alcohol), sl. sol. cold, v. sol. hot water. V. sol. alcohol and ether. Not attacked by furning HNO₂. Splice up by water at 150° into CO₂ and pyroterebic acid. On boiling with H₂SO₄ (2 pts.) and water (1 pt.) it is converted into the lactone of oxyisohexoic acid CMe₂ CH₂ CH₂, CO₂ being evolved. On distillation it yields pyroterebic (hexenoic) acid, oxy-isohexoic lactone, and a little teraconic acid. On heating for 15 hours at 160° with excess of a saturated solution of baryta it is converted into acctone and succinic acid (Frost, A. 226, 363). Fuming HIAq yields CH.Pr.CH.2CO.H. Alkalis form salts of diaterebic acid, of which terebic acid is the lactone.

Salts.—NH₄A': very soluble prisms.—
KA';aq.—NaA';aq.—BaA';2q: amorphous.—
AgA'. Prisms, v. sol. water.

Ethyl ether Eth'. (274° i.V.). S.G.

1. 1.111. Formed from terebic acid, alcohol, and HCl. Dilute NaOH dissolves it, forming monoethyl diaterebate; on cautious acidification the ether separates again, but only after warming (Ekmann). Sodium dissolves in its ethereal (F.Kinani). Southin dissertes in 100 emilies solution, giving off hydrogen and forming the sodium salt of acid ether of teraconic acid (q, v). Alcoholic NaOEt acts in the same way, excess torming a white pp. of disodic teraconate.

Diaterebic acid

CMe,(OH).CH(CO,H).CH,.CO,H. The salt BaA" 3aq is formed by boiling terebic acid with excess of baryta-water. It crystallises from Vot. IV.

alcohol, but on acidification at once yields the lactone, terebic acid. AgNO, added to a solu-

lactone, terebic soid. AgNO, added to a solu-tion of the Ba salt ppts. Ag, A".—CaA" Saq.— CaA".—PbA" 3aq.—Pb, A", (OH), aq.

Ethyl ether Et, A". Formed from Ag, A" and Etl. Oil. Converted by acetyl chloride into CMc_(OAc).CH(CO_Et).CH_.CO_Et, an unstable

β-Bromo-terebic acid C,H,BrO, i.e.

CMo₂ CBr(CO₂H) CH₂. [151°]. Formed by adding Br (1 mol.) to powdered teraconic acid (1 mol.) covered with water (Frost, A. 226, 363). Large crystals, m. sol. CS., v. sl. sol. chloroform and benzene. Decomposed by boiling with water into HBr and terebilic acid C.H.O. Reduced by sodium-amalgam to terebic acid.

References .- CHLOROand OXY-TEREBIO

TEREBILENIC ACID C,H,O, i.e.

 $CMe_2 < C(CO_H) > CH$ (?) [169]. Formed by herting a-chlord-terebic acid at 200° (Roser, B. 15, 296; A. 220, 261) and by evaporating B-chloro-terebio acid with water (Frost, A. 226, 370). Small prisms or needles (from water), v. sol. alcohol and other. Crystallises from alcohol or cone. HBrAq in trimetric forms; a:b:c=809:1: 858. May be sublimed. Excess of KOH forms the diaterebilenate K,C,H,O,, but this splits up on warming with water into KOH and potassium terebilenate. Does not combine with Bror HBr. Sodium-amalgam reduces it to terebio acid. -- CaA'₂.--AgA'. Prisms.

Reference.-- Chloro-threbulenic acid.

TERECHRYSIC ACID C. 11.03. A product of the action of HNO₄ (S.G. 1-2) on turpentine (Cailliot, A. 64, 376). Orange-red crystals, v. c. sol. water, alcohol, and ether. —PbA": crystals.

TERELACTONE C, II, O, i.e. C, II, O. [12°]. (210° i.V.). Formed by the action of boiling water on di-bromo-isohexoic acid derived from pyroterebic acid and Br (Geisler, A. 208, 47). Mobile liquid, sol. water. Douing out you converts it into amorphous Ba(C_qH_qO_q), which is sol. water and deposits BaCO_q on boiling.

TEREPHTHALIC ACID O_qH_qO_q i.e.

C_sH_s(CO₂H)₂. p-Phthalic acid. Mol. w. 166. H.C.p. 770,900. H.C.v. 771,200. H.F. 188,100

(Stohmann, J. pr. [2] 40, 139).

Formation.—1. By the action of HNO, on oil of turpentine (Cailliot, A. Ch. [3] 21, 28; De la Rue a. Hugo Müller, A. 121, 86; Schreder, B. 7, 704; cf. W. C. Williams, B. 6, 1094).—2. By the oxidising action of chremic acid mixture on p-xylene (Beilstein, A. 133, 32; 137, 301), p-xylene (Rentstein, A. 133, 32; 137, 301), cuminic acid, cuminic aldehyde, cymene (Hofmann, A. 97, 197), p-toluic acid (Beilstein a. Yssel, A. 137, 308), di-ethyl-benzene, and amyltoluene (Fittig, A. 141, 167).—3. By the action of boiling dilute HNO, on cymene and on terpenes (Schwanert, A. 132, 257; Homeyer, Ar. Ph. [3] 5, 326).—4. By oxidation of o-ethyltolura Picarcel B. toluene by aqueous KMnO₄ (Claus a. Pieszcek, B. 19, 3083).—5. By fusing potassium p-sulphobenzoate with sodium formate [Remsen, B. 5, 379]. - 6. From its nitrile, which is obtained by distilling K.FeCy, with potassium benzene p-disulphonate (Garrick, Z. 1869, 551), p-chlorobenzene sulphonate (Nölting, B. 8, 1113), or p-

bromo-benzene sulphonate (Irelan, Z. 1869, 164; Barth a. Senhofer, A. 174, 242; Limpricht, A. 180, 88).—7. The semi-nitrile is also formed by the action of a hot solution of cuprous potassium cyanide upon p-diazobenzoic acid (Sandmeyer, B. 18, 1497). - 8. By heating p-di-bromo-benzene with chloroformic ether and 1 p.c. sodium-amalgam at 110° and saponifying the product (Bonz, B. 18, 2305).—9. By the action of 5 p.c. KMnO₄ on an oil (258° 268°) which remains as a residue in the manufacture of aniline and toluidine (Hell a. Rockenbach, B. 22, 505).

Preparation .- 1. Br (2 mols.) is added to boiling p-xylene (100 g.), and the resulting C₄H₄(CH₂Br)₂ decomposed by alcoholic KOAc on the water bath. After evaporating the alcohol the C_rH_{*}(OAc)₂ is extracted with ether, and oxidised by adding 4.5 litres of 10 p.c. KMnO₄ to its solution in water (1 litre) and NaOH (500 g. of S.G. 1.22). Finally more KMnO, is added till the solution remains violet, the solution kept at 100° for 3 hours, filtered, and ppd. by HCl (Baeyer, A. 245, 139) .- 2. By oxidising p-xylene with chromic acid mixture (Beilstein, A. 133, 41). 3. From p-toluidine by Sandmeyer's reaction, the resulting p-toluic acid being oxidised by

KMnO₄ (Baeyer a. Herb, A. 258, 1).

Properties.—White crystalline powder, nearly insol. water, alcohol, ether, chloroform, and HOAc. Sublimes without previous fusion. Does not yield an anilide on boiling with aniline (Michael a. Palmer, B. 19, 1376). It is ppd. from its salts by pthalic &cid. Yields benzene when distilled with slaked lime. Reduced by sodium-annalgam in a current of CO_2 to the $\Delta^{2\ell}$ or (1,4) dihydride. If CO_2 be not used the Δ^{1,t} or (1,4) dihydride. If CO₂ be not used the product is the Δ^{1,t} or (3,6)- dihydride, which is also get by boiling the (1,4)-dihydride with NaOHAq (Baeyer, A. 269, 153; cf. Mohs, Z. [2] 3, 68). The (1,4)-dihydride gives benzoic acid on oxidation by MnO₂ and dilute H₂SO₃, while the (3,6)-dihydride forms terephthalic acid (Baeyer, A. 269, 182). By heating its alkaline solution with sodium, suglement terephthalic acid solution with sodium-amalgam terephthalic acid is reduced to a tetrahydride, and this is further reduced by HIAq at 240° to a hexahydride (Baeyer, B. 19, 1805).

(Baeyer, B. 19, 180a).

Salts. — (NH₁),A". Small crystals. —

CaA" 3eq. S. '08 at 6°.—BaA" 4eq. S. '28 at

5°.—SrA". S. '19 at 17°.—Ag₂A". Curdy pp.

Mono-methyl ether MeHA". [c. 230°].

Formed by the action of conc. H.SO, or alcoholic potash on the di-methyl other (Baeyer, A. 245,

141). Needles, sol. Na₂CO₂Aq and hot water.

Di-methyl ether Mc₂A'': [140°]. S. 3

at 100°. H.F. 172,300 (Stohmann, J. pr. [2] 43,

2). Formed by heating the acid with POl₃ on the water-bath and pouring the product into methyl alcohol. Trimetric plates; a:b:c =*843:1:3:083. Insol. cold water, sl. sol. hot MeOH, m. sol. EtOH.

OH, m. sci. Euch.

Di-ethyl ether Et.A". [44°]. Prisms.

Propyl ether Pr.A". [31°]. Needles.

Isopropyl ether Pr.A". [56°]. Plates.

n-Butyl ether (C.H.,)A". Liquid.

Isobutyl ether (C.H.,)L',A". [52·5'.

Callen y sol ether (Regner R 10 1742).

Isomery: ether (CH,!r),A". [52.5°]. Needles, v. sol. ether (Berger, B. 10, 1742).

Isomyl ether (C,H₁₁),A". Pearly scales. Phonyl ether !h₂A". [194°] (Baeyer, A. 258, 44). Formed from the chloride and phenol. Leaflets.

Chloride C.H.(COCI).. [78°]. (259°).

Amio acid C.H.(CONH.).CO.H. [214°].

Formed from p-diazo-benzoic acid by Sandmeyer's reaction (Sandmeyer, B. 18, 1498).

Minute plates (from water), m. sol. cold water.

Amide C₆H₄(CONH₂)₂. Formed from the chloride and NH₃Aq. Amorphous.

Nitrile C₆H₄(CN)₂. [220°] (Luckenbach, B. 17, 1428). Formed from the amide and P.O. Got also by distilling calcium brono-benzene p-sulphonate with K,FeCy. Conc. HIAq forms C,H,(CI_NH₂), (Biltz, B. 25, 2543). Γ cistrans $\Delta^{3.5}$ or (1,4)- Dihydride

CO₂H.CH<CH:CH>CH.CO₂H. S. 3 in the

cold. H.F. 182,600 (Stohmann, J. pr. [2] 43, 538). Formed by reducing terephthalic acid in a current of CO₂ by sodium-amalgam (Baeyer, $A.\,251,\,257;\,269,\,153$). Monoclinic prisms (from EtOAc); $a:b:c=\cdot982:1:1\cdot019$; $\beta=78^{\circ}$ 2'. M. sol. cther. Not attacked by sodium-amalgam in the cold. Unites with bromine (4 atoms). Transformed into the $\Delta^{1.5}$ isomeride by boiling with Not attacked by sodium-amalgam in the water, and into the $\Delta^{1.4}$ acid by boiling with NaOHAq. Alkaline KMnO, re-oxidises the acid to terephthalic acid. A warm solution of the acid readily reduces AgNO₂. On warming with aqueous cupric acetate it gives off CO2 and forms a white pp. which, on adding HOAc and warming, yields Cu₂O₂ the liquid then containing benzoic acid. The (3,6), (3,4), and (2,8) isomerides do not reduce AgNO₂ and cuprio acctate. The Ba salt crystallises in plates, and is v. sol. water.

Methylether Me. A". [77°]. Yields a diand a tetra-bromide. Br in CHCl, forms a dibromide [170°] and a tetrabromide [98°].

Di-phenyl ether Ph₂A". [146°]. Formed from the chloride and phenol at 100°. Small crystals, sl. sol. alcohol, ether, and ligroin.

 Γ cis $\Delta^{2,5}$ or (1,4)- Dihydride

CO_H.CH<CH:CH>C(CO_H)H. Extracted by

ether from the mother-liquor from which the preceding isomeride has separated. Closely resembles its cistrans isomeride, but the cis acid and its salts are the more soluble.

 $\Delta^{1,5}$ or (3,4)- Dihydride

 $CO_2H.CH < \stackrel{CH}{<} \stackrel{CH}{<} \stackrel{CH}{>} C.CO_2H.$ S. 042 in the

cold. H.F. 185,300. Formed by boiling the (1,4)-dihydride with water, and obtained, therefore, by reducing terephthalic acid with sodium-amalgam (Baeyer, A. 245, 142; 251, 257; 269, 148). Converted into the (3,6)- acid by NaOHAq. Sodium-amalgam in the cold reduces it to the Δ' tetrahydride.-BaA" 4aq. Trimetric orystals; a:b:c = :319:1: 352 (Baeyer a. Herb, A. 258, 22).

Methylether Me, A". [40°].

Δ1,4 or (3,6). Dihydride

CO₂H.C CH₂CH₂C.CO₂H. S. 0059 in the

cold. H.F. 191,900. Formed by reduction of terephthalic acid in a kaline solution by sodium. amalgam (Baeyer, A. 245, 142). Got also by boiling the (1,4)-dihydride with NaOHAq. Slender needles (from water), almost insol. ether. Much resembles terephthalic acid. On sublimation it is partially converted into terephthalic

acid. Immediately oxidised by KMnO4. Forms CH(CO,H) CH, .CHBr CH.CO,H by uniting with HBr. Sodium-amalgam in the cold reduces it to a slight extent, forming the two isomeric Δ² tetrahydrides.—BaA"4aq. Crystals,

resembling its $\Delta^{1,5}$ and $\Delta^{1,8}$ isomerides. Mono-methyl ether MeHA". [225°]. Got from Me,A" and alcoholic potash. Needles

(from hot-water).

Di-methyl ether Me.A". [130°]. H.F. 172,700. Formed from the dihydride by-successive treatment with PCl_s (2 mols.) and MeOH. Monoclinic plates (from EtOAc); a:bc=1·52:1:2·79; β =c. 74°. Sl. sol. water, m. sel. hot alcohol, v. e. sol. ether. Br in CHCl, yields a dibromide C, H, Br₂(CO,Me)₂ [90°] and a tetrabromide [150°]. Excess of Br yields CO₂Mo.C_eH_eBr

CO [188°]. HBr forms

C₂H_eBr₂(CO₂H)₂ which yields C_eH_eBr₂(CO₂Me)₂ [166°].

Di-phenyl ether Ph.A". [191°]. Formed by treating the chloride with phenol (Baeyer a. Herb, A. 258, 31). Small scales (from hot

MeOH), sl. sol. ether.

Δ ^{1,3} or (5,6). Dihydride CO₂H.C ≪ CH₂CH₂CH₂ ⊗ C.CO₂H. S. 0053 in the cold. Formed by the action of alcoholic potash on the dibromide of the \(\Delta^2 \) tetrahydride and on the tetrahydride of di-bromo-terephthalic acid got by bromination of the hexahydride. Unites with hydrogen bromide (2 mols.) forming CO_H.CH<CH_CHBr.CHBr>CH.CO_H. Easily reduced by Zn and HOAc and by sodium-amalgam to the two A2 tetrahydrides. Boiling water converts it into the (3,4)- isomeride. Boiling NaOIIAq forms the (3,6)- isomeride.—BaA" 4aq. Needles (from hot water).

Methyl ether Me.A".

Methyl ether Me.A". [85] Monoclinic plates; a.br. = 2'211:1:3'591; \$\beta = 87' 13'. Slowly converted by HBr into (2,3)-di-bromo-terephthalic acid hexahydride, which is reduced by since the state of t zinc-dust and acetic acid to the \(\Delta^2 \) tetrahydride of terephthalic acid. Yields a dibromide [61°].

Di-phenyl ether Ph.A". [175°]. Large needles (from MeOH), sl. sol. cold alcohol.

Δ' or (3,4,5,6). Totrahydride.

CH(CO_H) < CH_CH_SCLO_H. [above 300°]. S. 102 at 16°; 83 at 100°. H.F. 214,200 (Stohmann, J. pr. [2] 43, 5). Formed by boiling a solution of terephthalic acid (1 pt.) in NaOHAq for twenty hours with gradual addition of 4 p.c. sodium-amalgam (100 pts.) (Baeyer, B. 19, 1805; A. 245, 160; 258, 32). Prisms, more sol. water than terephthalic acid or its dihydrides. Combines with HBr and with Br (1 mol.). Immediately reduces alkaline KMnO, yielding oxalic acid.—BaA" 3 aq. M. sol. cold water. Reduced by HIAq at 240° to the hexahydride.—Ag.A". Amorphous.

Methylether Me.A". [39°]. H.F. 196,200. Plates. Its ethercal solution shows blue fluor-NaOEt. HBr gives C.H.Br(CO.H), whence Ma.A." [95°]. Bromine forms C.H.Br₂(CO₂Me), [81°].

Di-phenyl-sther Ph.A". [145°]. Formed

from the acid by successive treatment with PCl, and phenol. Monoclinic crystals; a:b:c=2.824:1:2.470, m. sol. cold alcohol and other.

Γ cistrans Δ2 or (1,4,5,6)- Tetrahydride CH(CO₂H) CH₂CH₂OH.CO₂H. [c. 220°]. S. 17. Formed, by reducing \$\Delta^{1,5}\$ dihydride and also the dibromide of the \$\Delta^{1,5}\$ dihydride. Oxidised by KMnO, in the cold to succinic acid and a soluble acid [150]. Alkaline K,FeCy, gives terephthalic acid. Yields three dibromides terephthalic acid. Yields three c CH(CO₂H) < CH₂ .CH₂ .CH₃ > CH.CO₂H. [51°], and [94°]. The Ba and Cd salts are more sol, water than those of the Δ^1 isomeride.

Methyl ether Mo.A". [0. 30].

Amide. Dimetric needles; a:c = 1:2:151.

Diphenyl ether PhA". Formed, in two modifications [107°] and [c. 190°] by the successive action of PCl, and phenol (Baeyer a. Herb, A. 258, 39). The modification [c. 190°] probably is a mixture containing the Δ^1 isomeride.

Dibenzybether (C,H,),A". [48°]. From

Ag, A" and benzyl chloride.

 Γ cis Δ^2 or (1,4,5,6)- Tetrahydride. [150°-155°]. S. 2.7 in the cold. Formed, together with the cistrans isomeride, by reducing the A1.4 dihydride by sodium-amalgam in the cold. The Ba, Cd, and Ag salts are amorphous. This acid and the cistrans isomeride are converted into the A1 isomeride by boiling with NaOHAq. l' cistrans Hexahydride

CO.H.CH. CH., CH., CH., CO.H. Funaroid or stable modification. [300°]. S. 086 at 16°; 13 at 100°. H.F. 236,500 (Stohmann, J. pr. [2] 43, 7). Formed by heating the tetrahydride with HIAq for 6 hours at about 240' (Baeyer, B. 19, 1806; 245, 170; 251, 257). Formed also by heating ethyl butane tetracarboxylate with NaOEt and ethylene bromide at 100°; the product being hydrolysed and heated at 220° till evolution of CO₂ ceases (Mackenzie a. Perkin, jun., C. J. 61, 174). Prepared by reducing the hexahydride of bromo-terephthalic acid zinc-dust and HOAc. Small prisms, sol. hot water. May be sublimed. Not oxidised by cold alkaline KMnO. Br (2 mols. at 100°) forms $C_aH_0Br(CO_2H)_2$ [71°], and a maleic isomeride Treatment with PCl, followed by Br at [203]. Treatment with Pol_a tollowed by B as 150° forms C_aH_aBr_a(CO_aH_b)₂ in a funaroid modification which yields Me_AA" [150°] and a maleic modification which yields Me_aA" [68°] and an anilide [200°]. The K and Ba salts are v. sol.

anima (2007). The K and Da sates are V. sol. water; the Ca salt is sl. sol. water.

Methyl ether Me.A". [71°]. S. .5 at 100°. H.F. 218,100. Exhibits no fluorescence. S. .5 at. Volatile with steam.

Diphenyl ether Ph.A". [151°]. Needles. r cis Hexahydride

CO₂H.CH CH₂CH₂CH₂C(CO₂H)II. Maleic or [162°]. H.F. 287,400. labile modification. Formed by reducing the very soluble hexa-hydride of bromo-terephthalic acid with zincdust and HOAc. Plates (from water), v. sol. alcohol and ether. Changes on heating with HClAq at 180° into its isomeride. Its Ba salt and methyl ether do not crystallise.

References. -BROMO-, CHLORO-, NITEO-- and

OXY- TEREPHTHALIC ACID.

TEREPRIHALIC ALDEHYDE

TEREPHTHALIC ALDEHYDE
C₄H₄(CH₀)₂[1:4]. [116°]. (247°). S. 1·7 at
100°. Formed by boiling C₂H₄(CH₂Cl)₂ or
C₄H₄(CH₂Br)₂ (1 pt.) with lead nitrate (1 pt.) and
water (20 pts.) (Grimaux, C. R. 83, 825°; Lōw,
A. 231, 363). Formed also by the action of
fuming HNO₂ on disweromo-pt-xylene (Lōw, B. 18, 2072), and by boiling C_cH₁(CHCl₂), with water (Colson a. Gautier, Bl. [2] 45, 6, 508). Obtained from CH₂(OH).C_cH₁.CH₂OEt by successive treatment with PCl₂ and water (Colson, Bl. [2] 42, 152).

Preparation.—p-Xylene (1 pt.) is heated with Br (6 pts.) at 140° to 200° with inverted condenser. The crystalline tetra-w-bromo-xylene [169°] thus obtained is heated with three times its weight of H2SO, (S.G. 1825 at 120°-130°), the product poured into water, and the needles that separate recrystallised from water (Hönig, M. 9,

Properties.—Long needles, v. sl. sol. hot water and cold ether, v. sol alcohol. Slightly volatile with steam. Dissolves in 25 pts. of saturated aqueous NaHSO₃ at 45°.

Reactions .- 1. Oxidised by chromic acid mixture to p-aldehydo-benzoic acid and then to terephthalic acid .- 2. Conc. NaOHAq forms terephthalic acid, w-oxy-toluic acid, and di-woxy-xylene.—3. KNO₃ and excess of H₂SO₄ at 110° form nitro-terephthalic aldehyde.—4. Cold cone. NH₃Aq forms tri-p-aldehydo-hydrobenz-amide (C_aH₄(CHO).CH)₃N₂, a crystalline powder, insol.water, alcohol, and ether, yielding on oxida-tion Bf KMnO₄ crystalline N₂(CH.C_aH₁,CO₂H)₃ (Oppenheimer, B. 19, 574).—5. Dry or alcoholic NH₄ forms crystalline C_aH₄(CH:NH)₂.—6, NaOAc and Ac.O give p-aldehydo-cinnamic acid.—7. Acetone and dilute NaOH give a white pp. of C_sH₄(CH:CH.CO.CH_s)₂, which crystallises from ether-acetone in matted needles [156°], insol. water and alcohol, and gives a deep-red soluwhite and alcohol, and gives a deep-led solu-tion in conc. H.SO. An intermediate body is C_aH₁(CH(OH).CH..CO.CH₃)₂.—8. NPhMe₂ and ZnCl₂form C_aH₄(CHO).CH(C_aH₁NMe₂)₂, the leuco derivative of the aldehyde of malachite green.-9. Cold conc. aqueous KCy added to a cold saturated alcoholic solution of the aldehyde ppts. amorphous C₁,H₁,O₁, which probably has the formula C₄H₄(CHO).CH(OH).CO.C₄H₄(CHO) [170°-174°]. This body reduces cold ammoniacal AgNO₃, forming a mirror. It also reduces warm Fehling's solution and combines with phenyl-hydrazine. KMnO₄ oxidises it to benzoin di-p-carboxylic scid. NaOHAq dissolves it, ferming benzoin di-p-carboxylic acid, di-a-oxy-p-xylene, and other bodies (Oppenheimer, B. 19, 1814).

Phenyl-hydraside [230°].

Oxim C-H_(CH:NOH).* [200°]. Formed

from the aldehyde and an alkaline solution of from the alderyde and an algaline solution or hydroxylamine (Westenberger, B. 16, 2994). Crystalline, v. sol. alcohol and ether, sl. sol. water. Yields $O_{\bullet}H_{\bullet}(CH:NOEt)_{\bullet}$ [55°] and $O_{\bullet}H_{\bullet}(OH:NOAc)_{\bullet}$ [156°]. Reference.—NITRO-TEREPHTHALIC ALDEHYDE. TEREPHTHALIO AMDINE $C_{\bullet}H_{\bullet}NN_{\bullet}$, i.e. $O_{\bullet}H_{\bullet}(OHN.NH)_{\bullet}$. The sait R"2HCI. formed

C.H.(C(M.).NH.). The salt B"2HCl., formed by digesting terephthalic imido-ethyl ether with alcoholic NH., is crystalline, and yields B"H_PCl. (Luckenbach, B. 17, 1436).
TEREPHTHALOPHENONE ... PHTHALO-

PHENOME.

TERPENES $C_{10}H_{16}$; also Sesquiterpenes $C_{13}H_{23}$ and Polyterpenes $(C_{10}H_{16})_n$. The greater number of these hydrocarbons exist ready formed as constituents of essential oils secreted by plants. Others are produced from the natural terpenes by the action of heat or of chemical agents. A dihydrocymene isomeric with the natural terpenes has been obtained synthetically from methylisopropyl succino-succinic ester and the homologous dihydroparaxylene and dihydrobenzene by corresponding processes (Baeyer, B. 25, 1840, 2122; 26, 232). The natural terpenes are generally optically active liquids, with right- or left-handed rotatory power. The only exception is the racemic compound dipentene (q. v.). The following isomerides are known :-

1. Pinene. This includes two varieties, australene or dextropinene and terebenthene or lævopinene. American spirit of turpentine conlevopinene. American spirit of turpename consists chiefly of dextropinene. (156°). [a]₁ = +21·5 (Berthelot, A. 83, 105; 88, 345, 110, 367, Suppl. ii. 226). S.G. $^{0}_{4}$ =8765; $^{25}_{52}$ =8586; $^{100}_{100}$ =8278 (Tilden, unpubl. expts.). French turpentine oil consists almost wholly of layopinene. (156°5°). $[\alpha]_{j} = -40.32$. S.G. $\frac{0}{0} = .8767$; $\frac{17.88}{17.88} = .8619$ (Riban, C. R. 78, 788; 79, 314). It is also present in oil of rosemary (Bruylants, J. 1879, 944), oil of lemon (Tilden, Ph. [3] 9, 654), sage and juniper (C. J. 31, 554), thyme and anise (Bruhl, B. 21,

156), and other essential oils.

For production and properties of turpentine oils v. Oils, ESSENTIAL, Thorpe's DICTIONARY OF

APPLIED CHEMISTRY.

Different specimens of the pinenes, both dextro- and levo-, obtained by fractional distillation from turpentine exhibit considerable variations in their rotatory power. An optically inactive liquid has been obtained by Wallach (A. 258, 343) from pinene nitrosochloride by treatment with aniline, whereby a diazo- compound is formed, which with the neighbouring chlorine atom gives rise to diazobenzenechloride and regenerates the hydrocarbon

- CCl -- C.NO -- + H.NC.H. $\begin{array}{ll} -\operatorname{CCl} -\operatorname{C(N:NC_0H_3)} - +\operatorname{H_2O} \text{ and} \\ -\operatorname{CCl} -\operatorname{C(N:NC_0H_3)} - + -\operatorname{C=C} - +\operatorname{ClN_0C_0H_3}. \end{array}$ The hydrocarbon thus obtained boils at 155°-156°, has a density 858 at 20°, a refractive index for D 1.46553 at 21°, and is supposed to be identical in constitution with the pinenes. It is apparently not resolvable into a mixture of dextro- and levo- pinenes, but with nitrosyl chloride and other reagents it behaves in the

same manner as pinene. Dry pinene unites with one molecule of dry hydrogen chloride, forming a crystalline com pound formerly called artificial camphor [125°], which appears quite saturated, as it is unacted upon either by excess of hydrogen chloride or bromine. The hydrochloride prepared from dex-tropinene is dextrorotatory, while that from levo-pinene is levorotatory. The compound is very pinene is laworotatory. The compound is very stable; it may be distilled almost without change, mere traces of hydrogen chloride being evolved; and it is unacted upon by aqueous solutions of the alkalis, except at high temperatures under pressure. Heated with sodium stearate, benzoate, or acetate, or with alcoholic potash, it loses the elements of hydrogen chloride and yields solid camphene (v. Camphene, infra). In the presence

of water, alcohol, ether, or acetic acid, pinene takes up two mols. of hydrogen chloride, producing a compound of different character [50°], which on the application of heat is readily split up into hydrogen chloride and a mixture of liquid into hydrogen chloride and a mixture of liquid hydrocarbons (v. DIPENTENE, infra). Nitrosyl chloride passed into a solution of pinene in chloroform at -10° yields a compound C₁₀H₁₀NOCI [103°], which is ppd. as a white crystalline powder on the addition of alcohol (Tilden, C. J., June 1875). The same compound is formed by adding hydrochloric acid to a cooled mixture of the terpene with amyl nitrite and glacial acetic acid (Wallach, A. 215, 245). The nitrosochloride gently heated with alcoholic potash yields a nitroso-compound, $C_{10}H_1$, NO [129°] (Tilden). For crystallography v. Story-Maskelyne (C. J., June 1875, and Phil. 'Mag.). Nitrosopinene unites with two atoms of bromine, forming a crystalline dibromide, which decomposes on melting [132°]. Mixed with alcohol and nitric acid both pinenes form crystallised terpin hydrate $C_{10}\Pi_{1}(OII)_{x}OH_{x}$ (Wiggers, A. 33, 358; 57, 247; Tilden, C. J. 33, 217; Hempel, A. 180, 71). Pinene dissolved in carbon tetrachloride and mixed with bromine yields a mixture of products, from which a well-defined crystalline dibromide $C_{10}H_{1a}Br_2$ [169°-170] may be isolated. On heating this with aniline it gives up hydrogen bromide, and ordinary cymene is produced. The yield, however, amounts only to about 10 p.c. of the bromide employed (Wallach, A. 264, 1). Exposed to the action of air or oxygen, in sunlight, the pinenes produce a crystalline compound $C_{\rm in}H_{\rm in}O_{\rm i}$ (Sobrero, C. R. 33, 66) which when distilled with dilute acid yields a compound called by Armstrong 'Sobrerone' (Armstrong a. Pope, C. J. 59, 311), which is identical with one of the products of the action of nitrous acid on pinene, isolated by Wallach a. Otto, and called by them 'Pinol' (A. 253, 249). Pinene distilled with bleaching powder and water yields a large quantity of chloroform. Pieric acid has no action upon pinenes in the cold, but at the b.p. of the latter a brisk reaction sets in, and if the liquid is afterwards allowed to cool a compound is deposited in colourless scales, which on boiling with alkali yield borneol (Lextreit, C. R. 102, 555; Tilden a. Forster, C. J. 63, 1388).

2. Limonene. This compound, like pinene, occurs in two optically active varieties. Dextrolimonene (175°-176°), S.G. 2°. 846, [a]_b = +106°8 (Wallach, A. 252, 145) occurs in oils of the fruit of oranges and lemons, also in caraway and dill, &c. The most convenient source is the essential oil of sweet orange, Citrus aurantium. Lavolimonene is obtained from the oil distilled from the leaves of Pinus sylvestris and P. picca. This oil occurs in the drug houses as 'Fir-Wool oil,' but is now much adulterated with common turpentine, and the commercial oil seldom yields more than a small percentage of limonene. (175°-176°), S.G. 2°° -846, [a]_b = -105° (Wallach, A. 227, 287, 246, 221). The limonenes, treated with perfectly dry hydrogen chloride, yield a liquid monochloride. In the presence of alcohol they give, with excess of hydrogen chloride, a quantitative yield of a dihydrochloride [50°], identical with the compound obtained from the pinenes. By the action of nitrosyl

chloride (Tilden a. Shenstone, C. J. May, 1877), or by the use of amyl or ethyl nitrite and hydrogen chloride (Wallach), they yield a crystalline nitrosochloride, which, whether formed from dextro- or lawo-limonene, is always a mixture of two isomerides separable from each other by cold chloroform or ether. There are therefore four isomeric limonene nitroso-chlorides, as follows:

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From d. Limonene: 

\alpha compound [103^{\circ}-104^{\circ}] \alpha_{\rm D}=+313^{\circ} 

\beta , [105^{\circ}-106^{\circ}] \alpha_{\rm D}=+240^{\circ} 

From l. Limonene: 

\alpha compound [103^{\circ}-104^{\circ}] \alpha_{\rm D}=-314^{\circ} 

\beta , [100^{\circ}] \alpha_{\rm D}=-242^{\circ}
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From the nitroso-chlorides by the action of heat (Tilden a. Shenstone), or by boiling with alcohol (Goldschmidt a. Zürrer, B. 18, 2220), is produced an isonitroso-limonene, which when made from lawo-limonene is identical in every respect with carvoyim C₀H₁, N.OH, from carvol, extracted from oil of caraway (Goldschmidt a. Zürrer, B. 18, 1732). For a comparison of the rotatory powers of the two limonenes and their derivatives, see Wallach (A. 252, 141). The limonenes are further characterised by the formation of a crystalline tetrabromide [104°-105°] by direct addition of bromine (Wallach, A. 227, 277)

By mixing together equal quantities of dextroand lawo-limonenes an optically mactive mixture is obtained, which behaves in many respects as a distinct hydrocarbon, and appearate be identical with dipentene (q. v.). Strong sulphuric acid acting upon citrene (d-limonone), causes polymerisation, the chief product being a colophene (310 '-320°) (Bouchardat a. Lafont, C. R. 115, 1083).

The oil of Licari kanali contains a compound, licarene C₁₀II₁₀O, from which a hydrocarbon, licarene C₁₀II₁₀O, from which a hydrocarbon, licarene C₁₀II₁₀O, from which a tation of acetic anhydride at 150° (Barbier, C. R. 114, 674, and C. R. 116, 993, and 1062). This terpene appears to consist of impure d-limonene, as it boils at 176°-178°, gives a tetrabromide [103°-104°], forms a nitrosochloride, from which carvoxim [72°] is formed by alcoholic potash; but its specific rotatory power is low, [a]₁₀ = 7.61°.

3. Sylvestrene occurs in Swedish turpentine (Atterberg, B. 10, 1206) and in Russian turpentine (Wallach, A. 230, 245), in company with australene and other hydrocarbons of higher boiling-point. (176°-177°). S.G. 18 = 8510; 29 = 8470. [a] = 66°32 (Wallach, A. 245, 197). The odour of sylvestrene differs from that of pinene and limonene, and resembles the odour of fresh firwood. It forms a liquid monohydrochloride, and a crystalline dihydrochloride [72°], from which the hydrocarbon may be recovered unchanged by heating with aniline. Sylvestrene also gives a nitrosochloride [106°-107°], which, by treatment with alcoholic potash, yields only oily products. The tetrabromide crystallizes in monoclinic tables [135°] (Wallach, A. 289, 29).

4. Phellandrene. The seeds of Phellandrium

4. Phellandrene. The seeds of Phellandrum aquaticum were found by Pesci (G. 16, 225) to yield about 2½ p.c. of a volatile oil, consisting chiefly of a dextrorotatory terpene (1712-1723). The same hydrocarbon is contained in the oil of bitter fennel, Foniculum vulgare (Wallach, 4.

239, 40), and in the oil of elemi. Lævo-phellandrene is found, according to Wallach (A. 246, 232), in the oil of Eucalyptus amygdalina. Phellandrene is characterised by the formation of a nitroso-nitrite $C_{10}H_{16}N_2O_3$. Pesci obtains it by the action of a nitrite and dilute sulphuric acid upon the hydrocarbon. It crystallises in needles [94°], and although obtained from the dextrorotatory hydrocarbon it rotates the plane of polarisation to the left. $[a]_0 = -183.5^\circ$ (Pesci). By reducing agents this compound is converted into a base $C_{10}H_{16}(NH_2)_2$ (20 $\hat{9}^{\circ}$ -214°). Ammonia converts it into nitrophellandrene

Ammonia converts it into introprenantierie C₁₆H₁₆NO₂ and an acid.

5. Dipentene, formerly called terpilene or terpinylene. As already stated, this compound is produced when equal quantities of dextroand lawo-limonenes are mixed together (see Pentylenes). It is formed by heating isoprene to a temperature of about 300°. It is also the chief constituent of 'isoterebenthene,' formed by the action of heat on lave-pinene. It occurs among the products of the destructive distillation of caoutchouc. Dipentene is also produced, together with terpinene, terpinolene, and terpineol, by the action of sulphuric acid or phosphoric acid on terpin, or by the action of sulphuric acid on the pinenes under certain condi-tions (Armstrong a. Tilden, C. J. November, 1879). It is also formed from the dihydrochloride [50°], whether made from pinene or limonene, either by the action of heat upon the chloride alone (Tilden, B. 12, 1133) or by boiling it with a mixture of sodium acetate and acetic acid, or with alcohol and aniline (Wallach). The products thus obtained were formerly supposed to consist of a single hydrocarbon, to which the name 'terpilene' was given. The hydrocarbons known as cinene and cajeputene formed from cineol and cajeputol respectively also consist of

dipentene. Dipentene occurs ready formed in the volatile oil of the camphor tree, also in oil of elemi and in Russian and Swedish turpentines (Wallach, A. 227, 296, &c.).
Dipentene boils at about 176°, and has a

pleasant smell of lemons. It combines with bromine forming a tetrabromide [124], and unites with 2HCl forming a chloride [50°], from

which it may be regenerated by methods given above. It is to be noted, however, that in all cases more or less isomeric change occurs, and the hydrocarbon, whether reproduced by heat

alone or by the action of aniline, always contains

terpinene and terpinolene, beside cymene and a small quantity of a paraflinoid hydrocarbon (Tilden a. Williamson, C. J. 63, 292). The nitrosochloride C₁₀H₁₆NOCl yields an inactive carvoxim C₁₆H₁₁NOH [98°] (A. 245, 267). A mixture of equal volumes of dextro- and levo-

limonene behaves in many respects as though it were a distinct hydrocarbon, as it was supposed to be previously to Wallach's researches. Thus the tetrabromide melts at 124°, while the limonene compound melts at 104°. The inactive

isonitrosodipentene or carvoxim, melting at 93°, is formed by mixing together equal quantities of lavo-carvoxim [72°] from dextro-limonene and dextro-carvoxim [72°] from lavo-limonene. The

resulting compound gives, by Raoult's freezingpcint method, a molecular weight corresponding to the simple formula C₁₀H₁₀NO (Wallach, A.

246, 280).

Certain derivatives of dipentene exist in two optically inactive forms. When d-limonenenitrosochloride, prepared from either dextro- or lævo-limonene, is warmed with an alcoholic solution of piperidine, a mixture of two crystallisable nitrolamines is formed in each case, as follows:

NITROLPIPERIDINES C10H16NONC4H16, FROM LÆVOLIMONENE :

> (a) [93°-94°] Rhombic, from alcohol. $[a]_{D} = -67.60^{\circ}$. Hydrochloride

dextrorotatory. (β) [110°-111°]. Monoclinic. $[a]_{D} = +60.18^{\circ}$ Hydrochloride almost inactive.

FROM DEXTROLIMONENE:

[93°-94°]. Rhombic. [a]_D = +67.95°. Hydrochloride lavorotatory.

(3) $[110^{5}-111^{\circ}]$. Monoclinic. [a]₀ = -60.48° . Hydrochloride (?). When the two a-piperidine bases [93°-94°] are dissolved in petroleum-spirit, and the solutions mixed, an inactive nitrolamine [154°] is at once precipitated. A second inactive compound [152°] is formed by mixing the β -piperidine bases (Wallach, A. 252, 123). Similar results have

been obtained by the employment of aniline and benzylamine. The salts of the bases thus produced possess a rotatory power opposite in direction to that of the free base. No method is at present known of producing from limonene active addition-compounds with two molecules of hydracid. With excess of hydrogen chloride the same inactive dipentene dihydrochloride [50°] is

always obtained. The corresponding dihydriodide seems to crystallist in two forms differing slightly in melting-point (Wallach, A. 239, 13). 6. Terpinene. (180° about). This compound

is formed, together with dipentene, by the action of acids upon pinene and terpin, &c. It is said to occur in oil of cardamoms (Ev. Weber, A. 238, 98). Terpinene has not been obtained in an absolutely pure state, but is characterised by

forming a nitrosonitrite $C_{10}H_{16}N_2O_3$ [155°] (Wallach, A. 239, 33). The tetrabromide is fluid, and it yields no crystallisable hydrochloride. The nitrosonitrite by the action of

the action ...

C₁₀H₁₅ < NOH₂ yields nitrolamines [116°-118°], C₁₀H₁₅<NOH_{NHC,H5} [130°-131°], &c. (A. 241, 315).

7. Terpinolene. (185° about). This hydrocarbon is formed along with dipentene and terpinene by the action of acids upon pinene, &c.

With hydrogen chloride and hydrogen bromide terpinolene unites to form the dipentene dihydrochloride [50°] and dihydrobromide [64°]. It forms an optically inactive tetrabromide which crystallises in monoclinic tables [116°] but is gradually converted at ordinary temperatures into a porcelain-like mass.

8. Fenchene. A liquid isomeride of camphor

(190°-193°), obtained from oil of fennel, is treated with alcohol and sodium, by which it is reduced with accordance solutine, by which is reduced to the alcohol $C_{10}H_{1}$, OH, a colourless crystalline compound. By treating this with phosphoric chloride the chloride $C_{10}H_{1}$, Cl is formed, and from this, by heating with aniline, fenchene $C_{10}H_{10}$ (158°-160°) may be obtained. Fenchene is optically inactive. It differs from other terpenes in resisting the action of nitrie acid unless heated (Wallach, A. 268, 149).

TERPENES.

SYNOPSIS OF TERPENES AND THEIR CHIEF DERIVATIVES. Boiling-points approximately stated. Rotatory power +, -, or 0.

Pinene (158°)	Limonene (176°)	Dipentens (176°)	Sylvestrene (175°)	Phellandrene (170°)	Terpinene (180°)	Terpinolene (185°)	Fgnchene (160°)
+ and -	+ and	±	+	+ and -	0	0	0
C ₁₀ H ₁₀ HCl saturated [125°]	O ₁₀ H ₁₄ HCl unsaturated liquid	C ₁₀ H ₁₀ HCl unsaturated liquid	O ₁₀ H ₁₀ HCl liquid	_		_	O, H, HOI liquid
O,.H,.2HCl [50°]	C,.H,.2HCl [50°]	O,.H,.2HCl [50°]	O ₁₀ H ₁₀ 2HCl [72°]				_
O, H, Br, [170°]	O, H, Br. [104°]	O ₁₆ H ₁₆ Br ₆ [124°]	Ο ₁₆ Π ₁₆ Βr ₆ [135°]		C, H, Br.	C, 11, Br.	C, H, Br,
O, H, NOCI [103°]	C ₁₀ H ₁₂ NOCl four isomerides [100° to 106°]	O, H, NOCI [101°-102°]	O ₁₀ H ₁₀ NOCl [106°]	0,.H,.N,0, [102°]	O,,11,,N,O, [155°]	_	_
0,.H,\(\sqrt{\text{NO}}\text{NHC,H,}\)	О, H, NO NHC, П,	C,.H,NO,H,	CHNIO,H,		C ₁₀ 1I ₁₀ N ₂ O ₂ [137°]		_
.0'*H'*NO	0 , H, N.OH [72°]	O,.II,.NOH [93°]					-

Isoterpenes.

Camphenes $C_{i0}H_{id}$. Pinene monohydrochloride [125°] was formerly described under the name 'artificial camphor,' from its resemblance to camphor in appearance and to a certain extent in odour. This compound is remarkably stable, but may be decomposed by heating with sodium stearate or benzoate, with potassium acetate, with alcoholic potash, or, better, with a mixture of sodium acetate and alcoholic soda (Brühl, B. 25, 147). The resulting hydrocarbon is a camphene [51°-52°] [160°), dextro- or lavorotatory or inactive according to the nature of the hydrochloride used and the reagent employed, though the exact conditions which determine the production of one or other are scarcely known (Riban, A. Ch. [5] 6, 353).

Camphene is also formed from bornyl chloride by the action of alcoholic potaslı (Riban), by the action of water and magnesia (Kachler, A. 197, 86), or by heating with aniline to the boiling-point of the latter (Wallach, A. 230, 234); it is also formed from camphor chloride and from pinene hydrochloride by the action of sodium (Montgolfier, C. R. 89, 102). In the last case it is accompanied by a liquid hydrocarbon (170), C₁₀H₂₀, which behaves like a paraflin, and is probably identical with a liquid obtained by the action of hydrogen iodide on turpentine (Berthelot), also by the action of iodine (Armstrong a. Gaskell, B. 12, 1756) and by the action of sulphric acid on turpentine (Armstrong, B. 12, 1759).

Camphene is also formed by the action of strong sulphuric acid on turpentine, and constitutes the characteristic ingredient in the liquid formerly known as 'terebene' (Armstrong a. Tilden, C. J. 1879, 733).

Camphene closely resembles camphor in appearance and even somewhat in odour. It is soluble in alcohol, ether, and benzene, and crystallises in leaflets from a concentrated solution. It is incapable of combining with bromine, but it forms a compound [157°] with hydrogen chloride, which is distinguished from pinene bydrochloride by its instability, being rapidly

decomposed by water with reproduction of camphene (Riban, C. R. 80, 1330). It is also dissociated into camphene and hydrogen chloride when volatilised (Ehrhardt, C. N. 54, 239). Camphene hydrochloride is said to be identical with bornyl chloride (Kachler a. Spitzer, A. 200, 310; v. also Brühl, B. 25, 160). Camphene does not combine with nitrosyl chloride. In contact with bromine it is slowly attacked, forming an oily monobrono- derivative (230*240*).

Oxidised by chromic liquor, camphene yields camphor, dextro-, laworotatory or inactive according to the character of the camphene.

By the action of phosphorus pentachloride on camphene, and subsequent treatment of the mass with an alkaline solution, salts of two phosphonic acids are formed (Marsh a. Gardner, C. J. 65. 35).

When camphene is heated to about 300° it is converted into liquid products which seem to include dipentene, but have not been sufficiently investigated.

Homologues of camphene.

Ethyl-camphene obtained by the conjoint action of sodium and ethyl iodide upon camphor monochloride C₁₀H₁₀Cl, is a colourless mobile liquid having a smell like turpentine (197-9° – 199-9°, bar. 742-1 mm.). Isobutyl-camphene is also a liquid (228°-229°, bar. 750-4 mm.) (Spitzef, B. 11, 1817).

Sesquiterpenes C15H24.

Oils of clove, calamus, cascarilla, patchouli, and cubebs contain a hydrocarbon of this composition (Gladstone, C. J. 1872), as also do the oils of galbanum, and savin and hulle de cade, a kind of tar made by distillation of the wood of Juniperus oxycedrus (Wallach, A. 238, 81). The hydrocarbon obtained from cade or cubebs (274°-275°) (S.G. \\ \frac{1}{2} = 921) forms the following crystalline compounds: C, \(\mathbf{H}_2\), 2HC[[17°-118°], C, \(\mathbf{H}_2\), 2HE [124°-125°], C, \(\mathbf{H}_2\), 2HI [105°-106°]. The hydrocarbon, especially when partially resinified by exposure to the air, gives the following characteristic colour reaction: dissolved in chloroform or glacial acetic acid and then

shaken up with a few drops of strong sulphuric acid, the liquid assumes an intense green and then blue colour, which, when heated, passes into red (Wallach). An attempt to prepare from isoprene a polymeride of the composition C₁₈H₂₈ proved unsuccessful (Wallach).

Conimene C_{1,}H₂₄, a liquid (264°) having a pleasant odour, is obtained from the incense resin (*Icica heptaphylla*) of British Guiana (Stenhouse a. Groves, C. J. 1871, i. 175).

Polyterpenes C .. H 32, &c.

This group includes (1) the constituents of certain natural essential oils; (2) products of artificial polymerisation of terpenes; and (3) caoutohoue and guttapercha.

1. Oleo-resin or so-called 'balsam' of copaiba (Copaifera Langsdorfii and other species) is a mixture of a resin with an oil (250°-260°). The latter unites with water and absorbs hydrogen chloride, with production of a deep violet colour but no crystalline hydrochloride. A similar hydrocarbon is obtained from Gurjun balsam or 'wood oil,' the product of various species of Dipterocarpus growing in the East, and from other essential oils.

2. When turpentine oil and other terpenes are heated for some time to about 300°, or treated with concentrated sulphuric or phosphoric acid or other agents, a large part of the hydrocarbon undergoes polymerisation. The name 'colophene' was given by Deville to the less volatile portions of the product obtained in this manner from French turpentine, apparently under the impression that it was closely related to the oil obtained by distillation of resin. Resin-oil, however, contains oxygen, and exhibits quite different characters.

Colophene is a yellowish viscid fluid, usually

fluorescent, which begins to boil at about 300°, but the distillation even under reduced pressure is attended by decomposition. The boiling-point continually rises, and even at a temperature approaching dull redness a viscid residue is left which on cooling becomes nearly solid (Armstrong a. Tilden, C. J. Nov. 1879). The portions which distil at 300° and upwards appear to consist of saturated compounds, for they absorb mere traces of hydrogen chloride. By the action of antimony trichloride upon turpentine a solid, C. M., is formed. This combines with hydrogen chloride to form two compounds Co. H., 14HCl., and Ci. H., 12HCl. (Riban, C. R. 1874, 389).

3. CAOUTCHOUG v. vol. i. p. 677. For further information concerning the products of its decomposition by heat v. Pentinenes (vol. iii. p. 807) and DIPENTENE (supra).

GUTTAPERCHA, v. vol. ii. p. 658.

Caoutchoue is formed from isoprene by polymerisation, which sometimes occurs spontaneously under circumstances not fully understood (Tilden, C. N., May 1892).

Oxidised compounds connected with terpenes.

A considerable number of oxidised compounds are known which are evidently closely connected with the terpenes, and in many cases directly derivable from them. Some of these, as, for example, borneol and camphor, occur as natural products in essential oils; others, such as terpin, are the products of the addition of water to a terpene, or, like camphor and some of its isomerides, may be formed from terpenes by oxidation. These compounds are enumerated in the following table, together with the hydrocarbons with which they are presumably immediately connected.

Hydrocarbons	Alcohols	Glycols	Ketones (?)		
Cymene C ₁₀ H ₁₄ (ii. 361)	Carveol C ₁₀ H ₁₅ OH (i. 711)		Carvol C, H, O (i.		
Pinene C ₁₀ H ₁₆ (v. supra)	Myristicol and ab-	Sobrerol C ₁₀ H ₁₆ (OH) ₂	711) Sobrerone (pinol)		
Dipentene C ₁₀ H ₁₆ (v. supra)	sinthol (v. infra) Terpineol C ₁₀ H ₁ ,OH (v. infra) Cineol C ₁₀ H ₁ ,OH (ii.	(v. infra) Terpin C ₁₀ H _{1s} (OH) ₂ (v. infra)	C ₁₀ H ₁₀ O (v. infra)		
Fenchene C ₁₀ H ₁₆ (v. supra)	187). Syn. Eucalyptol, cajcputol Fencheol C ₁₀ H ₁₇ OH (v. infra)	- -	Fenchone C ₁₀ H ₁₆ O		
Camphene C ₁₀ H ₁₀ (v. supra)	Borneol $C_{10}H_{17}OH$ (i. $5\frac{4}{2}$ 2) $C_{10}H_{17}OH$	Camphene glycol C ₁₀ H ₁₆ (OH) ₂ (v.infra)	Camphor C ₁₀ H ₁₆ O (i. 669) Pulegone C ₁₀ H ₁₆ O (v.		
	(ii. 609) Linalool C ₁₀ H ₁₇ OH (iii. 146)	-	infra) Puleone C ₁₀ H ₁₆ O (v. infra)		
- ,	` _	-	Tanacetone or Thu- jone C ₁₀ H ₁₀ O (v. infra)		
Menthene C ₁₀ H ₁₈ (iii.	Menthol C ₁₀ H ₁₉ OH iii. 203)	-	Menthone C ₁₀ H ₁₀ O		
Dihydrocamphene C ₁₀ H ₁₈ (v. Decinene, ii. 867)	_	-	(iii. 204) —		
Tetrahydrocamphene C ₁₀ H ₂₀ (v. Decylene, ii. 869, et infra)	- .				

Cymene $C_{10}H_{14}$ (176°); ii. 361.

Dipentene $C_{10}H_{16}$ (176°); v. supra.

Fenchene $C_{10}H_{16}$ (160°); v. supra.

Camphene $C_{10}H_{16}$ (160°); v. supra.

Menthene $C_{10}H_{16}$ (160°); v. supra.

Menthene $C_{10}H_{16}$ (160°); v. supra.

Dihydrocamphene $C_{10}H_{16}$ v. Decinene, ii. 367.

The liquid produced, together with the solid monohydrochloride, by passing hydrogen chloride into pinene, yields when treated with sodium a mixture from which a liquid hydrogenhom C. H mixture from which a liquid hydrocarbon C10H18 (148°-149°), having a smell of oranges, may be separated by fractionation, &c. (Bouveault, C. R.

116, 1067). Tetrahydrocamphene C₁₀H₂₀ (DECYLENE, ii. 367). A liquid obtained by the action of hydrogen iodide and phosphorus upon oil of turpentine (Berthelot) and another (160°) by action of phosphonium iodide on turpentine (Baeyer) have this composition. The same formula is ascribed by Armstrong (B. 12, 1758) to a liquid (160°-170°) obtained by the action of iodine upon oil of turpentine and upon camphor, also by the action of sulphuric acid upon turpentine. these products are insoluble in strong sulphuric acid, and resemble the paraffins in chemical

characters.

Carveol C₁₀H₁₅.OH (219°); i. 711.

Terpineol C₁₀H₁.OH. [35°]. (215°.218°).

Wiggers, A. 33, 358; 57, 247; List, A. 67, 362;
Tilden, C. J. 33, 247, and 35, 286; Wallach, B.
18, 618, Ref.; Kannonikoff a. Flawitzky, J. pr. [2] 32, 497; Bouchardat a. Voiry, C. R. 104, 996. Dextro- and lavo-terpineol are obtained by the action of alcoholic sulphuric acid upon d- and *l*-pinene respectively, or inactive by distilling terpin with very dilute sulphuric or hydrochloric acid. Terpineol as thus obtained is a viscous liquid, having an odour of white lilac. By fractional distillation under reduced pressure a portion is obtained (130°-135° at 40 m.m.), which may be crystallised by cooling to -50°, or by the introduction of a crystal of the same. These crystals melt at 30°-32°, and boil undecomposed at 218° (Bouchardat a. Voiry, C. R. 104, 996). Terpincol treated with sodium evolves hydrogen, but in consequence of its viscosity the action soon ceases. Contact with dilute acids converts terpineol into terpin hydrate. Hydrogen chloride and iodide react to form C10H18Cl2 [50°] and C₁₀H₁₈L₂ [77°] respectively. Potassium hydrogen sulphate at 200° produces dipentene. Terpineol unites with two atoms of bromine, but excess of bromine gives rise to dipentene tetrabromide. With phenyl cyanate it yields phenyl-terpinyl-urethane C₆H₃.NH.CO.OC₁₀H₁, [110°]. These and other reactions have been repeated by Wallach, using crystallised terpineol (A. 275, 103). Terpineol oxidised by permanganate yields a substance C₁₀H₂₀O₃ [121°-122°], which probably has the constitution of an oxyterpin C₁₆H₁₇(OH)₂. Further oxidised by means of chromic acid this yields a crystalline compound

C₁₆H₁₀O₂ [62°-63°] (Wallach, A. 275, 145). Cincol C₁₆H₁₀O (176°); ii. 187. Cincol appears to contain no hydroxyl, since it is not acted upon by metallic sedium nor by benzoyl chloride at 120°. It is also unaffected by hydroxylamine and by phenylhydrazine. Hence it appears to be neither an alcofiol nor a ketone. Its relation to terpineol (infra) is shown by the fact that when heated with

alcohol and sulphuric acid cineol is converted into terpinene and terpinolene; also that terpineol, and therefore also terpin, are partly converted into cineol by prolonged heating with phosphoric acid. Cineol oxidised by permanganate of potassium yields the potassium salts of carbonic, oxalic, and cineolic acids, with a small quantity of acetic acid. Cineol yields 45 p.c. of its weight of cincolic acid. This compound forms well-defined anhydrous crystals, which dissolve in 70 pts. of water at 15°, and in 15 pts. at 100°. They melt with decomposition at 196°-197°.

Calcium cineolate C₁₀H₁₁CaO₃.4H₂O is soluble in cold water, but is completely precipitated by boiling the aqueous solution. Silver cincolate C10H11Ag2O2.H2O is soluble in both water and alcohol, but cannot be crystallised. Ethyl cineolate C.H. (C.H.), O. obtained by passing hydrogen chloride gas into an alcoholic solution of the acid. is a colourless liquid (155° under 11-12 mm.). By dry distillation cineolic acid yields cineolic anhydride, water, carbon dioxide, and a liquid which appears to consist of a monobasic acid (A. 246, 265).

(A. 240, 265).

Fencheol C₁₆H₁,.(OH). Fenchyl alcohol
[40°-41°]. (201°). (Wallach, A. 293, 143; 272,
99-125). S.G. 22 933 (W.). [a]_D = ± 10·36 (W.). Dextro- and lavo-fenchyl alcohols are obtained by the reduction with sodium and alcohol of lavo- and dextro-fenchones respectively, Concentrated HNO₂ oxidises Henchyl alcohol to defenchone. PCl₃ gives rise to fenchyl chloride C₁₀H₁₁Cl (84°-86° at 14 mm.).

Borneol C₁₀H₁₂OH, ii. 522.

Geraniol C₁₀H₁₂OH, iii. 146. Linalool is said

to be convertible into the isomeric geraniol by treatment with acetic anhydride, and saponifying the resulting ester with alcoholic potash (Bouchardat, C. R. 116, 1253).

Menthol C₁₀II_{1p}(OII), iii. 203. Terpin C₁₀H₁₈(OH)₂ [104°-105°]. (258°) (Wiggers, A. 33, 358; 57, 247; Tilden, C. J. 33, Ter-247; 35, 286; Wallach, A. 230, 225-272). pin is best known in the form of its hydrate $C_{10}H_{20}O_2$. H_2O [116-117°], a beautifully crystalline compound which on heating to 100° loses water and leaves terpin as a vitreous mass. Terpin hydrate is readily obtained by shaking turpentine oil with alcohol acidified with sulphuric or nitric acid (Flawitzky, B. 12, 1022; Tilden, C. J. 33, 247; 35, 286), and leaving the liquid to evaporate. It is an optically inactive, saturated compound, slightly soluble in boiling water, soluble in alcohol and crystallising in rhombic prisms (Rammelsberg, P. 63, 570; Maskelyne, P. M. 1879). It possesses the characters of a glycol and with hydrogen chloride yields dipentene dihydrochloride [50°]. Boiled with water containing a mere trace of mineral acid, terpin dissolves with production of ter-pineol and water.

Camphene glycol O₁₀H_{1a}(OH)₂ [192°] (G. Wagner, B. 23, 2311).

Formation .- By the oxidation of camphene benzene solution with a 1 p.c. solution of KMnO, (l.c.).

Properties.—Colourless prismatic needles (from benzene) very readily soluble in ether, alcohol, CS, and chloroform. Exhibits the

same phenomenon as camphor when thrown on water. Sublimes when heated above 100°. Melts when warmed with water,, but only dissolves in it with difficulty. Heated with acetic anhydride in a closed tube at 120°, the greater part loses water, only a small portion being converted into the acetic erter. Treatment with difute HCl results in the loss of 1 mol. of H,O, giving rise to a solid body, C10H10O, isomeric with camphor, which reduces ammoniacal AgNO, and reacts with hydroxylamine.

Carvol C₁₀H₁₀O (228°), v. i. 711.

Fenchone C₁₀H₁₀O. [5°-6°]. (192°-193°)
(Wallach, A. 263, 130; 272, 102). S.G. 12 9465
(W.). R_A 44·23 (W.). [a]₁ + 71·70 and -66·94.

Occurrence.—Dextro-fenchone is present in

fennel oil, the fraction boiling between 190° and 195° consisting almost exclusively of the ketone, together with traces of anethol; derived from Thuja oil, fenchone possesses levorotatory optical properties. D- and l-fenchone form a series of derivatives which bear to one another a relation similar to that subsisting between the two tartaric acids, and the analogy extends to the formation of racemic modifications when equal proportions of the two classes of derivatives are mixed together.

Preparation.—The fraction of fennel oil boiling between 190° and 195° is treated with concentrated HNO₃, the ketone remaining unattacked. After being freed from acid and distilled in a current of steam, the dry oil is cooled,

and the fenchone crystallises out.

Reactions .- With bromine in the cold, an addition compound is formed, substitution taking place if the mixture becomes heated. P₂O₃, P₂S₃, and PCl₃ have the same action upon fenchone as upon camphor. Fenchone is dissolved by cold concentrated HCl, being thrown out of solution on warming. HNO, has but little action in the cold, but in a scaled tube at 120° HCN is formed (A. 263, 134). KMnO, oxidises fenchone to a mixture of oxalic, acetic, and dimethyl-malonic acids. D- and l-fenchone yield d- and l-fenchyl alcohols respectively on reduction with Na and alcohol (v. Fencheol). On heating d- and t-tenchone with ammonium formate, t- and d-fenchylamines respectively are formed. Fenchone does not react with phenyl-hydrazine or with alkaline sulphites, but both varieties form oxims [161°] with hydroxylamine.

d-Fenchon-oxim C₁₀H₁₈NOH [161°] (240°) loses water on treatment with dilute H.SO., an unsaturated dextrorotatory nitrile (218°) being formed.

l-Fenchon-oxim C₁₀H₁₈NOH [161°] behaves in a similar manner on treatment with dilute H₂SO₄. The resulting nitrile yields with potash a laworotatory α-isoxim C_νH₁₂.CONH₂ [114°-115°] which is readily converted by dilute H₂SO₄ into the \$-isoxim [136° 137°].

into the B-180xim [130*—137*].

Camphor C₁₀H₁₀O (0.669) (iii. 204).

Menthone C₁₀H₁₀O (206°) (iii. 204).

Palegone C₁₀H₁₀O (130°—131° under 60 mm.).

(Beckmann a. Pleissner, A. 262, 1; Wallach, A. 272, 122; Semmler, B. 25, 3515). S.G. 22. 9323 (B. a. P.); R₄ 45·55 (B. a. P.); [a]_D 22·89 (B. a. P.). Pulegone is the chief constituent of Spanish oil of pennyroyal (Mentha pulcgium). It is a dextrorotatory colourless liquid, having an odour of peppermint, and rapidly becoming yellow on exposure to the air.

Reactions. - With HBr it combines forming a lævorotatory ([a]_p = -33·8) addition compound C₁₀H₁₆O.HBr [40·5°]. When heated with ammonium formate, Wallach (A. 272, 123) failed to obtain a base isomeric with fenchylamine and thujonamine, a mixture of bases being formed. Slow exidation with KMnO, gives rise to acetone and \$\beta\$-methyl-adipic acid [84.5°]. Rapid oxidation with the same reagent yields a γ-valero-lacton-γ-acetic acid (Semmler, B. 25, 3516). Pulegone combines with hydroxylamine to form pulegonoxim $C_{10}H_{18}NO_2$ [157°]. The oxim contains one molecule of H_2O more than camphoroxim. It is levorotatory ([a]_D -83.4) and forms a hydrochloride [117-118°], a benzoyl ester [137°-138°], and an acetyl ester [149°]. On heating its hydriodide pulegonamine C10H18O.NH is formed.

Pulegone hydrobromide C10H10O.HBr [40.5°] is levorotatory; it forms an oxim [38°] which becomes converted on standing into normal pulegonoxim [157°]. Pulegone hydrobromide, on treatment with moist silver or lead oxide, loses HBr, pulegone being regenerated. Distillation with zinc dust gives rise to an oil which resembles menthone in every respect but the melting-point of its oxim (85° instead of 59°).

Constitution. - From the results of oxidation

experiments carried on under various conditions with KMnO, Semmler (B. 25, 3519) attributes to pulegone the constitution:

Puleone is the name given to a compound isomeric with camphor, obtained by Barbier (B. 25, 110c), from pennyroyal oil, described as boiling at 222°-223°, and possessing the following physical properties: S.G. 9482; 23 9293; [a]₀+29·15. Its oxim C₁₀H₁₀.NOH is an oil $[\alpha]_0 + 29.15$. Its oxim $C_{10}H_{10}$.NOH is an oil (170° under 48 mm.) yielding a liquid anhydride C₁₀H₁₅N on treatment with dilute H₂SO₁. Chromic acid mixture oxidises it to carbonic. acetic.

and propyl-succinic [89°-91°] acids.

Tanacetone C₁₀H₁₀O (195°-196°; 84.5 at 13 mm.), identical with the thujone of Wallach (A. 272, 109; Bruylants, B. 11, 450; Semmler, B. 25, 3343, 3519; Wallach, l.c.). S.G. 26 9126 (S.). R. 44.54 (S.).

(S.). R. 44-54 (S.). Tanacetone occurs in tansy, sage, wormwood, possesses an optical rotatory power amounting to +38° 30' in a 2-dcm. column.

Reactions .- Sodium in alcoholic solution reduces it to tanacetyl alcohol (92.5° at 13 mm.). With alkaline hypobromite it yields bromoform and tanacetogen-dicarboxylic acid (113.5° at 15 mm.). Oxidised with KMnO, it yields tanaceto-carboxylic acid, which exists in two modifications, the a and & thujal etonic acids of Wallach (l.c.), [75°-76°] and [78°-79°] respectively. Heated with ammonium formate, it gives the acetylamine (198°-199°), the same body being formed when tanacetoxim (see below) is reduced with sodium and alcohol. The hydrochloride of this base on dry distillation yields tanacetene (172°-175°), a hydrocarbon of the formula $C_{10}H_{10}$, identical with Wallach's thujene. Tanacetone reacts with hydroxylamine to form tanacetoxim $C_{10}H_{10}$. NOH [51·5°] (135°-186° at 22 mm.), which yields tanacetylamine on reduction, while treatment with dilute alcoholic H_{10} SO, converts it into a cymidine (Pr.NH₂:Me:1.3:4), which gives carvacterol with nitrous acid. Tanacetophorone $C_{10}H_{10}$ O (89°-90° at 13 mm.). R_{10} SO. When tanacetogen-dicarboxylic acid (produced by the action of NaBrO upon tanaceto-carboxylic acid, is heated with soda-lime, tanacetophorone is formed. It has ketonic properties, and combines with hydroxylamine.

Constitution.—Semmler (B. 25, 3519) suggests for tanacetone and tanacetogen-dicarboxylic acid the formulæ

Sobrerone C₁₈H₁₈O. Pinol. (183°-184°) (Wallach, A. 253, 254; Armstrong, C. J. Proc. 1890, 100). S.G. $\frac{29}{5}$ 953 (W.); $\mu_{\rm b}$ 1469 (W.). Sobrerone is obtained from the mother-liquors accumulated in the preparation of pinene nitrosochloride; also by boiling sobrerol with dilute H₂SO₄ (Armstrong, Le.).

Reactions.—It combines readily with Br to form a dibromide [94], from which, on treatment with alcoholic potash, sobrerone is regenerated. Sobrerone and its dibromide yield terebie acid [175°-176°] on oxidation with KMnO, HNO, produces the same result. It forms a nitroso-chloride [103°] which, by the action of bases, is readily converted into nitrolamines, egsobrerone-nitrol-pierdidne [164°] and sobrerone-nitrol-benzyl-amine [133'-131°]. The dibromide C₁₈H₁₀O.Br₂ [91°] (143°-144° at 1 mm.) yields on treatment with alcoholic potash, in addition to sobrerone, its glycol-ether C₁₀H₁₀O(OC₂H₃)₂ [52°-53°]. Sobrerone-glycol-diacetate is easily obtained by heating the dibromide to 150° with lead acetate in glacial acetic acid solution. When heated at 100° for three hours with formic acid, sobrerone dibromide is converted into pinene.

Constitution.—Its behaviour towards bromine and nitrosyl chloride and its molecular refraction indicate the existence of one ethylene linking, while its indifference towards acid chlorides, hydroxylamine, phenylhydrazine and 11. Srender it probable that the O- atom is united to two different C- atoms. From these facts, and from its behaviour on oxidation, Wallach (.1. 253, 259) assumes the constitution

Sobrerol C₁₀H₁₀O₂. [150°] (Sobrero, C. R. S. 66; Armstrong, C. J. Proc. 1890, 100; C. J. 59, 315). Sobrerol is obtained by oxidising French and American turpentines in

sunlight. It occurs in two optically active forms, both melting at 150°, and on allowing a mixed solution to crystallise inactive sobrerol. [181°] separates out. When boiled with dilute H₂SO, it loses 1 mol. of H₂O, sobrerone—identical with Wallach's pinol—being formed.

Eucalyptol C₁₀II₁₀O (176°) (Jahns, B. 17, 2941; Bouchardat a. Voiry, C. R. 106, 663). Identical with cincol, spicol, cajeputol, and terpan (B. a. V.).

Myristicol C₁₀H₁₀O (224°) (Wright, B. 6, 1320; Gladstone, C. J. 23, 147; 25, 1; Brühl, B. 21, 471). S.G. ¹² 9446 (G.). R_s 46-42 (G.). Myristicol is a dextrorotatory alcohol, obtained from the ethereal oil of nutneg, Myristica aromatica. It yields a chloride with PCl_s and beconverted into cymene by the action of ZnOl₂.

Absinthol C_{1a}H_{1.}O (217°) (Beilstein a. Kupffer, B. 6, 1183; Wright, Lc. 1320; Gladstone, C. J. 45, 241; Brühl, B. 21, 471). S.G. 33 9128 (G.). R_A 44·62 (G.). Absinthol is obtained from oil of wormwood, and is dextrorotatory. It is converted by ZnCl₂ and P₂S₃ into cymone. In what form the oxygen exists is at present unknown.

Constitution of the terpenes.

I. Pinene. The following facts must be taken into consideration:

1. Dry pinene combines with one molecule of hydrogen chloride to form a saturated compound, from which hydrogen chloride is with-drawn with difficulty, the resulting hydrocarbon being a solid camphene. Moist pinene combines with 21ICI, yielding dipentene-dihydrocalboride. This also is saturated. The formation of both these compounds is undoubtedly attended by isomeric change, inasmuch as pinene cannot be recovered from either of them; but on removal of the elements of hydrogen chloride a new hydrocarbon results.

2. Pinene seems to combine with two atoms or with four atoms of bromine, according to the method of operating. By adding bromine to a cooled solution of pinene in carbon tetrachloride, Wallach has obtained a crystalline dibromide C₁₀H₁₈Br₂ [170°]. The yield is, however, very small, about 7 p.c. of the hydrocarbon employed (A, 264, 1). By shaking up a solution of pinene in chloroform, with an excess of sodium hypobromite, acidified with hydrochloric acid, so as to liberate the bromine, and immediately afterwards determining the unabsorbed excess of bromine, Telden obtained results which pointed to the union of the terpene with four atoms of bromine. The combination is, however, very unstable, and hydrogen bromide is soon evolved (C. J. 53, 882). Schtschukaroff finds that a chloroform solution of pinene takes up, in the dark, four atoms of bromine, but the bromide formed is unstable, and quickly gives off hydrogen bromide, thus C10H1.Br. HBr + C10H15Br. (B. 23, 432, Ref.; J. pr. 47, 191-6).
3. Pinene combines with NOCl to form a

3. Pinene combines with NOCl to form a saturated compound which is not an oxim but a nitroso compound, and yields up the NO.Cl by the action of aniline, with liberation of an optically inactive pinene.

4. By addition of two atoms of bromine to pinene, and subsequently heating the product alone, or, better, with aniline (Oppenheim, B. 5.

629), cymene is formed.

5. In contact with slightly diluted mineral acids, or when heated above its boiling-point, pinene is gradually converted into an optically inactive mixture of dipentene with terpinene, terpinolene, and polymerised terpene ('colo-

phene').
6. When heated to a temperature short of visible redness, pinene yields a considerable quantity of isoprene C_aH_s, together with a notable amount of meta-xylene.

7. Pinene submitted to oxidation yields about 1 p.c. of its weight of p-toluic or terephthalic acid. This is perhaps due to the presence of a little cymene. It must, however, be remembered that the oxidising agent usually employed is either nitric acid or acidified chromic liquor, and hence that the pinene is first changed into dipentene or one of the other hydrocarbons referred to above (5). When nitric acid is used oxalic acid is the most abundant product, accom-

Beckurts, B. 18, 826). By treatment with chromate and sulphuric acid pinene yields much acetic acid, together with some terebic acid and

8. Natural pinene rotates the plane of polarisation to the right or to the left. therefore must be supposed to contain an asymmetric atom of carbon.

In order to epitomise these facts many formula have been proposed. The most important fall under two classes—namely, those in which pinene is represented as a dihydrocymene, and those in which a cross- or para-linkage is assumed.

Of the former class, the first example is the formula given many years ago by Oppenheim (B. 5, 98)-

This kind of formula is now attributed with greater probability to limonene, and it must be remarked that of the possible formulæ of this type there are only four which contain an asymmetric carbon atom and iso-propyl.

It has been shown that cymene, with waich pinene is closely connected, contains iso- and not normal propyl (Widman, B. 24, 439). Hence pinene and its isomerides are believed also to be isopropyl compounds.

Formula containing cross- or para- linkages have been proposed as follows:-

II. Limonene.—1. Dry limonene combines with one molecule of hydrogen chloride, but unlike the hydrochloride derived from pinene the resulting compound is optically active and is not saturated, as it combines with halogens. with nitrosyl chloride, and, in the presence of moisture, with a second molecule of hydrogen chloride (Wallach, A. 270, 188). Limonene in the presence of water or alcohol readily yields dipentene dihydrochloride [50°], identical with the product formed from pinene. The dihydrochloride is optically inactive.

2. Limonene unites with four atoms of bromine, forming a crystalline tetrabromide.

3. Limonene unites with one molecule of nitrosyl chloride. The product, of which two (stereo?) isomerides occur, gives the reactions of an oxim.

4. Limonene readily yields abundance of cymene identical with that which is obtained from pinene (Oppenheim, B. 5, 628).

5. Limonene is polymerised by heat much less readily than pinene, and is not convertible into camphene.

6. Limonene vapour at a low red heat yields isoprene in the same way as pinene.

7. Limonene oxidised by nitric acid or by chromate yields oxalic, acetic, terebio or terpenylic acids according to circumstances, usually without any trace of toluic or terephthalic acid.

8. Limonene is dextro- of lavo-rotatory.

mixture of equal volumes of the active hydrocarbons constitutes dipentene, which, on account of its peculiarities, quite different from those of its components, was long regarded as a distinct hydrocarbon.

The formula which agrees best with the characters of limonene is either I. or II. given

above (see Pinene).

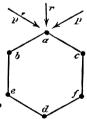
In both of these there is an asymmetric carbon atom, and as the mono-hydrochloride is optically active while the dihydrochloride is inactive, these compounds will probably be represented by the following formula:-

Limonene nitrosochloride deprived of the elements of hydrogen chloride yields a compound which has been identified with carvoxim. If the following formule be assumed for carvacrol and carvol, the interrelation of these compounds is obvious.

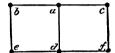
The corresponding formula for limonene should be No. II., but if that correctly represents the constitution of the hydrocarbon, the production of the nitrosochloride, or of the oxim from it, must be attended by isomeric change involving a re-distribution of the hydrogen and of the double linkages. Thus:

The oxim is optically active.

The very ready conversion of pinene into dipentene (= limonene) is a point of considerable importance, and it appears probable that the products formed by the action of heat and acid oxidising agents are in reality derived, not directly from pinene, but from the isomeric hydrocarbon into which it is first converted. The splitting up of pinene by heat into isoprone has been regarded (Wallach, A. 239, 48; Collie, B. 25, 1111) as supporting the formulæ already given VI. and VII., in which a para-or cross linkage is adopted. But remembering that isoprene is converted by polymerisation, not back again into pinene, but into dipentene, this evidence is of little importance. On the other hand, the difficulties involved in the assumption of a cross link in a cycloid of six carbon atoms are very considerable. In any closed ring of carbon atoms, the stability of the ring is easily accounted for upon simple mechanical principles. For if we consider six carbon atoms situated at the angles of a regular hexagon, and each attracted to its two neighbours on either side, whatever be the forces of attraction between them the resultant of those forces will have the effect of urging each carbon atom toward the centre of the figure. Thus, if the carbon atom a is attracted towards the carbon atom b with a force represented by p, and towards c with a force represented by p', in the figure, the resultant of these two pressures will be r, which acts towards the centre; and so with each of the five other atoms.



This conception is, of course, independent of any hypothesis concerning the fourth unit of valency, and the formula has no reference to the well-known 'centric' formula. The modern hypothesis according to which the carbon atom is supposed to be situated at the centre of a regular tetrahedron while the radicles with which it is united are placed at the angles of the same supplies no distinction between the force and the direction of the unit of affinity. The difference of specific volume observed between carbon compounds of the aromatic and fatty series seems to indicate that carbon atoms in the former are more closely united together. but it appears that no compounds are known in which the specific volume of carbon differs very greatly from its normal value. Hence it appears probable that the carbon atom, in uniting with other atoms, preserves a nearly constant distance from them, and in the figure above to suppose that a is combined with d as firmly as with b or c requires the assumption that a carbon atom is capable of acting through a distance twice as great in one case as in another. If this is possible, and we imagine the force of attraction between a and d to be as great as between a and b or c, then, unless c acts upon e and b acts upon f at the same time with the same force the figure will be changed from the hexagon to a double square.



A compound of this kind would be incapable of many of the changes which are characteristic of pinene, and a second cross linkage between c and e, or between b and f, would be impossible. Hence the following formulæ, which are attributed by Wallach to nitrosopinene and pinylamine cannot be accepted even if a single diagonal is allowed in the formula of pinene.

Formulæ III. and IV. now remain to be considered. So far as the writer is aware, formulæ of this type have not been proposed for any of the terpenes. Nevertheless there is much to be said in favour of an expression of this kind for a compound so unstable as pinene, which appears to be incapable of withstanding the action of heat or of contact with any reagent without isomeric change. For example, the conversion of pinene into dipentene, terp nene, and terpinolene may be explained with the minimum amount of hypothesis by the following formulæ, in which the tendency towards the conversion of an unsymmetrical into a symmetrical molecule is clearly shown. The question as to the relative positions of the methyl and propyl groups is left open.

The conversion of pinene into dipentene through the dihydrochloride is readily shown.

Such a formula for pinene also explains the extreme instability of its tetrabromide.

III. CAMPHENE. Camphene behaves towards all reagents-such as bromine and nitrosyl chloride—as a saturated compound, but with hydrogen chloride it unites, forming a compound which in external appearance resembles pinene monochloride, but differs from that compound by its instability. When camphene is oxidised by chromic acid it yields camphor, but when treated with permanganate a glycol is formed. This compound crystallises in odourless small monoclinic prisms, which sublime at temperatures above 100° (192° ca.). Its most characteristic property is seen in its reaction with dilute acids, whereby water is separated and a compound isomeric with camphor formed. This reaction appears to indicate the existence of one ethylenic bond in camphene (G. Wagner. B. 23, 2307). Brühl (B. 25, 160) also finds, as the result of his latest determinations of the molecular refraction and dispersion of camphene, that this hydrocarbon contains one ethylenic linkage. Wallach (B. 24, 1555) upon other grounds appears to hold the same view. phene is, however, so closely connected with camphor that the constitution of the latter compound when settled may serve as a guide in determining the constitution of the former. The formula for camphor given by Kekulé (B. 6, 931) was based upon the supposed intimacy of its relation to cymene and carvacrol.

There can be no serious doubt of its character as a ketone, inasmuch as it yields an oxim, though it gives no compound with NaHSO₃; but the action of dehydrating agents upon camphor is very complicated, and there can be no doubt that the production of cymene is attended by isomeric change. Armstrong a. Kipping (C. J., Jan. 1893) have shown that among the products of the action of strong sulphuric acid upon camphor

there is a considerable quantity of acetylorthoxylene (O.H.Me.Me.Ac, Me:Me:Ac = 1:2:4). From observation of its molecular refraction Brühl (B. 21, 467) suggests a formula containing a para- linkage, either

The former of these two formulæ has also been used by Wallach (B. 24, 1555). These expressions are equivalent to representing camphor as a derivative of tetramethylene.

A formula of a different character has been suggested by Armstrong a. Miller (B. 16, 2260) (v. vol. i. p. 670), and another of somewhat similar type by Collie (B. 25, 1114):

Camphor by oxidation with nitric acid yields camphoric acid in large quantity, and as the characteristic and chief product. Camphoric acid is therefore probably derived from camphor by an operation of a simple kind without con-stitutional disturbance. The following formula proposed by Collie (B. 25, 1116) has been shown to possess a very high degree of probability (Walker, C. J., April 1893):

This formula sufficiently accounts for the chief facts concerning camphoric acid, viz. that it is a saturated dibasic acid, which readily yields the anhydride by heating; that it is optically active, and when treated with hydrogen iodide yields tetrahydro- and hexahydro-

m-xylene.

From this formula are deducible the following formulæ for camphor and camphene:

This formula for camphene explains pretty well all its relations, except its derivation from pinene, if either of the formulæ containing a para-linkage be adopted. The chief objections to such formule are stated above.

J. Bredt (B. 26, 3047) has recently proposed formulæ for cymphene, camphor, and camphoric acid, which are derived from a pentamethylene ring.

Synthesis of Terpenes.

Von Baeyer in a series of papers has shown that various dihydro-derivatives of benzene and its homologues may be synthetically produced. Starting with succino-succinic ester, this compound, by treatment with dilute sulphuric acid. yields diketo-hexamethylene, and this, by reduction with sodium-amalgam, gives the corresponding glycol. This glycol possesses the characters of a sugar, and has been named chinite or quinite (B. 25, 1037). It occurs in two isomeric forms, which by treatmens with hydrogen bromide yield two dibromohexamethylenes. Both of these by heating with quinoline yield dihydrobenzene (B. 25, 1840), a liquid which has nearly the same boiling-point as benzene, but combines with HBr and with Br. It also reduces permanganate. By a corresponding series of processes dihydro-p-xylene was obtained from dimethylsuccino-succinic ester (B. 25, 2122). Dihydrop-xylene (134° circa) smells of turpentine, unites with hydrogen bromide, but forms no crystallisable nitrosite.

In order to produce a dihydrocyruene it is necessary to start from the methyl-propyl com-This compound of succino-succinic ester. pound was obtained by heating the sodium compound of the monopropyl ether with methyl iodide (B. 26, 233). Methyl-isopropyl-dihydrobenzene boils at about 174. It smells like tur-pentine and resinifies in the air. It decolourises permanganate and unites with bromine, forming an uncrystallisable bromide. Although closely resembling a terpene, however, it is obvious that this hydrocarbon is not identical with any natural terpone known, containing, as it does, no asymmetric carbon. It may be identical with terpinene. The relations of the paradibromohexamethylene, or of its alkyl derivatives, to the corresponding hydrocarbon is shown in the following formulæ (B. 25, 1840, 2122):

TERPENYLIC ACID C,H,2O,. [72°] (Fittig); [58°] (Wallach). Formed, together with terebic acid, by oxidising oil of turpentine and other terpenes with chromic acid mixture (Hempel, B. 8, 357; A. 180, 77; Fittig a. Kraft, A. 208, 71). Formed also by oxidising pinol hydrate [131^o] with KMnO₄ (Wallach, A. 259, 318). Monoclinic prisms (containing aq).

Reactions. - 1. Yields acetic acid and CO₂ on

further exidation by chromic acid.-2. On dry distillation it yields teracrylic acid (218°), a very little oxy-heptoic lactone (212°) and other bodies (Amthor, J. pr. [2] 42, 388).—3. Reduced by HI and P to \$\beta\$-isopropyl-glutaric acid (Schryver, C. J. 63, 1344).

Salts.—BaA'₂. Amorphous powder, v. e. sol. water. Converted by boiling with baryta into barium diaterpenylate Ba(C₈H₁₃O₈)₂ aq. which separates in needles on heating the cold saturated solution and is v. sl. sol. water. On adding an acid the liberated disterpenylic acid at once changes to its lactone, terpenylic acid. -CuA'₄ xa₁...-AgA'. Crystalline mass. Silver diaterpenylate AgC₈H₁₃O₄ is ppd. by adding AgNO₄ to a solution of barium diaterpenylate.

Ethyl ether EtA'. [38°]. (305° i.V.).

Monoclinic crystals; a:b:c=1.051:1:381; $\beta=50^{\circ}$ 58'. V. sol. alcohol and ether, sl. sol. cold water. Sodium converts it into (α)- and

cold water. Sodium converts it into (α)- and (β)-diterpodilactone $O_{1,1}^{-1}O_{2,.}^{-1}$ (154°).

(α)-Diterpodilactone $O_{1,1}^{-1}O_{2,.}^{-1}$ [154°].

Formed as above (Fittig, A. 256, £13). Long, needles (from water), m. sol. alcohol. Yields CaO_{1,1}H_{2,1}O, 6aq, Ag₂O_{1,1}H_{2,1}O, and BaC_{1,1}H_{2,1}O, 6aq erystallising in monoclinic prisms; a:b:c=935:1:595; β=65°54', which, when decomposed by HCl and immediately extracted with ether wields (a)-diterpolactonic acid C. H...O. [160°]. yields (a)-diterpolactonic acid $C_{15}H_{24}O_8$ [160°]. This acid decomposes above 160° into water and its lactone.

(β)-Diterpodilactone C₁₅H₂₂O₃. [135°]. A product of the action of Na on terpenylic ether (Fittig, A. 256, 122). Needles, in. sol. alcohol. Converted by baryta into (β)-diterpolactonic acid [187°] and (β)-diterpoxylic acid C₁₈H₂₀O₂. (8)-diterpolactonic acid forms trimetric crystals; a:b:c = .732:1: 259 and is re-converted by heat into the lactone. (3)-Diterpoxylic acid forms the salts BaA" 33aq, CaA", and Ag.A".

(a)-Diterpylic acid C, al. O, (a)-Diterpodilactone carboxylic acid. [2169]. An interpolacid card.

mediate product of the action of Na on terpenylic ether. Needles, m. sol. alcohol. Converted by boiling HClAq or by heating above 216° into

(a)-diterpodilactone.
TERPILENE v. TERPENES.

TERPILENOL C₁₀H₁₈O. [c. 32°]. (c. 130° at 50 mm.). S.G.c. 95. H.C. (inactive) 113,318; (active) 102,923 (Louguinine, C. R. 107, 1165). Got by saponification of the terpilene acetates C10H18HOAc or terpilene formates C10H18CH2O2 by alcoholic potash (Latont, A. Ch. [6] 15, 205). Crystals, insol. water, v. sol. oil of turpentine, alcohol, and ether. Boils with decomposition at 220°. Occurs in several forms varying in their action on polarised light.

Reactions.-1. HCl forms (1.0H1.2HCl [48°], Reactions.—I. Hot forms \(\text{L}_0,\text{H}_1\) \(\text{2}\) Hold [48], which is inactive even if the terpilenol were active.—2. Alcohol and HNO, give \(\text{C}_1\text{H}_1\text{O}_3\) \((\text{L}_1\text{O}_4\) \((\text{L}_1\text{O}_4\) \((\text{L}_1\text{L}_1\text{O}_4\) at 100° forms the acetyl derivative or terpilene acetate.

C₁₀H_MOAc or .971. V.D. 6.6. derivative Acetys aerivative C_{0,6}H₁₆OAc or C_{0,6}H₁₆HOAc. (220°). S.G. 2 '971. V.D. 6·6. Obtained by heating terpilene with HOAc at 150°. Liquid (Bouchardat a. Lafont, C. R. 102, 1555).

Formyl derivative $C_{10}H_{17}O.CHO$. [a]_D = -69° 25'. S.G. 2 999. Formed from oil of turpentine and cold formic acid (Lafont, C, R.

106, 140). By heating with water at 100° 65 p.c. of the ether is saponified.

TERPIN v. TERPENES.

TERPINEOL v. TERPENES.

TERPYLONIC ACID C₉H₁₄O₈. [135°]. A product of the oxidation of turpentine by chromic acid mixture (Schryver, C. J. 63, 1328). Needles, v. e. sol. water, m. sol. ether. Differs from camphoronic acid in electrical conductivity.

TETANINE v. PTOMAÏNES.

TETRADECANAPHTHENE C14H20. TETRADECANAPHTHERE Co. 1. Cor.). S.G. 2 839. Occurs in petroleum from Baku (Markownikoff a. Ogloblin, J. R. 15, 339). Dihentul. [4:50]. n-TETRADECANE O₁, H₁₀. Diheptyl. [4:5°]. (253°). S.G. § '775; § '76s. Formed by heatmyristic acid with HI and P (Krafft, B. 15, 1700). Got also by the action of Na on n-heptyl iodide (Krafft, B. 19, 2223; Sorabji, C. J. 47,

Reference. - DI-BROMO-TETRADECANE.

TETRADECENOIC ACID C₁₄H₂₅O₂ i.e. C₆H₁₃.CH:C(C₅H₁₁).CO₂H. Amylhexylacrylic acid. Formed by the action of alcoholic potash on cenanthol (Perkin, B. 15, 2803; 16, 211). Liquid, boiling in vacuo at 275° to 280°.

TETRADECENOIC ALDEHYDE C, H20 i.e. CH₃(CH₂), CH:C(CHO)(CH₂), CH₃. (278°). S.G. 15° 849. Formed by the action of alcoholic potash or of ZnCl₂ on conanthol (Perkin, C. J. 43, 47). Oil, not solid at -20°. Forms crystalline C₁, H₁₀, ONa HSO₂. Yields hexoic and heptoic acids on oxidation

TETRADECENYL ALCOHOL (282°). S.G. 13 852. Formed by reducing the preceding aldehyde with sodium amalgam (Perkin, B. 15, 2808). It is also a product of the action of sodium-amalgam on a solution of cenanthol in HOAc (Perkin, C. J. 43, 68). Oil. May be reduced to C₁₁H₃₀O.

Acetyl derivative C₁H₂OAc. (285°-290°). S.G. 15 °868. Combines with Br (2 atoms).

TETRADECINENE $C_{14}H_{26}$ i.e. $CMeiC.C_{11}H_{22}$. $[6.5^{\circ}].$ $(134^{\circ}$ at 15 mm.). S.G. $\frac{6^{\circ}5}{4}$ ·8064; $\frac{15^{\circ}3}{4}$ 28000. Formed from tetradecylene bromide and alcoholic potash at 150° (Krafft, B. 17, 1372; 25,

TETRADECOIC ACID C₁₁H₂₀O₂ i.s. C₃H₁₁.CH(C₇H₁₈).CO₂H. (300²-310²). Got by the action of moist Ag₂O on the corresponding aldehyde (Perkin, C. J. 43, 74). Liquid, not solid at -10°.

Tetradecoic acid v. Myristic ACID. Reference. - OXYTETRADECOIC ACID.

TETRADECOIC ALDEHYDE 0,1H₂O i.e. C.H₁₁,CH(O,H₁₃).CHO. [30°]. (267°). S.G. ³⁶/₃₀° 827. A product of the action of Na on an ethereal solution of cananthol (Perkin, C. J. 43, 71). Tables, v. sol. alcohol. Reduces ammoniacal AgNO₃. Yields heptoic, hexoic, and acetic acids on oxidation.

Isomeride v. Myristic aldehyde.

n-TETRADECYL ALCOHOL C_{1,}H₁₀O. [88°]. (167° at 15 mm.). S.G. \(\frac{9}{2} \) *8153. Formed by reducing myristic aldehyde (Krafft, B. 16, 1720). Acetyl derivative C_{1,4}H₂₀OAc. [18°]. (176° at 15 mm.).

Tetradecyl alcohol C₃H₁₁.CH(C₇H₁₃).CH₂OH. (270°-275°). S.G. $\frac{15}{15}$ 8368. Formed by reducing the corresponding aldehyde or the alde-

hyde C, H20 (Perkin, B. 15, 2811; C. J. 43, 76). hyde C₁H₂₀U (Ferkin, B. 20, 2011) — Liquid, solidifying at -10°. Acetyl derivative C₁H₂₀OAc. S.G. 15 ·856. Oil, not solid at -10°. n-TETRADECYLENE C₁H₂₃ i.e. (c. 278°).

CH_:CH_C, H_B. [-12°]. (127° at 15 mm.) S.G. 2 '7852; \frac{1}{2}' '7745. Formed by distilling tetradecyl palmitate at 500 mm. (Krafit, B. 16, 3021). Liquid.

Bromide v. DI-BROMO-TETRADECANE. TETRADECYLENE GLYCOL v. Di-iso-BUTYL

TETRADECYL-MALONIC ACID C₁₇H₃₂O₃ i.e. C₁₁H₂₅CH(CO₂H)₂. [118°]. Formed by boiling its nitrile with alcoholic potash (Hell a. boiling its nitrile with alcoholic potash (Hell a. Jordanoff, B. 24, 988). White powder (from HOAc), insol. water, v. sl. sol. ether, sl. sol. cold alcohol. At 150°-170° it is split up into CO₂ and palmitic acid.—Ag,A": white pp.

Anide C₁₁H₂₀CH(CO₂H)(CONH₂). Pearly scales. At c. 140° it yields palmitic amide.

Nitrile C₁₁H₂₀CH(CO₂H).CN. [76°]. Formed by heating p-bromo-palmitic ether with alcoholic KCr. Silker plates (from HOAc)

alcoholic KCy. Silky plates (from HOAc). **n-TEFRA-ICOSANE** C₂H₃₀. [51°]. (213° at 15 mm.). S.G. 70° 763°, 748. Formed by the action of HI and P on C₁H₃₀. CCl., C₄H₁, made from the ketone obtained by distilling barium stearate with barium heptoate (Krafft, B. 15,

TETRA-ICOSOIC ACID C₂₃H₁₇.CO₂H. [72·5°]. Occurs in the soap got by heating carnaüba wax with aqueous NaOH (Stärcke, A. 223, 307). Crystalline powder, v. sol. hot alcohol.--PbA', [111°]. Sol. toluene and hot HOAc.

TETRAZOLE N\left\(\sigma_{\text{CH,NH}}^{N'=N}\). [155°]. Formed by treating amido-phenyl-tetrazole carboxylic acid with alkaline KMnO, followed by HNO, (Bladin, B. 25, 1412). Plates (from toluene). Reddens blue litmus.

TETRAZYL-HYDRAZINENH, NII.C NII.C [199°]. Formed from amido-tetrazotic acid by diazotisation and reduction by SnCl, (Thiele, A. 273, 155). Yellowish crystalline aggregates, v. sol. hot water. — B"2HCl. [176]. Acctoactic ether forms CMc.NIL > N.C. N. N. N. [215]

crystallising in needles.

TETRIC ACID Clu H₁₂O₄ i.e.

CH₂:C(OH).CMe CO CMe.C(OH):CH₂

CH₂:C(OC) CMe.C(OH):CH₂

CH₂:C(OC) CMe.C(OH):CH₂

(Nef. A. 266, 92) or CH₂CO.C(CO₂H):CH₂Acetyl-acrylic acid. [189°]. (262°). S. 1·5 at 14°. Electrical conductivity: Walden, B. 24, 2027. Got by heating CH₂CO.CMeBr.CO₂Et at 100°, but not by heating the isomeric acid CH₂Br.CO.CHMc.CO₂Et (Nef; cf. Pawloff, B. 16, 448). Formed by suggestive action of heminal 486). Formed by successive action of bromine and alcoholic potash on methyl-acetoacetic ether (Demarcay, C. R. 87, 351; 88, 126). Triclinic prisms (from water), v. sol. hot water, alcohol, and ether. Gives a violet-red colour with FeCl., PCl, gives rise to several compounds boiling between 169° and 185° which take up chlorine forming O₂H₂Cl⁴₂O (Pawloff, Bl. [2] 45, 181; C. R. 97, 99). Demarcay obtained oily C₄H₂Cl⁴₂O(?) which united with Cl and-Br forming O₄H₂Cl⁴₂O [48°] and C₄H₄Cl₂Br₂O [67°]. Resinified by dilute HClAq at 150°. Potash-Vor. IV. (Demarcay, C. R. 87, 351; 88, 126). Triclinic Vot. IV.

fusion gives formic and propionic acids. Distillation with lime forms methyl ethyl ketone.

Sodium-amalgam has no action.

Salts.—(NH₄)₂A". Crystals, v. sol. water.

—Na₂A" 6aq.—K₄A".—BaA" 3aq. Needle's, v. o.
sol. water.—BaA" 2aq.—Ba₂(OH)₂A". Sl. sol.
water.—CaA" 2aq.—MgA" 10aq.—ZnA" aq.—
CuA".—Ag₂A". i Needles, sl. sol. water.

Ethyl ether CO-CH₂>0 (?).

(180° at 70 mm.) (Moscheles, B. 21, 2607).

Amide C, H, NO... [212°]. Got by heating the acid with alcoholic NH.

TETROLE CYANURAMIDE v. Nitrile of

PYRROLE CARBOXYLIC ACID.

TETROLIC ACID C₄H₁O₂ i.e. CH₃·C:C.CO₂H. Butyrolic acid. Mol. w. 84. [77]. (208). Formed by boiling β -chloro-crotonic acid or β chloro-iso-crotonic acid with dilute potash (Geuther, Z. 1871, 215; Friedrich, A. 219, 343; Kahlbaum, B. 12, 2338). Formed also by the action of Na and CO2 on allylene chloride (Pinner, B, 14, 1081).

Preparation .- From acetoacetic ether and PCl, the product being freed from POCl, by heating to 115', mixed with water, and freed from chloro-crotonic acid by distillation with steam. The residue is treated with alcoholic potash (Fittig a. Clutterbuck, A. 268, 96; cf. Friedrich, A. 219, 322).

Properties .- Plates (from ligroin). May be sublimed. V. e. sol. water, alcohol, and ether. Not reduced by sodium-amalgam to erotonic acid (F. a. C.; cf. Aronstein, B. 22, 1181). Slightly volatile with steam.

Reactions. - 1. Br forms di-bromo-crotonic acid [120°], which is reduced by sodium-amalgam to tetrolic acid. Bromine also yields C, H, Br, O2. [97°] (Pinner). 2. HBr forms bromo-crotonic acid [91°] .- 3. Heated with conc. KOHAq it forms acetone. - 4. Fuming HClAq at 15° in a few weeks converts it into β -chloro-crotonic acid [94.5°] .- 5. Boiling with Na and McOH yields butyric acid (A.). - 6. Chlorine forms C, H, Cl, O2. 7. On heating with iodine in CHCl, in scaled tubes it yields di-iodo-erotonic acid (B. 26, 843) .-8. Split up at 211° into CO, and allylene. -9. KMnO, forms acetic acid.

Namo, torms accue acid.
Salts.—NaA'. Crystalline.—KA' (dried at 100°). Prisms (from alcohol). - NH,A'. -LiA' aq. —MgA', 3aq. -BaA', 3aq. —CaA', 3aq. Small needles.—ZnA', 2aq (Lagermark, J. R. 12, 290). —ZnA', 2aq (Fittig). Groups of prisms.—CdA', 4aq.—PbA', aq. S. 1-5 in 92 p.e. alcohol at 20°.

alcohol at 20°.

Chloride C.H. OCl. Fuming liquid, carbonised by heat. Quickly decomposed by water (Lagermark, Bl. [2] 35, 171).

DI-TETROLUREA v. CARBONYL-PYRROL. TETROLE-URETHANE v. Ethyl ethyl of

PURROLE CARBOXYLIC ACID. TEUCRIN C₂₁H₂₁O₁₁ or C₂₁H₂₀O₁₁. [230°]. A glucoside occurring in Tenerium fructicans, a plant used in Sicily as febrifuge. Extracted by alcohol (Oglialoro, G. 9, 440; 13, 498). Slender yellow prisms. Boiling dilute nitric acid forms anisic, tartaric, and oxalic acids. Boiling dilute H2SO, yields glucose and a yellow insoluble

residue TEWFIKOSE. [a]_D = 53·1°. A sugar occurring in the milk of the Egyptian buffalo (Bos bubalus). Yields glucose on hydrolysis (Pappel a. Richmond, C. J. 57, 759), v. Sugars.

THALICTRINE. Macrocarpine. Occurs in Thalictrum macrocarpum (Hanriot a. Doassans, Bl. [2] 84, 83). Yellow needles, insol. water, sol. alcohol and ether. Resembles aconitine, but is less poisonous.

THALLIN v. OXY-QUÍNOLINE."

THALLIUM. Tl. At. w. 203-64. Mol. w. 407-28 as gas at c. 1700° (v. infra). Melts at 293-9° (Crookes, C. J. 17, 123; cf. Lamy, A. Ch. [3] 67, 385). Boils at full red heat. S.G. pressed 11-88, cast 11-81, in wire 11-91 (Crookes, L.c.; cf. Lamy, L.c.; Worther, J. pr. 91, 385; de la Rive, C. R. 56, 588). V.D. 232-7 at 1636°, 203-7 at 1728° (Biltz a. V. Meyer, B. 22, 725). S.H. -0325 (Lamy, L.c.); 0335 (17°-100°) (Regnault, A. Ch. [3] 67, 437). C.E. (linear) 00003021 at 40°, 00003135 at 50° (Fizeau, C. R. 68, 1125). E.C. 5-225 at 0° (Hg at 0° = 1) (Bénoit, P. M. [4] 45, 314; cf. Matthiossen, P. 118, 431). H.C. [Tl²,0] = 42,240 (Tk. 3, 354). Latent heat of fusion c. 1010 for 203-6 g.-u/Heycock a. Neville, C. J. 65, 35). The characteristic green line of the emission spectrum has the wave-length 5347 according to Huggins (T. 1864. 139), 5349-6 according to Mascart (Ann. de Vécol. norm., 4, 7 [1867]), and 5349-5 according to Thalén (Determin. des long. d'onde des raies métalliques (Upsala, 1868)). Concerning the emission spectrum of Tl v. also Crookes, Pr. 12, 530; Nicklès, C. R. 58, 132; Kirchoff a. Bunsen, A. 155, 230, 366; Lockyer a. Roberts, Pr. 23, 344; Liveing a. Dewar, Pr. 27, 132; Hartley a. Adeney, T. 1884. 104; Becquerel, C. R. 99, 376; Wilde, Pr. 53, 369.

Historical.—In 1861 Crookes was preparing

Historical.—In 1861 Crookes was preparing Se from the flue-dust of a sulphuric acid manufactory at Tinkelrode in the Harz mountains, when on distilling the impure Se he obtained a residue which showed a marked single green line in the spectrum; this line was not known to belong to the spectrum of any element, hence Crookes supposed that the impure Se contained a new element. Crookes isolated the element towards the end of 1861, and called it thallium. (from \$\theta \text{Ab} \text{d} = \text{a} \text{green bud} \text{) c. C. N. 3, 193, 303}. Lamy (A. Ch. [3] 67, 385) noticed a new green line in the spectrum of a leaden chamber deposit about the same time as Crookes was investigating the cause of the line he had observed; in 1862 Lamy isolated a specimen of the metal which Crookes had obtained a few months before.

Occurrence. — Never uncombined. Compounds of Tl are widely distributed, but only in very small quantities. The sulphide occurs in minute quantities in many specimens of copper pyrites and iron pyrites (v. Crookes, C. J. 17, 112; Lamy, Lc.; Wöhler, A. 142, 263; Carstanien, J. pr. 102, 65; Gunning, Ar. N. 3, 86); also in native sulphur from Lipari and Spain. Compounds of Tl are found in small quantities in many ores of As, Bi and Hg, and in preparations from these ores; also in commercial Se and Te, probably as selenide and telluride (v. Crookes, Lc.; Röppler, Am. S. [2] 35, 420; Herapath, Ph. 4, 302; Werther, J. pr. 89, 129). Some specimens of Lepidolite contain small quantities of Tl compounds (v. Schrötter, W. A. B. 48 (ii.) 734; 50 (ii.) 268). A Swedish

mineral called crookesite was found by Nordenskjold to contain from 16·3 to 18·55 p.o. Tl as selenide, along with selenides of Cu and Ag (Bl. [2] 7, 409). Small quantities of TlCl are found in some mineral springs and in the saline deposits from such springs (v. Böttger, J. pr. 89, 378; 90, 22; 96, 294). Traces of Tl alum have been found accompanying the double sulphates of Cs, Li, and Rb in alumite from the island of Volcano (Cossa, Acad. dei Lincei [3] 2). Small quantities of Tl compounds have been noticed in carnallite, sylvine, and kainite (Schramm, A. 219, 374). Many specimens of commercial sulphuric and hydrochloric acids contain traces of Tl compounds (v. Crookes, l.c.).

Tl compounds (v. Crookes, L.c.).

Formation.—(Crookes, L.c.; or T. 1872.)—1.

By reducing Tl_CO₂ by fusion with KCN.—2. By electrolysis of Tl_CO₃ covered with water.—3.

By electrolysis of Tl_SO₄.—4. By heating Tl_CO₄ in a covered crucible.—5. By ppg. by zinc from solution of a thallous salt to which excess of NH₂Aq or NaOHAq has been added.

Preparation.—The most economical source is the flue-dust from sulphuric acid manufactories where pyrites or sulphur containing Tl compounds has been used. Many specimens of flue-dust contain no Tl compounds; in some specimens 8 p.c. Tl has been found, but only in a very few does the quantity amount to 25 p.c. Tl (Crookes). After having been heated to dull redness, to remove any HCl, the dust is well stirred in wooden tubs with its own weight of boiling water and allowed to settle for 12 hours; the liquid is siphoned off, and the residue is again stirred with boiling water and let settle; the mixed liquids are ppd. by a considerable excess of conc. HClAq; the pp., which is crude TICI, is well washed on a calico filter and squeezeddry. About 68 lbs. crude TlCl were thus obtained from 3 tons flue-dust (Crookes, T. 1872). The crude TICl is heated with its own 18/2). The crude 1101 is neated with its own weight of pure cone. H₂SO₄ in a Pt dish till all HCl and most of the H₂SO₅ are removed; the TlHSO₄ is dissolved in c. 20 times its weight of water, the solution is nearly neutralised by CaCO₂, filtered, ppd. by cone. HClAq, and the TlCl so obtained is well washed, and is then boiled for a few minutes with (NH_i)₂SAq; the pp. of Tl₂S is filtered off, well washed with water containing H₂S, and dissolved in dilute H.SO.Aq; the solution is boiled to remove H.S, ammonia is added in slight excess, and after boiling the solution is filtered and crystallised; (NH₄)₂SO₄, being much more soluble in water than Tl₂SO₄, remains in solution when Tl.SO, crystallises out.

If small quantities of Tl are to be prepared

If small quantities of Tl are to be prepared from Tl,SO,, the salt is dissolved in c. 20 times its weight of water, the solution is acidulated with H SO,, and electrolysed, Pt electrodes being used. If large quantities of Tl are to be prepared, Tl,SO, is placed in a deep porcelain dish (holding about 4½ litres) and covered with water (c. 3 kilos Tl,SO, are used at a time) and plates of pure zinc are arranged vertically around the sides of the vessel; heat is applied, and the whole of the Tl separates in a few hours as a spongy mass easily detached from the zinc by shaking... The spongy Tl is washed several times, pressed by the fingers, and then fused with KCy in a porcelain crucible to get it into a

tump (for details v. Crookes, I.c.; v. also Gun-

ding, J. pr. 105, 843).

Crookes (l.c.) gives several methods for preparing pure Tl. If the starting-point is comparing pure Tl. If the starting-point is com-mercial Tl₂SO₄, he recommends to dissolve this salt in water, to saturate the cold solution with pure H.S. filter, heat to boiling, and pour into boiling, dilute, pure HClAq; to filter while hot, and allow to cool; to wash the TlCl that crystal- lises out, by decantation, till the washings are free from H.SO., and to purify by re-crystallising twice from water. The TICI thus obtained is dried, mixed with pure Na₂CO₂, and projected, in small successive portions, into molten pure KCy in an unglazed porcelain crucible; reduction to metal is rapid. After cooling, the contents of the crucible are treated with water, the ingot of TI is boiled for some time in water, dried, and fused over a spirit lamp (coal-gas should not be used on account of the S compounds in it) in an unglazed porcelain crucible, with free access of air and frequent stirring with a piece of unglazed porcelain, to facilitate oxidation, and the metal is poured into a porcelain mould.

Properties .- A white metal without any tinge of blue; when fused under coal-gas, liquid Tl is exactly like Hg; may be highly polished by rubbing under water; very sott, may be cut with the nail, or scratched by lead. Less tenacious than lead; does not become brittle between -18° and its m.p.; very malleable, Lamy (A. Ch. [3] 67, 385) says that plates $\frac{1}{15.000}$ mm. thick

can be obtained; can be squeezed, but not drawn, into wire; very inelastic. Tl crystallises very easily in octahedral forms; it crackles like tin when bent; a wire of Tl seems amorphous when prepared, but under water it soon becomes crystalline. Tl quickly tarnishes in air; the film of oxide formed protects the mass of metal. The metal may be kept unchanged for years under water that has been deprived of air (v. Böttger, D. P. J. 197, 374). The melts easily (at 294°) without first becoming pasty; it expands considerably before melting is complete, and con-tracts much on cooling. TI boils below white heat; it may be distilled in a current of H. Pieces of the metal may be welded together by pressure at the ordinary temperature. Tl is nearly as diamagnetic as bismuth. Tl gives an intense green colour to a non-luminous flame (v. infra, Detection). Heated in air, Tl readily burns to Tl.O; it combines with S, Se, P, Cl, Br, I, &c., when heated with these elements; it dissolves in solutions of most acids (v. Reactions). The compounds of Tl are very poisonous, producing symptoms like those of lead poisoning.

The at. w. of Tl has been determined (1) by The at. w. of Ti has been determined (1) by ppg. Cl as AgCl from TlCl by AgNO, Aq (Lamy, A. Ch. [3] 67, 385 [1862]; Hebberling, A. 134, 11 [1865]); (2) by ppg. I from TII by AgNO, (Werther, J. pr. 92, 136 [1864]); (3) by converting Tl, SO, into BaSO, (Lamy, Lc.; Hebberling, Lc.); (4) by converting Tl into TlNO, (Crookes, T. 1873. 277); (5) by determining S.H. of Tl (Lamy, Lc.; Regnault, A. Ch. [3] 67, 437 [1862]); (6) by determining V.D. of TlCl (Roscoe, Pr. 27, 426).

The mol. w. of Tl in the gaseous state is double the at. w.; in other words, the gaseous molecule is diatomic (Biltz a. Meyer, B. 22, 725). Ramsay (C. J. 55, 521) determined the depression produced in the vapour pressure of Hg by dissolving Tl in that solvent; assuming that equal volumes of dilute solutions contain equal numbers of molecules, and that the mol. w. of liquid Hg is 200, the results obtained by R. indicated the molecule of Tl dissolved in Hg to be monatomic.

Tl is distinctly a metallic element; no compounds have been isolated wherein Tl certainly forms part of the negative radicle, although there are indications of the existence of such compounds (v. THALLIUM DIOXIDE, p. 680); the compounds which TIBr, TICl, and TII, form with alkali halides may contain TI in the negative radicles. TI is the last element in the odd-series family of Group III.; this family comprises Al, Ga, In, and Tl. The element Tl also shows marked resemblances to the alkali metals; and in its physical properties it is more like lead than any other element. The position assigned to Tl by the periodic classification of the elements clearly indicates the relations between this element and other elements. The relations of Tl (III .- 11) to Al (III.-3) should be similar to those of Hg (II.-11) to Mg (II.-3), and also similar to those between Pb (IV.-11) and Si (IV.-3). The re-semblances between the compositions and properties of the oxides of Hg and Mg on the one hand, and of the oxides of Pb and Si on the other hand, are shown only in the highest oxides of these elements: there is Hg.O but no Mg.O. there is PbO but no SiO; HgO and MgO are basic, PbO, and SiO, are feebly acidic. Neverbasic, 100, and 310, are feely availed than HgO and PbO₂; these lower oxides, Hg₂O and PbO, are basic; Hg₂O feely, and PbO strongly, basic. Hence it is likely that the resemblances between the exides of Tl and Al will be shown in the highest exides. This supposition is confirmed; TlO₃ and Al₂O₃ are basic, forming salts M₂X₃, where X = the radicle of a dibasic acid; these oxides are more basic than PbO₂ and SiO₂, but less basic than HgO and MgO. As Hg and Pb form lower oxides than HgO and PbO₂, and these lower oxides are more basic than HgO and PbO, so Tl will likely form an oxide lower than Tl,O. and this oxide will be more basic than Tl₂O_{3,7} Tl forms the strongly basic oxide Tl₂O. Then consider the position of Tl in series 11. Consider the oxides of the members of this series: the lower oxides Hg₂O, PbO, and Bi₂O₂ are basic; the higher oxides HgO, PbO₂, and Bi₂O₄ pass from basic (11gO) to feebly acidic (PbO₂ and Bi₂O₃); therefore it is probable that the higher oxide of Tl will be less basic than HgO, but that it will not be acidic; Tl2O2 is a feebly basic oxide.

If the chlorides of series 11 are considered, the position of Tl in III .- 11 is seen to be justified: HgO gives HgCl., which can be gasified unchanged, PbO, gives PbCl., which is very easily decomposed by heat, no chloride corresponding with Bi,O, has been isolated; therefore sponding with D₁O, has been isolated, therefore Ti₂O₂ will probably give a chloride more stable towards heat than PbCl₄, but less stable than HgCl₂. TlCl₄ is decomposed by heating to c. 80° into TlCl and Cl. Hg₂O gives HgCl, PbO gives PbCl₃, and Bl₂O₄ gives BiCl₄, and these chlorides can all be gasified unchanged; there-

fore the chloride of Tl corresponding with Tl.O will probably not be decomposed by heat; TiOl has been gasified unchanged. The relations between the elements Hg, Tl, Pb, Bi, and Mg, Al, Si may be summarised in the expressions Tl: Hg: Pb = Al: Mg: Si; and Tl: Hg = Pb: TlBi: Pb. (For a further working out of the relations of Tl. v. Mendeléeff, C. N. 1880. 2; v. also Alkalis, metals of the, vol. i. p. 114; and Earths, metals of the, vol. ii, p. 424.) The atom of Tl is monovalent in the gaseous molecule TlCl: the V.D. of no other compound of Tl has been determined.

Reactions and Combinations .- 1. Exposed to air or oxygen, a film of Tl2O is at once formed; when heated in air or O to somewhat below redness (c. 300°) Tl burns to Tl₂O₃, and at a higher temperature this gives Tl₂O and O (Lamy, A. Ch. [3] 67, 385). Moist ozone acts on Ti giving TlO.H. - 2. A compact piece of Ti does not decompose boiling water, decomposition begins at a red heat; but spongy Tl, as ppd. by zinc, dissolves in water forming TlOHAq. -3. Tl dissolves in solutions of most acids, forming thallous salts Tl, X, where X = 2Cl, 2NO3, SO4, &c.-4. Tl combines with sulphur and selenion (v. sulphides and selenides). 5. Forms alloys with many metals (v. alloys). 6. Forms compounds with antimony and arsenic (v. antimonide and arsenide) .-7. A phosphide is formed by heating Tl in vapour of phosphorus (v. phosphide) .- 8. Combines with chlorine, bromine, and iodine, when heated with these elements (v. chlorides, bromides, and iodides -9. Tl ppts. the noble metals, also copper, lead, and mercury from solutions of salts of these metals (Reid, C. N. 12, 242).

Detection and Estimation.—TI is best de-

tected by the intense green colour which the metal and its compounds give to the non-luminous flame of the Bunsen lamp; according to Lamy (l.c.) 1 mgm. can be detected by the use of the spectroscope; if induction sparks are used it is said that $\frac{1}{80,000,000}$ mgm. can be detected (Cappel, P. 139,628). This generally estimated as Th or The So,; it can also be determined volumetrically by KMnO₄Aq (Willm, Z. 1863.

Thallium, alloys of. Several alloys of Tl were prepared by Carstanjen in 1867 (J. pr. 102, 82) by heating the metals together. Many of the alloys are soft, and most of them readily tarnish in the air; the alloy with ; pt. Sb is fairly hard; and those with Bi and Pb, Bi and Cd, and Bi and Sn are hard and brittle. Alloys are described with Al, Sb, Cd, Cu, Pb, Mg (v. also Mellor, C. N. 19, 245), Hg (v. also Crookes, l.c., and Regnauld, C. R. 64, 60), K, Na, and Zn; also with Bi and Od, Bi and Pb, and Bi and Sn.

Thallium, antimonide of. A hard, grey, crystalline solid was obtained by fusing together Tl and Sb in the ratio Tl: Sb; with cold dilute H.SO.Aq the substance gave off SbH, (Carstanjen, l.c.)

Thailium, arsenide of. Carstanjen (l.c.) obtained a white, crystalline, soft substance by fusing Tl and As in the ratio Tl: As; with cold

Thallium, bromides of. The compounds compounds the simplest formulæ of which are Tl₂Br₂ and TlBr₂. As none of the bromides has been gasified, the formulæ are not necessarily molecular; but from the analogy of TiCl, the formula TIBr probably represents the composition of the gaseous molecule of this compound.

THALLOUS BROMIDE TIBr. (Thallium mono. mide.) TI reacts very slowly with Br. bromide.) Thallous bromide is obtained, as a white pp., by adding HBrAq or solution of a bromide to solution of a thallous salt; almost insoluble in water (Willm, A. Ch. [4] 5, 28). TlBr melts at 458° to a brownish-yellow liquid, which solidifies to a yellow solid (Carnelley, C. J. 33, 278).

Thomsen gives H. F. [Tl,Br] = 41,290 (Th. 3, 354).

THALLIC BROWIDE TIBr₃. (Thallium tribromide.) Prepared by adding Br to TIBr sus-

pended in water until solution is effected, and evaporating in vacuo. TlBr, forms a yellow crystalline solid; it is very deliquescent, becoming gradually brown and giving off Br. Very soluble in water, also in alcohol. Reduced to TIBr by SO, Aq and other reducing agents (Willm, l.c.). Thomsen gives H.F. [Tl,Br,Aq] = 56,450(Th. 3, 354). TIBr₃ combines with NH₃ to form TIBr₃.3NH₃; a white solid that gives off NH₃ and Br at 100°, and when more strongly heated leaves TIBr (W., l.c.). Also combines with NH₄Br and KBr, forming TlBr, NH, Brand TlBr, KBr. 2aq (W., l.c.; Nicklès, C. R. 58, 537). Rammelsberg (P. 146, 597) described 2TlBr₃.3KBr. 3aq.

Thallum dibbonide Tibr₃, which sade TLBr₄). Obtained in long, yellow, needles by adding Tibr to boiling Tibr₄Aq, in the ratio Tibr₄Tibr₃, and cooling. Not decomposed at 100°; water forms TiBr₃Aq and Tl₂Br₃ (v. infra) (W., l.c.).

Thallium sesquisseomide Tl₂Br₃, or TIBr₄-3TiBr = Tl₁Br₆. (Thallo-thallic bromide.) Orange-red hexagonal leaflets; obtained by adding HBrAq to a mixture of a thallous and a thallie salt in solution; also by adding TIBr to TlBr, Aq, or by adding a little water to TlBr, (3TlBr₂ + Aq = Tl₂Br₃ + TlBr₃Aq) (W., Lo.). Thallium, chlorides of. Tl and Cl combine

to form at least four compounds: TlCl, Tl,Cl,

TICl, and TICl,

Thallors Chloride TiCl. Mol. w. 239-01.
Melts at 427° (Carnelley, C. J. 33, 277). Boils at 708°-719° (C. a. Williams, C. J. 33, 284). S.G. 7-02, after fusion (Lamy, J. 15, 184). V.D. at 830° to 1025° = 117.8 (Roscoe, Pr. 27, 426). 11 530 16 163 = 117 (168566; 77. 27. 25). S. 19 at 0°, 27 at 16°, 28 at 16:5°, 16 at 63° (Hebberling, A. 134, 15). H.F. [Tl,Cl] = 48,580; [Tl,Cl,Aq] = 38,480 (Th. 3, 354). Formation.—1. By heating Tl in Cl, keeping

the Tl in excess .- 2. By boiling powdered Tl in HClAq, and dissolving the film of TlCl that forms in much boiling water.—3. By adding

SO, Aq to TlCl, Aq.

Preparation. — HClAq, or solution of a chloride, is added to the solution of a thallous salt; the white curdy pp. that forms is washed with cold water, dissolved in a large quantity of boiling water, and the salt that separates as the solution cools is purified by two or three recrystallisations from boiling water (Crookes, C. J. 17, 112).

Properties and Reactions.—A white, crystal-line solid; resembling PbCl, but separating from solution in hot water in smaller and less shining crystals than PbCl. Becomes slowly

violet coloured when exposed to light (Hebberling, A. 134, 15). Melts at 427° to a clear vellow liquid, which solidifies to a white crystalline Very slightly soluble in water (v. supra); mass. less soluble in water containing a little HCl; insoluble in alcohol; insoluble in ammonia; soluble in hot Na₂CO₃Aq, KOHAq, or Na₂SO₄Aq. Hot conc. sulphuric acid forms Tl₂SO₄ and HCl; oxidisers such as ClAq, aqua regia, KMnO,Aq and HClAq, form TlCl₃, Tl₂Cl₃, or TlCl₂ (v. these chlorides). TlCl is reduced to Tl by zinc and sulphuric acid, also by adding aluminium to TiclAq at 90° (Cossa, Acad. dei Lincei [3] 2). Fusion with sodium hydrogen sulphate produces Tl.SO₄ (Krause, D. P. J. 217, 323; Nietzki, D. P. J. 219, 262).

Combinations.—1. With platinic chloride to form 2TICl.PtCl₁ (= Tl.PtCl₂); obtained, as a pale-yellow, crystalline powder, by mixing solutions of TlCl and PtCl₁; this salt is extremely insoluble in water, one part dissolving in 15,585 parts water at 15°, and in 1948 parts boiling water (Crookes, l.c.) .- 2. With mercuric chloride, to form TlCl.HgCl2; white lustrous chrome, to form 11Cl.HgCl₂; white lustrous needles, separating from a hot solution of TlCl in HgCl₂Aq; all HgCl₂ is removed at 200° (Carstanjen, J. pr. 102, 141; Jörgensen, J. pr. 12] 6, 82).—3. With ferric chloride to form 3TlCl.FeCl₂; small red prisms; obtained by adding TlCl to a hot solution of FeCl₂ in HClAq, and crystallising the red pp. from hot cone. HClAq; decomposed to its constituent salts by water (Willer, 4, 144, 3.50).—4 With chromic water (Wöhler, A. 144, 350) .- 4. With chromic chloride, to form 3TlCl.CrCl3 (v. Neumann, A. 244, 328). -5. According to Lepierre a. Lachaud (C. R. 113, 196), a conc. solution of chromium trioxide reacts with TICl to form small red prisms of CrO, TICl [CrO.(OTI)Cl], which are decomposed by water to TlCl and CrO,Aq.

THALLIC CHLORIDE TICI, Mol. w. not certainly known; from analogy of AlCl, GaCl, and InCl, the formula TlCl, is probably molecular.

Formation .- 1. By heating TICl with hot aqua regia and evaporating the solution in Cl (Willm, A. Ch. [4] 5, 28).—2. By dissolving treshly ppd. TlO₃H₂ in HclAq. adding HNO₂Aq, and evaporating in Cl.—3. By heating TlCl at its melting-point in Cl; it is doubtful whether the product is pure TlCl₂, or contains also TlCl₂ or Tl₂Cl₂ (Lamy, l.c.).

Preparation .- Cl is passed into water containing TICl in suspension until a little of the solution ceases to give a turbidity with PtCl,Aq; excess of Cl is removed by a stream of CO., and the solution is evaporated in vacuo. Crystals of TlCl, H2O separate, which lose water at c. 40°

(Werther, J. pr. 91, 385).

Properties and Reactions. — The hydrate forms large colourless prisms; the dehydrated salt is a white crystalline solid. Werther (l.c.) also obtained a hydrate 2TlCl.15H2O from a solution of TlCl₂ prepared as described. Cl begins to be given off at c. 50° to 60°; at 100° a mixture of TlCl and chlorides intermediate a mixture of TICI and enforteds intermediate between TICI and TICI, remains (Werther, *l.c.*; Lamy, *l.c.*). TICI, is very deliquescent; it dissolves very easily in water. Thomsen gives [Tl,Cl²,Aq] = 89,250 (Th. 3, 354). On diluting a concentration of the considerable conside aqueous solution considerable quantities of TIO.H, and HClAq are formed. Reducing agents, such as SO., form TlCl.

Combinations.-1. With ammonia to form TiCl., 3NH, (Willm, A. Ch. [4] 5, 28). A white, crystalline powder. Obtained by passing NH, over TiCl,; by adding an alcoholic solution of NH, to TiCl, suspended in absolute alcohol; or by boiling TlO, H, with cone. NH, ClAq, ppg. by NH, Aq, washing with alcoholic ammonia, then with absolute alcohol, and drying in vacuo. The compound is anchanged in air; water forms NH₄ClAq and Tl₂O₄; when heated NH₄, NH₄Cl, and N are given off and TlCl remains. Dissolves in HClAq, forming TlCl, 3NH, Cl. With ammonium chloride to Ticl, 3NH, Cl; obtained by adding NH, Cl to a solution of TlO, H, in HClAq, and evaporating in vacuo; large, white, quadratic crystals, probably with 2H.O (Rammelsberg, P. 146, 597; p. also Nicklès, J. Ph. [4] 1, 25) .- 3. Compounds with potassium chloride, caesium chloride, and rubidium chloride, TlCl_x-3MCl, xaq, have been obtained (v. Rammelsberg, l.c., also W. 16, 709; Godeffroy, Zeit. des allganein. österr. Apothekerver. 1880 No. 9; Neumann, A. 244, 348; Willm. Neumann (l.c.) also describes a compound of TICl, with beryllium chloride .- 4. Willm (l.c.) describes a compound with cupric chloride, 2TlCl_s.CuCl_s.-5. According to Nickles (C. R. 58, 537) TICl, forms a compound with ether and hydrochloric acid, to which he gives the composition TlCl, Et,O.HCl.H,O; it is described as a yellow fuming liquid.

Thallium dichloride TlCl, (or TlCl.TlCl. = Tl.Cl.). Lamy (A. Ch. [3] 67, 402) obtained a yellow, slightly hydroscopic, easily fusible solid, to which he assigned the composition TICL, by heating Tl and TlCl in a stream of Cl so that the product always remained liquid, and allow ing to cool when saturated; the substance gave off Cl, and Tl₂Cl₃ remained.

Ti,Cl,; THALLIUM SESQUICHLORIDE TIGL, 3TICL = TI Cl. (Thatlothallic chloride.)

Formed by heating dry TICl, somewhat above 100° as long as Cl is given off; the brown liquid cools to a clear yellow, crystalline mass (Lamy, l.c., p. 403). Also formed by the direct combination of Cl with molten Tl (L., l.c.); also by ppg. a solution containing a thallous and a thallic salt by HClAq (Willin, l.c.). Also obtained by dissolving Tl or TlCl in aqua regia, evaporating, heating till Cl ceases to be given off, and crystallising from water slightly acidified with aqua regia (Lamy, l.c.; Crookes a. Church, C. N. 8, 1). According to Werther (J. pr. 91, 390) the product of this reaction, dried at 100°, is a mixture of compounds of TiCl and TiCl_a, besides Tl₋Cl_a. Tl₋Cl_a crystallises in yellow, hexagonal leaflets: unchanged in air; melting between 400° and 500° to a dark-brown liquid that solidifies with much contraction, forming a yellowish mass with S.G. 5.9 (Lamy, l.c.). Very slightly soluble in water; S. 26 at 15°, 29 at 17°, 1.9 at 100° (Crookes; Hebberling, A. 134, 21). The solution is said to show the reactions both of thallous and thallie compounds. Heated above 500° Cl is given off compounds. Heated above 500°C is given off; heating in H₂S produces Tl₂S, S, and HCl (Hebberling, l.c.). Heating in NH, produces TlCl, NH₂Cl, and N (Crookes a. Church, C. N. 8, 1). Tl₂Cl, reacts with KOHAq to form TlO₂H₂, TiCl, and KCl.

OTHER THALLO-THALLIC CHLORIDES. According to Werther (J. pr. 91, 890), two compounds

besides TLCl, are obtained by evaporating TlCl in aqua regia, heating till Cl ceases to be given off, crystallising from water slightly acidified with abua regia, and drying at 100°. To these with aqua regia, and drying at 100°. To these compounds W. gives the formule 3TlCl.4TlCl, = Tl,Cl, and TlCl.15TlCl, = Tl,cl, and TlCl.15TlCl, = Tl, and TlCl.15TlCl, = Tl, and TlCl.15TlCl, = Tl, and TlCl.15TlCl, = Tl, and TlCl.15TlCl, = Thallium, oyanide of; v. vol. i. p. 347.

Thallium, ferrocyanide of; v. vol. ii. p. 337.
Thallium, fluorides of. Only one fluoride of TI has been isolated with certainty; there are indications of the existence of another.

THALLOUS FLUORIDE TIF. Formula probably molecular, from analogy of TlCl. Prepared by dissolving Tl,CO, in HFAq, evaporating to dryness, heating gently to remove HF, and crystallising from water; forms white, lustrous, regular octahedra (Büchner, J. pr. 96, 404). TIF is also said to be formed as a white sublimate by heating Tl₂O in HF gas (Kuhlmann, C. R. 58, 1037). Sol. in water: S. = 80 at 15°, and increases with increase of temperature; solution in water has alkaline reaction; somewhat sol. in alcohol. A hydrate TIF.H.O forms in monoclinic crystals by evaporating a solution of Tl₂O or Tl₂CO₃ in HFAq; it is deliquescent, and acts on glass (Kuhlmann, l.c.; Willin, A. Ch. [4] 5, 5). A compound with fluorhydricacid, TIF.HF - THF₂. is obtained by evaporating a solution of TlF in HFAq over H.SO. Decomposed above 100° to TlF and HF. V. sol. water; S. = 100 at ordinary temperature: the solution has an acid reaction (Büchner, l.c.).

THALLIO FLUORIDE. By digesting TIO,II, with RFAq, and also by adding HFAq to TI(NO₈),Aq, Willm (A. Ch. [4] 5, 5) obtained a dark olive-green solid, becoming brown when heated, and melting to an orange-yellow liquid that became white on cooling, insoluble in water and in cold HClAq. This substance was probably thallie fluoride, or perhaps a thallothallie fluoride; no analyses are given.

Thallium, hydride of. Horapath (Ph. 4, 802) supposed that a compound of Tl and H existed; but Crookes (C. J. 17, 132) failed to obtain any compound either by the interaction of an acid with Tl-Zn alloy, or by heating Tl in a stream of H; the escaping H burnt with a green flame, but this was found to be due to particles of Tl carried by the stream of H.

Thallium, hydroxides of. Tl forms three compounds with O and H, namely, TIOH, TIO.H

(or TlO.OH), and TlO,H,.
THALLOUS HYDROXIDE TIOH. (Hydrated thallous oxide Tl₂O.H₂O.) Mol. y. not known with certainty. Thomsen (Th. 3, 354) gives H.F. [Tl₂O,H'O] = 3,230.

Formation.—1. By dissolving T1 in water containing air, and evaporating.—2. By decomposing Tl₂So₄Aq by BaOAq, filtering, and evaporating.—3. By the interaction of CaOAq and Tl₂C₄O₄Aq.—4. By dissolving Tl₂O in water and evaporating.

Preparation .- 1. Tl ppd. by zinc is allowed to oxidise in warm, moist air, and the oxide is dissolved in boiling water; these operations are repeated till a saturated hot solution is obtained, and this solution is evaporated a little, filtered from any Tl₂CO, that may have separated, and allowed to crystallise (Crookes, O. J. 17, 132).— 2. Tl₂SO₄Aq is mixed with the proper quantity

of BaOAq, and the solution, filtered from BaSO, is crystallised in vacuo; this method is tedious, and there is much difficulty in getting rid of all BaO.—3. Thin plates of Tl are suspended over a shallow dish containing absolute alcohol, within a bell-jar from which air has been exhausted, and pure O is passed into the jar, the temperature being kept at 20°-25°; after several hours or days, C.H.TlO is formed as an oil in the dish; excess of alcohol is removed by to warm dry air till all water and alcohol are

removed (Lamy, A. Ch. [3] 67, 385).

Properties and Reactions. — Pale-yellow, prismatic crystals. At 100° in air, or in vacuo over H₂SO₄ at the ordinary temperature, the crystals become black from formation of Tl₂O₅ without altering their crystalline form. Easily soluble in water; Thomsen (Th. 3, 354) gives [TIOH,Aq] = - 3,155. The solution in water resembles KOHAq and NaOHAq in its properties; it is strongly alkaline, absorbs CO2, ppts. heavy metals as hydroxides or oxides, feels soapy to the touch, stains the skin, neutralises acids, &c. The solution absorbs a little O on heating; when evaporated to dryness and the residue re-dissolved, a little Tl.O. generally re-

THALLIC HYDROXIDES. Two thallie hydroxides. are known, TlO.OH and TlO,H3.

I. Monohydrated thallic oxide, TlO.OII = Tl2O3.H2O. Mol. w. not known with certainty.

H₂O₃, H₂O. Mol. W. not known with certainty. Formation.—1. By ppg. TlCl₃Ag by alkali and drying at 100° (Lamy, A. Ch. [3]67, 385).—2. By passing ozonised air through TlOHAq (Schönbein, J. pr. 93, 35).—3. By the action of H₂O₃Aq on Tl; according to Weltzien (A. 138, 129) a mixture of TlOH and TlO.OH is thus obtained .- 4. Various oxidisers -- e.g. KMnO Aq, hypochlorite solutions, &c .- convert TlOH into TIO.OH (Schönbein, l.c.) .- 5. By electrolysing a neutral or ammoniacal solution of Tl2(SO4) or Tl(NO3)3; the hydroxide separates on the posi-

tive (Pt) electrode (Flemming, J. Z. 1869, 292).

Preparation.—TICl, Aq is ppd. by a slight excess of KOHAq or NH, Aq, the pp. is thoroughly washed, and dried at 100° (Iamy, A. Ch. [3] 67, 397; Crookes, C. J. 17, 132; Werther, J. pr. 91, 388). The air-dried pp. has the composition TIO.OH (Carnelley a. Walker, C. J. 53, 88).

Properties and Reactions .- A brown powder ; insoluble in water and dilute alkali solutions. Heated to c. 60° begins to lose water; completely dehydrated at 115°, according to Werther (J. pr. 91, 385), but the residue contains some TLO. as well as Tl₂O₃ (cf. Birnbaum, A. 138, 133). According to Carnelley a. Walker (C. J. 53, 88). dehydration is complete at 230°, and the residue is Tl₂O₂, which is stable to 360°. Dissolves in HClAq, forming TlCl3; in conc. acid Cl is given off and some TICl is produced. Dissolves in dilute H2SO, Aq; with conc. acid some O is given off. H_SU_Aq; with cone. acid some U is given off. Dissolves in SO_Aq, As_O_Aq, hot tartaric acid solution, and boiling oxalic acid solution, in each case forming a salt of Tl_O. TlO.OH dissolves in warm cone. NH,ClAq, giving off NH, and forming TiCl_3NH,; on adding water Tl_O, is ppd. as a black powder (Willm, A. Ch. [4] 5, 5).

II. Trinydrated thallic oxide, TlO.H. —
TlO.BH O. Formed as light hown, lustrose.

Tl.O.3H.O. Formed, as light-brown, lustrous,

microscopie, hexagonal plates, by dissolving TlO.OH in molten KOH, fusing for some time, cooling, washing with hot water, then with alcohol, and drying at 100°. Insoluble in water. Not decomposed at 340°; soluble in dilute acids (Carnegie, C. N. 60, 113).

Thallium, iodides of. TI combines directly with I. At least two compounds are known:

TII and Tl₂I₁; TII₁, and probably one, or perhaps more than one, other compound of TII and TII₃, seem also to exist.

THALLOUS IODIDE TII. (Thallium monoiodkile.) Mol. w. not known with certainty, but
formula TII is probably molecular from analogy
of TICl.

Formation. — 1. By heating together Tl and I in the ratio Tl:I.—2. By adding KIAq to solution of a thallous salt.

Preparation.—KIAq is added to a dilute solution of a thallous salt, and the yellow pp. is thoroughly washed with water and dried at 100° (Lamy, A. Ch. [3] 67, 405; Crookes, C. J. 17, 137).

Properties and Reactions.—A citron-yellow powder; melts at 439° (Carnelley, C. J. 33, 278), and boils at 800°-806° (C. a. Williams, C. J. 33, 284). S.G. 7-072 at 15-5°, after fusion 7-04-75 at 14-7° (Twitchell, Clarke's Table of Spec. Grav. [2nd edit.] 35). Very slightly soluble in water. Determinations of solubility vary considerably; Werther (J. pr. 92, 130) says that 1 pt. requires 20,000 pts. water to dissolve it at 15°, and Crookes (l.c.) gives solubility as 1 in 450 of water at 15° (v. also Hebberling, A. 134, 16). Crookes says TII is somewhat more soluble, Hebberling says it is decidedly less soluble, in KIAq than in water.

When heated to c. 190° TII becomes red, and when it melts a red liquid is formed which solidifies to a red crystalline mass having the composition TII (Hebberling, *l.c.*, p. 18); the red variety is also obtained by crystallising from hot KOHAq (Willm, A. Th. [4] 5, 28); also by crystallising from hot KC.H.Q.Aq (Werther, *l.c.*). The red form of TII is produced by adding KIAq to a warm cone, solution of a thallous salt (Hebberling, *l.c.*, p. 16). Red TII crystallises in octahedral forms (W., *l.c.*). The red variety alowly changes on keeping to the yellow form.

When freshly ppd. yellow TlI is exposed to the sun's rays it becomes green and crystalline without any change in composition. The green variety of TlI is somewhat more soluble in hot water than the yellow form; it crystallises from hot water in green microscopic crystals that are very refractive. The green variety changes is hastened by heating in water containing I or KI, but not by heating with pure water. When strongly heated, green TlI becomes red (v. Knösel, B. 7, 576, 893).

TII is decomposed by warm HNO, Aq, with separation of I. It is dissoived, without I being separated, by ClAq or agua regia; Willm (l.c.) supposes that an iodochloride is formed. Fusion with KCN produces TI (Werther, l.c.).

THALLIG IODIDE TII, This compound has the individual with cartainty. Pay treating

THALLIG IODIDE TIL. This compound has not been isolated with certainty. By treating TI with an ethereal solution of I, Nickles (C. R. 88, 537) obtained a brown liquid from which brown needles gradually separated. These crys-

tals may have been TlI,; no analyses are given.

Double sales of TII, with alkali iodides have been prepared by digesting TII with solutions of I and alkali iodides in ether; these salts have the composition TII, MI.xH.O, where M = NH, and K (v. Mic'des, J., Ph. [4] 1, 25; Willm, A. Ch. [4] 5, 5; Rammelsberg, P. 146, 597). A compound TII, CuI_NNI, is described by Jörgensen (J. pr. [2] 6, 82).

THALIUM SERQUI-IODIDE TI₂I₃ or TII₄.3TII = TI₄I₄. (Thallothallic iodide.) Black, lustrous needles; insoluble in water, slightly soluble cold alcohol, decomposed by boiling alcohol; decomposed slowly at ordinary temperature, quickly on heating; obtained by long-continued heating yellow TII with excess of IAq (Knösel, B. 7, 576, 893).

OTHER THALLO-THALLIC IODIDES. By evaporating a solution of TII in HIAq, in presence of I, at 70°, small, brown, rhombic, crystals were obtained by Jörgensen (l.c.). The composition of the crystals is represented by J as 6TII.TII, or perhaps 5TII.TII,. The same compound is said to be obtained by digesting TII with an ethereal solution of I. Heating to c. 100°, drives off I, and leaves yellow TII; boiling alcohol, and also KIAq, withdraws I, forming TII.

Thallium, oxides of. Two oxides have been isolated, TLO and TLO; there is evidence in favour of the existence of a third oxide, probably

That bous oxide TI₂O. (Thatlium monoxide.)

That bous oxide TI₂O. (Thatlium monoxide.)

Mol. w. not known with certainty. [\$\mathbb{P}\$\text{?},0] = 42,240 (Th. 3, 354). Prepared by heating TI in air to not above 100° (to prevent formation of Ti₂O₃); also by heating TIOH to 100° out of contact with air; also by heating Ti₂O₃ to full redness. A black powder; melting at c. 300° to a dark-yellow liquid, which acts on glass, forming a silicate of Tl. Ti₂O absorbs moisture from the air, forming TIOH; it dissolves easily in water, forming a strongly alkaline solution of TIOH (v. Thallous hydroxide, p. 678). Soluble in absolute alcohol, forming C,H₂OTI, a colourless, heavy oil (S.G. 3:55); this oil is decomposed by a little water with separation of TIOH (v. Thallous hydroxide, Preparation, No. 3, p. 678). (Crookes, C. J. 17, 128; Lamy, A. Ch. [3] 67, 385). Tl₂O is reduced to Tl by heating to redness in II, or in CO, or with Mg (Winkler, B. 23, 788).

THALLE OXIDE TI₂O₂. Mol. w. not known with certainty. Prepared by ppg. a thallie salt with KOHAq or NH₂Aq, washing the pp. thoroughly, drying, and heating it to c. 260° (Crookes, Lc., p. 132). Also formed by burning Tl in air to a light below redness; at a lower temperature the product is chiefly TI₂O, and at a full red heat TI₂O₃ is decomposed to TI₂O and O (Lamy, Lc.). TI₂O₃ is also formed by passing an electric current (from a couple of Grove cells) through neutral TI₂SO₂Aq, using Pt₃electrodes, Tl deposits on the negative electrode, and TI₂O₄ forms, as a brown cake, on the positive slectrode; the H₂SO₂Aq formed should be neutralised from time to time by NH₂Aq (Crookes, Lc.). For other methods of formation v. Wöhler (A. 146, 263, 375), and Willm (A. Ch. [4] 5, 19). TI₂O₃ is a brownish-black solid; insoluble in water Melts at c. 760° (?) (Carnelley a. O'Shea, C. J.

Tl.SO, Aq and giving off O. Soluble cold HClAq, forming TiCl, Aq, and some TiCl with evolution of Cl. Takes fire in dry H₂S, forming Tl₂S, (Carstanjen, J. pr. 102, 65). A mixture of Tl₂O, and S takes fire, when struck (Böttger, J. pr. 90, 27). Reduced by heating in H or CO to Tl.O, and then to Tl. Tl.O, absorbs NH, when heated in that gas; no definite compound has been isolated. For compounds with H.O v.

THALLIC HYDROXIDES, p. 678).

THALLIUM DIOXIDE (?TIO2). When a rapid stream of Cl is passed into conc. KOHAq, holding freshly ppd. TlO.OH in suspension, a violetcoloured solution is obtained; mineral acids added to this solution form thallous salts, and give off O, or Cl with HClAq. Carstanjen (J. pr. 101, 55) supposed the violet solution to contain a thallate of potassium. Piccini (G. 17, 450) obtained a violet pp. by adding Ba(NO_s)₂Aq to the violet solution; analyses of this pp. were not satisfactory, but the results indicated that an oxide of Tl of the composition TlO, is formed by the method described. Piccini says that the same violet solution is obtained by electrolysing 30 p.c. KOHAq, using a plate of Tl as anode; also by digesting 1 pt. KOH with 4 pts. KClO.

in water, and adding Tl₂SO₄.

Thallium, phosphide of. No compound of Tl and P has been isolated with certainty. According to Crookes (C. J. 17, 135), the black substance formed by passing P hydride into an moniacal Tl. SOrtq is a phosphide of Tl. Carstanien (J. pr. 102, 80) failed to obtain a phosphide by reducing Tl_aPO₄ by C or II, or by heating the elements together. Flemming (Bi. [2] 10, 35) noticed that a thin, black coating formed on molten Tl when pieces of P were thrown on to it; by heating solution of a thallous salt with P in a scaled tube, he obtained a black solid. perhaps a phosphide, and also a phosphite and hydride of P (cf. Willm, A. Ch. [4] 5, 5). Thallium, platino-cyanide of; v. vol. ii. p.

Thallium, salts of. Two series of salts are formed by replacing the H of acids by Tl; thallous salts, Tl,X, and thallic salts, Tl,X, where X = SO,, CO,, 2NO,, 2IO,, 2FO, &c. The chief thallous salts of oxyacids are arsenates, carbonates, chlorate and perchlorate, chromate, dichromate and trichromate, dithionate and trithionate, hypophosphite, iodate and periodate, molybdates, nitrate, phosphates, selenite and selenates, silicates, sulphates and sulphite, tellurate, thiosulphate. The principal thallic salts are arsenate, iodate and periodate, nitraie, phosphates, sulphates (v. CARRONATES, NITRATES, SULPHATES, &c.). Several double salts of both series are also known.

Thallium, salts of oxyacids of. pounds of this kind have been isolated with certainty, but there is evidence in favour of the existence of salts of the hypothetical thallic acid, probably analogous to plumbates (v. Thallium

DIOXIDE, supra).

Thallium, selenides of. Tl Se has been isolated; another selenide, perhaps Tl₂Se₂, pro-

bably exists.
THALLOUS SELENIDE Tl.Se. Mol. w. not known. Obtained by fusing the elements toge-

ther in the ratio 2Tl:Se (Willm, A. Ch. [4] 5, 5; Carstanjen, J. pr. 102, 79); also by ppg. Tl.CO.Aq by H.Se (Kuhlmann, Bl. [2] 1, 330). A grey, lustrous, crystalline solid; melting at c. 840° (Kuhlmann, l.c.). Dissolves in H.80,Aq and HClAq, giving off H.Se.

THALLIO SELENIDE (? Tl.Se.). By fusing the elements together in the ratio 2Tl.3Se, Carstanjen (l.c.) obtained greyish-black prismatic crystals, resembling Sb; not acted on by dilute H.SO,Aq; decomposed by hot conc. H.SO, with separation of Se and evolution of SO, composition of this substance has not been deter-

mined.

Thallium, silicofluoride of, Tl2SiF. tained by dissolving Tl.CO, in H.SiF.Aq, and evaporating. Colourless, regular, octahedra (Werther, J. pr. 91, 385). According to Kuhlmann (Bl. [2] 1,330), the crystals are Tl_SiF, H O. Easily soluble in water. Volatile without decomposition, according to Kuhlmann (l.c.).

Thallium, sulphides of. TLS and TLS, have been isolated, and also probably more than one

compound of these two sulphides.

THALLOUS SULPHIDE TLS. Mol. w. not known.

Formation.—1. By fusing the elements toge ther in the ratio 2Tl:S (Carstanjen, J. pr. 102, 76).—2. By ppg. an alkaline solution of a thallons salt by H.S.—3. By ppg. slightly acidified Tl.SO, Aq by H.S. (Hebberling, A. 134, 11).— 4. By heating an alkaline solution of a thallous

salt with Na₂S₂O₃ (C., l.c.).

Preparation.—A cold, fairly cone., aqueous solution of Tl.SO, is acidulated with a trace of H.SO,Aq, and saturated with H.S, and the bluish-black pp., consisting of microscopic crystals, is washed with H.SAq and dried over H.SO.

(Hebberling, l.c.).

Properties and Reactions.—Prepared by ppn. from slightly acidulated Tl.SO,Aq, Tl.S forms very minute, blue-black, lustrous tetrahedra; prepared by heating together Tl and S it is a black, crystalline, brittle solid; prepared by ppn. from alkaline solutions it is a black amorphous solid. When the amorphous solid is dried, and strongly heated, it melts, and After melting. S.G. is 8°0 (Lamy, J. 15, 185).

H.F. [Tl',S] = 21,660 (Th. 3, 354). Moist ppd.

Tl.S oxidises in air to Tl,SO₄. On long continued heating Tl₂S is completely decomposed (Lamy, l.c.). Tl₂S is insoluble in solutions of (lamy, t.c.). 11.50 is insoluble in soluble in soluble as alkalis, alkali sulphides, carbonates, and cyanides; it dissolves readily in H₂SO, Aq and HNO, Aq, and less readily in HClAq. By ppg. from a very dilute solution of a thallous salt, and dialysing, when the solution of a thallous salt, and dialysing, the solution of a solution o Winssinger (Bl. [2] 49, 452) obtained a reddishbrown aqueous solution of colloidal Tl.S

Combination .- By passing H.S into Tl, SO, Aq containing As,O,Aq, and acidulated with dilute H.SO,Aq, Gunning (Ar. N. 3, 86) obtained a red pp. of Tl₂S.As₂S₃; the same compound was obtained by mixing a solution of As,S, in NH,Aq with an ammoniacal solution of a thallous salt. Heat decomposes the compound into its constituent sulphides; alkali solutions dissolve out

As,S., leaving Tl.S.

Thallic sulphide Tl.S.. Obtained as a black, amorphous, easily fusible, solid, by melting Tl with excess of S, and removing uncom-

bined S by heating out of contact with air (Carstanjen, J. pr. 102, 65). Below 12° Tl.S., is hard and brittle; above 12° it is so soft that it may be drawn out like pitch. It dissolves in warm dilute H₂SO₂Aq without separation of S. Strecker (J. pr. [2] 2, 162) obtained a lustrous, brownblack pp. by passing H.S into a solution of a thallic salt mixed with sodium tartrate and excess of NH, Aq, followed by boiling; this pp. was Tl, S, according to Strecker. When H.S is passed into an aqueous solution of a thallic salt, the pp. is a mixture of Tl₂S and S. Tl₂S₂ combines with potassium and sodium sulphides, forming Tl.S. K.S and Tl.S. Na.S. These compounds are obtained by fusing together 1 pt. Tl.SO, 6 pts. S, and 9 pts. K₂CO₃ or Na₂CO₃, and washing the fused mass with water. The K compound is more stable than the compound of Na; when heated it melts, and then gives off S, leaving K.S and Tl.S; it is not changed by water or alkali solutions, but is decomposed by mineral acids (v. Schneider, A. 135, 215; cf. Krüss, B. 19, 2738). These compounds may be regarded as KTlS₂ and NaTlS₂, that is, as salts of a hypothetical thio-thallic acid.

THALLO-THALLIC SULPHIDES. By adding (NH₁), SAq to a solution of Tl₂Cl₃, a black pp. is obtained which is more fusible than Tl.S, and after melting solidifies to large greyish-black prisms. This pp. contains Tl and S. Similar substances are formed by heating together Tl.S and Tl2S3, and by melting Tl with more S than 2Tl:S, and less than 2Tl:3S; Carstanjen (J. pr. 102, 65) gave the formule 5TLS.3TLS₃ = Tl₁₀S₄, and Tl₂S.TLS₃ = Tl₅S₄, and Tl₂S.TLS₃ = TlS to compounds obtained in this way. By heating Tl₂S₄Na₂S (v. supra) with water, Schneider (A. 135, 215) obtained a compound to which he gave the formula

 $Tl_2S.2Tl_2S_3 = Tl_2S_3$

Thallium, sulphocyanide of; v. vol. ii. p. 352. Thallium, thiosalts of. The compounds of TLS, with K2S and Na.S may be regarded as K and Na thiothallates (v. THALLIC SULPHIDE, M. M. P. M.

THALLIUM ETHIDE TIEt. Has not been

obtained in the free state.

Ethylo-chloride TlEt,Cl. S. 2.76 in the cold; 3.37 at 92°. S. (alcohol) 33 at 78°. Formed from TlCl, and ZnEt, in ether (Hartwig, A. 176, 257). Scales (from water), explodes salts forming: TlEt₂NO₃, S. 5:67 at 70', exploiding at 230'°, exploding at 250° and converted by BaI, into TlEt₄I, S. 1, exploding at 195°.—
(TlEt₄)₂PO₄, S. 23-7 in the cold; 20.7 at 75°.—
(TlEt₄)₂PO₄, S. 23-7 in the cold; 20.7 at 75°.—

exploding at 189°.—TiEt,OA orystallising in needles [212°] (245°), exploding if rapidly heated. Ethylo-hydroxide TlEL,OH. S. 15-1 in the cold; 8 at 88°. Formed from (TlEL,).SO, and baryta. Silky needles (from water). More and baryta. Silky needles (from water). More sol. cold than hot water, forming an alkaline solution. Does not unite with CO₂, but forms the above salts with other acids.

THAPSIC ACID C, H₂₀O₂. [124°]. Obtained from the root-bark of *Thapsia garganica*. The bark is extracted with ether, which leaves on evaporation an amber-coloured resin. The resin dissolves in potash with evolution of heat, and the solution, on acidification, yields a neutral resin, n-octoic acid and thapsic acid.

alkaline solution on standing deposits potassium thapsate (Canzoneri, G. 13, 514). White scales (from alcohol), nearly insol. water and benzene, sol, alcohol and ether.

Salts .- K.A" zaq. Prisms .- BaA" (dried at 120°). Crystalline pp.—Ag.A": amorphous.

at 120°). Crystalline pp.—Ag,A": amorphous. Anhydle;de $C_{10}H_{20}O_s$. [71°]. Crystalline powder (from benzene). Antide $C_{c_1}H_{c_2}O_s$. [163°]. THEBAINE $C_{10}H_{c_1}O_s$. [193°]. S.G. 1·8. [a]₁ = -219° in 97 p.c. alcohol at 15°; = -230° in CHCl₃; S. (ether) · 7 at 10°; S. (isoamyl alcohol) 1·67 in the gold · S. (houseast feet 1.4). hol) 1:67 in the cold; S. (benzene) 5:27 in the cold (Kubly, J. 1866, 823). Occurs in opium to the extent of about :6 p.c. (Pelletier, J. Ph. 21, 569; Couerbe, A. Ch. [2] 59, 155; Kane, A. 19, 9; Anderson, A. 86, 179; Hesse, B. 3, 367; A. 153, 47; 176, 196). Prepared by treating the aqueous extract of opium with Na,CO, or lime, exhausting the filtrate with other, agitating the ether with dilute acetic acid, and pouring the acid liquid into dilute KOHAq. The pp. is collected after 24 hours, warmed with dilute alcohol and dilute HOAc is added till just acid. The alcohol is evaporated off at 50°, papaverine and narcotine removed by filtration, and thebaine acid tartrate ppd. by adding powdered tartaric acid to the filtrate. The tartrate is re-crystallised from water (Hesse, A. Suppl. 8, 262). Thebaine may also be obtained by adding NaOAc to a solution of the hydrochlorides of the opium alkaloids, allowing to stand, filtering, evaporating, again filtering, and adding sodium salicylate. After 24 hours thebaine salicylate crystallises (Plugge, Ar. Ph. [3] 24, 993; 25, 343).

Properties .- Colourless leaflets (from dilute alcohol) or prisms (from conc. alcohol). Tasteless. Alkaline in reaction. Very poisonous. Begins to sublime at 135°; at 160° the sublimate contains needles, onbes, and prisms (Blyth). V. sol. alcohol and chloroform. Ppd. by alkalis and alkaline carbonates, the pp. being slightly soluble in NH, Aq and lime-water. Conc. H.SO, gives a deep-red solution. Boiling dilute H.SO, converts it into thebenine and thebaïcine. Hot conc. HCHAq at 90° yields McCl and morphothebañae (Howard, B. 17, 527). III \q gives McI (2 mols.) (Howard a Roser, B. 19, 1597). Bromine-water forms C18H28BrNO3, a flocculent pp. converted by excess of Br into C19H20Br3NO3, a yellow pp. Solutions of its salts give a pp. of the dichromate

on adding K.Cr.O..

Salts.—B'HClaq. Large trimetrio prisms.

S. 63 at 10°. [a] = -168·32 + 2·33p. —

B'_2H_2PtCl_2aq. Amorphous pp., quickly chan-B_{211,2}ttol₂2ad. Amorphous pp., questy changing to orange prisms. Decomposed by boiling water (O. De Coninck, Bl. [2] 45, 131).—B'₂H₂C₂O₅6aq. S. 1·03 at 10'.—B'H₂C₂O₅aq. S. 23 at 20'.—B'C₄H₂O₈aq. Prisms, very soluble in hot alcohol. S. 77 at 20'.—Meconate B'₂C₂H₂O₅6aq. White prisms (from alcohol).— B' H. FeCy. (Plugge, Ar. Ph. [3] 25, 793).

Methylo-iodide B'MeI. Crystallises from

alcohol in prisms (containing EtOH), m. sol.

water.

Ethylo-chloride B'EtCl. Needles. Ethylo-iodide B'Etl. Needles (from alcohol) (Howard, B. 17, 527)

Benzylo-chloride B'C,H,Cl. Crystals.

Morpho-thebaine C₁,H₁,O₂N [191°]. Obtained by heating thebaine with strong aqueous HCl or

HBr, McCl (or EtCl) being split off; the yield being 50 p.c. of the thebaine. Yellowish crystals. Soluble in alcohol, ether, and benzene, sparingly in water. It dissolves in H2SO, to a colourless solution.

Salts.—B'HCl. Small glistening crystals, sol. water, insol. alcohol.—B'HR' fine silky needles.—B'HNO, 2aq: small white crystals, v. sol. water and alcohol.—A',H,SO, 7aq: small small should. The crystals, v. sol. water, insol. alcohol. The oxal at e is a sparingly soluble amorphous pp. The picrate is a yellow pp. which melts under water. Insoluble pps. are produced with potassium ferrocyanide, ammonium molybdate, HgCl₂K₂I₂, K₂Cr₂O₃, and bismuth-potassium iodide.

Acetyl derivative C₁,H_{1e}AcO₃N. [183°]: glistening plates (Howard, B. 17, 529).

Ethylo-iodide *B'Etl. Crystallises from

acetic acid.

Methylo-iodide B'MeI. Dimetric tables, insol. alcohol, sol. HOAc.

Benzulo-chloride *B'C.H.Cl. Needles, m. sol. water, sl. sol. alcohol (Howard a. Roser, B. 19, 1596).

Thebenine C₁₀H₂₁NO₃. Formed by boiling thebaine with HClAq (S.G. 1.04) (Hesse, A. 153, 69). Amorphous. Insol. benzene and ether, st. sol. boiling alcohol. Conc. H₂SO₄ forms a blue solution. V. sol. KOHAq.—B'HCl 3aq. S. 1. Plates.—B'₂H₂HgCl, 2aq. Very long efflorescent solution. V. soi. AUIIIII.—B INCOMP.

Plates.—B',H,HgCl, 2aq. Very long efflorescent prisms.—B',H,SQ, 2aq. Plates, insol. cold water.

—B'H,C₂O₄ aq. Prisms, sl. sol. hot water.

Thetaicine. Formed by boiling thebaine or

thebenine with conc. HClAq (Hesse). Yellow amorphous pp., insol. ether, benzene, and water, sl. sol. hot alcohol, v. sol. KOHAq. Conc. H. SO. forms a dark-blue solution. The salts are resinous.

Theine v. Caffeine. THEOBROMINE C,H,N,O, i.e.

CO NMe.C:CH.NMe Mol. w. 180. methyl-xanthine. S. 062 at 17°; .7 at 100°. S. (alcohol) '02 at 17°; '2 at 78°. S. (ether) '006 in the cold; '17 at 35°. S. (boiling CHCl.) 1. Occurs in the seeds of Theobroma cacao to 1. Occurs of 13 to 46 p.c. (Woskresensky, A. 41, 125; Glasson, A. 61, 335; Keller, A. 92, 71; Rochleder, A. 71, 9; 79, 124; Strecker, A. 118, 151). Formed by heating the lead salt of xa hine C₄H₂PbN₄O₂ (4 pts.) with MeI (5 pts.) for twelve hours at 130° (Fischer, B. 15, 454; A. 215, 311). Prepared by ppg, the aqueous extract of the seeds with lead acetate, filtering, removing excess of lead by ILSO,, adding MgCO,, evaporating to dryness, and extracting with alcohol (Dragendorff, Ar. Ph. [3] 12, 1). Got also by freeing cacao from oil by pressure, adding slaked lime, and extracting with 80 p.c. alcohol (Schmidt a. Pressler, A. 217, 287).

Properties.—Minute trimetric crystals, sl. sol. hot water, alcohol, and ether. Tastes bitter. At 184° it begins to sublime; at 170° (Blyth) or 290° (S. a. P.) it yields a crystalline sublimate. Very slowly attacked by pure HNO. (Franchimont, R. T. C. 6, 223). Not attacked by boiling KOHAq. Its salts are more or less easily de-composed by water. Ammoniacal AgNO, gives a gelatinous pp. which dissolves on warming, and deposits, on boiling, crystalline C,H,AgN,O₂ (Strecker). Theobromine is ppd. by sodium phosphotungstate (Wolfram, O. J. 36, 406; Fr. 18, 346).

Reactions.-1. Yields methyl-parabanic acid on exidation by CrO₈.—2. KClO₃ and HClA₂ at 50° yield methyl-alloxan and methyl-urea (Fischer, A. 215, 304). Chlorine-water yields amalic acid.—3. Will not combine with MeI to form a methyloiodide. But in presence of dilute alcoholic KOH it reacts with MeI, forming caffeine, even in the cold; better at 100°. But the reaction is never complete, some theobromine being decomposed.—4. Conc. HCl has no action below 200°. At 250° it decomposes it, producing formic acid, carbonic acid, ammonia, methylamine and sarcosine, C,H₈N,O₂+6H₂O
= 2CO₂+NMeH₂+2NH₃+C₃H,NO₂+CH₂O₃; the
NH₃ and NMeH₂ occur in the proportion indicated by the formula (Schmidt, A. 217, 298). Boiling aqueous Ba(OH), effects in 40 hours the same decomposition.—5. HNO, forms CO, methyl-parabanic acid and methylamine, but no ammonia.

Salts .- B'HClaq. Rosettes of needles .-B'HBr aq. Tables. — B'₂H₁PtCl₃ 4aq. — B'₂H₂PtCl₅5aq. — B'HAuCl₁. — B'₂HNO₃. — Manulu black prisms, de-B'HOAc. -B'2H2I8. Nearly black prisms, B'HOAc.—B'_H,I,. Nearly black prisms, decomposed by alcohol (Jörgenssen, Z. [2] 5, 675).—B'HAg(NO₃). Silvery needles, v. sl. sol. water.—C,H,AgN,O₂13aq.—Ba(C,H,N₄O₂). (dried at 105°). Got by adding the obromine to barytaat 105°). Got by adding the obromine to barytawater (Maly a. Andreasch, M. 4, 379). Needles (from hot water).

Bromo-theobromine C,H,N,O2Br. From theobromine and bromine (Fischer, A. 215, 305). Crystalline powder. Sl. sol. hot water. HČl, but reppd. by water. Sol. aqueous NaOH, not in NH3. Does not give an ethoxy-derivative with alcoholic KOH (unlike bromo-caffeine). After warming with ammonia it gives with ammoniacal AgNO, a silver salt that can be converted by EtI into bromo-ethyl-theobromine C,H_sEtN₄O₂Br, whence alcoholic KOH forms eth - oxy - ethyl - theobromine C,H_sEtN₄O₂(OEt) [153°] as needles. Boiling HCl converts this into EtCl and oxy - ethyl - theobromine C,H_aEtN,O.(OH), whence bromine and alcohol form the di-ethyl derivative of tri-oxy-di-hydroethyl-theobromine C,H,EtN,O,(OH)(OEt),[152°] This body on treatment with hot dilute HCl gives methylamine and apo-ethyl-theobromine (?); and with chlorine at -10° forms hypothyl-theobromine $C_1H_2N_3O_3$ [142°].

Methyl-theobromine is CAFFEINE.

Ethyl-theobromine C,H,EtN,O₂. [above 270°]. Formed from C,H,AgN,O₂ and EtI (Philips, B. 9, 1308). Small crystals, m. sol. hot water. Weak

THEOPHYLLIN C, H, N,O, i.e.

CO NH.C:CH NMe [264°]. Occurs in alco-

holic extract of tea, from which it may be separated by means of its Ag salt (Kossel, B. 21, 2164). Monoclinic tables (containing aq, v. e. sol. warm water and very dilute ammonia. May be sublimed. When evaporated with chlorinewater it yields a scarlet residue, which is coloured violet by NH,Aq. MeI converts its Ag salt into cafferne. KClO, and HClAq yield dimethyl-alloxan.

Salt.—AgC,H,N,O, laq. Amorph which may be crystallised from NH,Aq. Amorphous pp.,

A name given by Crum-THETINES. Brown and Letts to compounds of the form CO.H.CH.SR.OH or their anhydrides CHrSR₂ where R is a hydrocarbon radicle; v. ĊO-Ò DI-ETHYL-THETINE and DI-METHYL-THETINE.

THEVETIN C₃₄H₈₄O₂₄3aq. [170°]. S. 8 at 14°. a = -85.5°. A poisonous glucoside occurring in the kernels of Thevetia nereifolia (Blas, J. 1868, 768; De Vrij, R. T. C. 3, 167; Warden, Rh. [3] 12, 417). Crystalline powder, v. sol. hot water and alcohol, insol. ether. Sol. acids and alkalis. Lævorotatory. Conc. H₂SO, gives a dirty-brown colour. Decomposed by boiling dilute HClAq into glucose and theveresin C48H70O1, 2aq, a white powder [140°], v. sl. sol. cold water, sol. alkalis.

THIACETIC ACID v. THIO-ACETIC ACID. THIALDINE C. H, NS. i.e.

NH CHMe.S CHMe. Mol. w. 163. [43°]. Formed by passing H2S for four hours into a soluformed by passing H₂S10 rotar hours into a solu-tion of aldehyde-ammonia (1 pt.) in water (15 pts.), and a little NH₂Aq (Wöhler a. Liebig, A. 61, 2; Hofman, A. 103, 93; Brusewitz a. Cathander, J. pr. 98, 315). Monoclinic crystals (from ether-alcohol). May be distilled with steam. V. sl. sol. water, v. sol. alcohol, v. c. sol. ether. Boilsol. water, v. sol. alcohol, v. c. sol. ether. Boiling dilute H.SO, forms thio-acetic aldehyde. KMnO, forms CH., CH(SO, K). (Guareschi, B. 11, 1384, 1692). Boiling AgNO, Aq forms aldehyde. Hofinan, A. 103, 93). I in KI forms amorphous (CHM-9S, (Hassbender, B. 20, 460).

Salts.—B'HCl. Prisms, v. sol. water.—B'HBr.—B'HCl. B'HNO,—B'H.SO,- Prisms.—

B'H,PO, aq. Needles, v. sol. water.

THIAZOLE N CH.S. (116.8° cor.). S.G.

17 1.1979; 17 1.1998. Formed by the action of boiling alcohol on the diazo-compound of amidothiazole, obtained from di-chloro-di-ethyl oxide and thio-urea (Hantzsch a. Popp, B. 21, 2582; A. 250, 274). Formed also from N CH:CH and the corresponding a-bromo-thiazole by reduction with zine-dust and HOAc (Schatzmann, A. 261, 12). Mobile liquid, very volatile, hygro-A. 261, 12). Mobile liquid, very volatile, hygroscopic, and highly refractive. Miscible with water, alcohol, and ether. Insol. KOHAq. Smells like pyridine. Neutral in reaction.—Salts.—B'2H_PtCl₂ 2aq.—B'HAuCl₄. [250°].—B'C,H_NAO., [151°].—B'HHgCl₄. [104'].—B'HgCl₄. [204°]. Crystalline pp., sl. sol. water.

 μ -Amido-thiazole $N \ll_{CH}^{C(NH_2).S}$ ane. Thiazylamine. [90°]. Formed by the action of chloro-acetic aldehyde on thio-urea (Traumann, A. 249, 36). Prepared by boiling CH_Cl.CHCl.OEt (1 pt.) with thio-urea (1 pt.) and water (5 pts.). Yellowish plates, sl. sol. water, alcohol, and ether. Strong base.—B'HCl aq. Needles.—B'H.PtCl. Yellow tables.

Acetyl derivatibe. [203]. Needles.

Thiazo-

Acetyl derivative. [203°]. No THIAZOLE TRIAZOLE (so called)

 $CH \stackrel{S-C:N}{\diamond} CH$. Formed by the action of HClAq on methyl-nitroso-imido-thiazoline (Näf, A. 265, 123). Liquid, v. sol. water. Alkaline;

reduces Fehling's solution. Nitrous acid reproduces nitroso - methyl - imido - thiazoline. -B'HCl 2aq. [220°]. Needles.—B'HBr 2aq.
THIENONE is DI-THIENYL KETONE.

THIENVIK IS DI-THIENYIK RETONE.

DITHIENYIC, H.S., i.e. C.H.S.C.H.S. [88°].

(266° cor.). Formed on passing thiophenethrough a sed-hot tube (Nahnsen, B. 17, 789,
2197). Plates (from alcohol). Conc. H.SO.,
gives a reddish-brown solution with deep-green
fluorescence. On warming with isatin and
H.SO, it gives a violet-blue colour.

Sulphonic acid C.H.S.(SO) H. Got be-

Sulphonic acid C8H3S2(SO3H). Got by heating with H2SO, (20 pts.) at 100°. Yields a

crystalline BaA', aq.

Reference.—Hexa-bromo-dithienyl.

THIENYL-ACETIC ACID C,H,S,CH,CO,H. [76°]. Formed from C.H.S.CH(OH). CO.H [115°], HIAq, and P (Ernst, B. 19, 3281). Crystalline, sol. hot water, alcohol and ether. - Ba'A, (dried at 130°). Crystals .- AgA': pp.

Reference.—OXY-THIENYL-ACETIC ACID.
THIENYL-ACRYLIC ACID C,H.SC C,H,SO, Formed C.H.S.CH:OH.CO.H. [138°]. boiling thiophenic aldehyde with NaOAc and Ac.O (Biedermann, B. 19, 1855). Needles (from water), sol. hot water and alcohol, FeCl, gives an amorphous orange pp. -AgA': white pp.

THIENYLAMINE v. AMIDO-THIOPHENE. THIENYL-BROMO-ETHANE Вкомо-THIENYL-ETHANE

THIENYL BROMO-ETHYLENE v. BROMO-THIRNYL-ETHYLENE

THIENYL BROMO METHYL KETONE

ω-Bromo-aceteMienone. C.H.S.CO.CH.Br. Formed by adding Br (2 at.) to thionyl methyl ketone (1 mol.) dissolved in CS, (Brunswig, B. 19, 2891). Pungent yellow oil, may be distilled in vacuo. V. sol. alcohol and other. Solidified in vacuo. by cold. Alcoholic NII, forms a deep-blue colour. Oxidised to (a) thiophenic acid [126.5°]. Anilina yields C,H,S.CO.CH,NHPh [80°].

Thienyl di-bromo-methyl ketone C.H.S.CO.CHBr. [c. 0°]. Formed from thienyl methyl ketone and Br. Pungent oil, almost

insol. ligroïn. (B)-THIENYL-CARBINOL O.H.S.CH.OH. (207° cor.). Formed by shaking (B)-thiophenic aldehyde with aqueous potash (Biedermann, B. 19, 639). Liquid. HCl forms C,H,S.CH,Cl, a pungent oil boiling with partial decomposition

at 175 THIENYL CHLORO-ETHANE v. Culoro-THIENYL-ETHANE

THIENYL-CHLORO-ETHYLENE v. CHLORO-THIENYL-ETHTLENE.

(a)-THIENYL CHLORO-METHYL KETONE 6.H.S.CO.CH.Cl. [47]. (259° cor.). Formed by chlorination of thienyl methyl ketone (Peter, B. 18, 539). Pungent white crystals. Yields (a)-thiophenic acid on oxidation.

C.H.NS THIENYL ETHYL AMINE C.H.S.CHMe.NH. (186). Got by reducing the oxim of thienyl methyl ketone in alcoholic solution by adding sodium amalgam and HOAa (Goldschmidt a. Schulthess, B. 20, 1700). Liquid, sol. water. Absorbs CO, from the air.— B'HOAc. Needles, v. e. sol. water.

[95°]. Needles. Benzoyl derivative. THIENYL ETHYL KETONE C.H.S.CO.C.H. Propiothicnone. (228° cor.). Formed from propionyl chloride, thiophene, and AlCl. (Krekeler. B. 19, 677). Liquid. Hot conc. H.SO, forms propionic and thiophene (a)-sulphonic acids Chromic acid mixture yields (a)-thiophenic acid Oxim C,H,S.CEt:NOH. [56°].

THIENYL DIETHYL PHOSPHINE

(C,H,S)PEt,. (225°). Formed from thienyl-chloro-phosphine and ZnEt, in ethel (Sachs, B. 25, 1517).

Ethylo-iodide (C.H.S.PEt,I. Methylo-iodide (C.H.S.PEt,MeI. [122°]. White powder, v. sol. water insol. ether.

THIENYL-GLYCOLLIC ACID v. OXY-THIENYL-ACREIG ACID

(a)-THIENYL-GLYOXYLIC ACID

C,H,SO, aq i.e. C,H,S.CO.CO,H. [91°]. Formed by oxidising thienyl methyl ketone with alkaline (837; Bradley, B. 19, 2115). Formed also, together with thiophene (a)-carboxylic acid, by oxidation of (a)-cthyl-thiophene by alkaline KMnO₄. Crystals (containing aq, possibly as C₄H₄S.C(OH)₂.CO₂H), who lives my water. Melts at 59° when hydrated. May be extracted by ether. from its aqueous solution. If a drop of crude benzene, followed by H₂SO₄, be added to its solution in HOAc, a brown colour is formed, which on addition of more H₂SO₄ passes through blue-green, green, violet, red, and bluish-violet to blue.

Reactions .- 1. On heating it splits up into CO₂ and thiophenic aldehyde.—2. On heating with di-methyl-aniline and ZnCl₂ it yields the leuco-base of a green dye C4H2S.CH(C6H4NMe2)2. -3. PCl, forms thiophenic chloride.

-3. PCl, forms thiophenic chloride.

Salfs. — BaA'₂aq. Slender efflorescent needles, v. sol. water.—CaA'₂2aq.—CuA'₂2aq.—ZnA'₂2aq.—AgA'aq: amorphous pp., probably C,H₃S.C(OH)₂CO₂Ag.

Methyl ether McA'. [28·5°].

Ethyl ether Eth'. (265° uncor.). Oil.

A mide C,H₃S.CO.CO.NH_{...} [88°]. Needles, almost insol. water, v. sol. alcohol and ether.

Oxim C,H₃S.C(NOH).CO₂H. [146°].

Hantzeh R 24 48). Slewler white needles

(Hantzsch, B. 24, 48). Slender white needles. Exhibits Liebermann's reaction (Bradley, B. 19, 2119).—BaA', 1',aq.—AgA': amorphous pp.—
MeA' [105°]. Converted by NaOMe and MeI into liquid C₄H₃S.C(NOMe).CO₂Me. — EtA'. [123°]. Needles.

Acetyl derivative of the oxim. [87°].

Phenyl-hydrazide

C,H,S.C(N,HPh).CO,H. [165°]. Deen-vellow needles (from ether).

Heference.—NITRO-THIENYL-GLYXXYLIG ACID.
THIENYL HEXYL KETONE C₁₁H₁₆SO i.e.
C₁H₃SO.O₄H₁₃. (304° cor.). Formed from
thiophene, heptoyl chloride, and AlCl₄ in ligroin
(Schleicher, B. 19, 664). Yellow oil, yielding
(a) thiophenic acid on oxidation. Conc. H₂SO₄ forms thiophene (a)-sulphonic and heptoic acids.

Oxim [49°]. -Crystals (from alcohol).

THIENYL-INDOLE C₁₂H_uNS i.e.

C,H, < CH >C.C,H,S. [162°]. Formed by heating the phenyl-hydrazide of thicnyl methyl ketone with ZnCl₂ (Brunck, A. 272, 201). Lightyellow needles, insol. water, v. sol. ether, m. sol. alcohol. Colours pine-wood, moistened with HCl, bluish-violet. Yields C, H, Br, NS [278°] and C, H, CH(C, H, NS), [245°]. — B'C, H, NO, [187°]. Dark red plates, v. sol. alcohol.

Nitrosamine C, H, (NO)NS. [241°].

DI-THIENYL KETONE (C.H.S),CO. (326° uncor.). Formed from thiophene, COCl, and AlCl. Obtained also by distilling calcium And Alois Obsained also by discharge and a state of the s

THIENYL MERCAPTAN (C.H.S).SH. (166°). Got by reducing thiophene (a) sulphinic acid with zinc and HClAq (Biedermann, B. 19, 1616). Got also in small quantity from succinic acid and P₂S₅ (V. Meyer a. Neure, B. 20, 1757). Stinking oil, volatile with steam.—AgS.C₄H₂S.

Methyl ether (C,H,S)SMe. (186°).
DI-THIENYL METHANE C,H,S,: i.e.

CH₂(C₄H₂S)₂. (267°). Got by adding H₂SO₄ to a solution of thiophene and methylal in HOAc (Pcter, B. 17, 1345). Oil, smelling like oranges, Volatile with steam. Gives a red colour with isatin and H.SO

(a)-THIENYL METHYL KETONE C_sH_aSO i.e. C.H., S.CO.CH., Acetothicnone. (213° cor.).
S.G. 21 1167. Formed from thiophene, AcCl, and AlCl., (Peter, B. 17, 2643; Biedermann, B. 19, 636; Bradley, B. 19, 2115). Formed also from C.H., (HgCl)S and AcCl (Volhard, A. 267, 178). Liquid, smelling like acctophenone. Gives a blue colour with isatin and H_2SO_1 . Oxidised by $KMnO_4$ to (α)-thienyl-glyoxylic and thiophenic acids. Mercuric chloride and NaOAc form the compound (CH₃.CO.C.H₃S)HgCl₂ crystallising in white needles. Oxalic ether (1 mol.) and NaOEt give C₄H₃S.CO.CH₂.CO.CO₂Et [42°], which forms large yellow crystals, converted by boiling alcoholic hydroxylamine hydrochloride into the compound $C_4H_4S.C \leqslant_{N}^{CH:C.CO_2Et}$

CO.Et.C $\stackrel{\text{CH:C.C.}_4H_2S}{N}$ crystallising in colour-less needles [489] (Angeli, $B.\ 24,\ 232$).

Oxim C₀H₀S(NOH). [112°]. Phenyl-hydrazide C₀H₀S(N₂HPh). [96°]. Reference.-BROMO-, CHLORO-, IODO-, and

NITRO-THIENYL METHYL KETONE

THIENYL PHENYL - AMIDO - METHYL XETONE C,H,S.CO.CH,NHPh. [80°]. Formed by mixing C,H,S.CO.CH,Br with aniline in alcohol (Brunswig, B. 19, 2892). Plates. Yields a nitrosamine C₄H₄S.CO.CH₂.NPh(NO) [81°], and acetyl derivative C,H,S.CO.CH,NPhAc [142°].

ŤHIENYL PHĖNYL KETONE C₁H₂S.CO.C₂H₃, [55°]. (c. 300°). Formed by the action of AlCl, on a mixture of thiophene and BzCl (Comey, B. 17, 790). Formed also by heating C,H,(HgCl)S with BzCl at 100° (Volhard, A. 267, 179). Long needles (from dilute alcohol), insol. water. Gives a blue colour on heating with isatin and H₂SO₄. Yields thiophene and benzoic acid on heating with soda-lime.

Oxims C₁H₄S.CPh:NOH. Hydroxylamine

forms two stereo-isomeric (?) oxims [98°] and [114°] (Hantzsch, B. 23, 2332; 24, 59).

THIENYL-PHENYL-METHANE

CH2Ph.C4H3S. (265°). Formed by the action of H₂SO, on a mixture of thiophene and benzyl alcohol dissolved in HOAc (Peter, B. 17, 1346).

Thienyl-di-phenyl-methane CHPh.:C,H,S. [63°]. (330°-340°). Formed from thiophene, di-phenyl-carbinol, and P.O. (Levi, B. 19, 1624).

Plates (from alcohol) or needles (from ligroin), v. sol. HOAc, alcohol, and ether. Crystallises from cold benzene in needles C, H, SC, H, [48°]. THIENYL ISOPROPYL KETONE

C.H.S.CO.CHMe.. (282° cor.). Formed from isobutyryl chloride, thiophene, and AlCl, (Krekeler, B. 19, 675). Liquid. Yields (a)-thiophenic acid on oxidation. Fuming H.SO, reacts with formation of the sulphonic acid C.H.(SO,H)S.CO.CHMe., which yields the salts BaA', PbA', xaq, and is converted by phenyl-hydrazine into C.H.(SO,N,H,Ph)S.C(N,HPh).CHMe... cystallising from hot water in plates.

Oxim C₁H₃S.C(NOH).CHMe₂. [108°]. Pearly plates (from dilute alcohol).

THIENYL STYRYL KETONE v. STYRYL THIENYL RETONE.

THIRM'L DISULPHIDE (C,H,S),S₂. [56°]. Formed by atmospheric oxidation of a solution of thenyl mercaptan in alcoholic NH₂ (Meyer a. Neure, B. 20, 1757). Needles.

Meure, B. 20, 1757). Needles.

THIENYL SULPHOCYANO - METHYL

KETONE CH. (SCy). CO. C., H., S. [88°]. Formed
from CH., Br. CO. O., H., S. and KSCy in alcohol
(Brunswig, B. 19, 2893). Plates (from ether), sl.
80, water and ligroin, m. sol. alcohol.

DI-THIENYL-THIOPHENE C₁SH₂(C₄SH₃)₂. [147°]. (357°). V.D. 8°6. One of the products of the passage of benzene and sulphur-vapour through a red-hot tube (Renard, C. R. 112, 49). Yellowish needles (from alcohol), m. sol. benzene. H_SO₄ forms a rose-coloured solution, turned violet and finally blue on heating. Fuming H₂SO₄ at 120° forms a trisulphonic acid, which yields (O₁H₂S₄(SO₃)₃)₂Ca₃ at an amorphous powder, v. sol. water. Fuming HNO₄ at 160° forms C₁₂H₄S₂O₄ [313°], crystallising in white plates, v. sl. sol. benzene. Br forms C₁₂H₂Br₂S₂[282°], and amorphous C.H. Br S.

amorphous C_{1,2}H_{1,8}C₃, Third S_{1,2}C_{1,2}S_{1,2}S₂S₃ and amorphous C_{1,2}H_{1,6}S₃.

THIENYL TOLYL KETONE C_{1,2}H_{1,0}SO i.e.
C₀H<sub>1,Me.CO.C,1H₂S. Formed from o-toluic chloride, thiophene, and AlCl₂ (Ernst, B. 19, 3279). Oil. Yields an oily oxim.

THIO-. This prefix is employed to denote the replacement of O by S. Most inorganic salts</sub>

THIO. This prefix is employed to denote the replacement of O by S. Most inorganic salts of thio-acids are described under the heading of the oxy-salts; thus thio-carbonates are described under Carbonates. In some cases thio-salts are described under the heading of the characteristic element of the salts: thio-arsenates are to be found under Ausenic. Certain thio-salts are described under headings placed in their strictly alphabetical position; for instance, Thiosulphates. Thiocyanides are described as Sulphocyanides.

The following addition should be made to the sub-article Thio-oxyorhiophosphates (p. 147). By heating metallic chlorides or sulphides with excess of P.S. Glatzel has prepared a number of tetrathio - oxyorthophesphates, i.e. salts of the hypothetical acid H.PS. (Zeit. für anorg. Chemie, 4, 186). These salts are crystalline—generally green to black in colour; they are burnt in air, giving off SO₂; some are decomposed to sulphides and P.S., but the mercuric and arsenic salts distil unchanged when heated out of contact with air. These salts are insol. en dilute acids; they are decomposed by strong acids. G. isolated the thiophosphates of Sb. As, Bi, Cd, Cu(ous), Fe(ous), Pb, Mn, Hg(io), Ni, Ag, Tl, Sn(ous), and Zn; he sould not obtain the salts of Ca, K, Na, or Sr.

THIOACETAMIDE CH., CS.NH., [108°]. Formed from acetonitrile and H.5 (Bernthsen, A. 192, 46), and from acetonitrile and H.5 (Bernthsen, A. 192, 46), and from acetamide and P.S. (Hofmann, B. 11, 340). Monoclinic plates, v. sol. water and alcohol, m. sol. ether. Hgo forms HgS. AgNo. gives AgS. CuSO, and Pb(OAC), give, on boiling, CuS and Pis. HgCl, forms a crystalline compound. A promo facetoacetic ether forms CH., C(NH).S.CH., CO.CH., CO.Et. [94°]. and

gives Ag.S. CuSO, and rolOAc), give, on coling, CuS and Pigs. HgCl, forms a crystalline compound.

of brome aceteacetic ether forms CH, C(NH).S.CH, CO.CH, CO, Et [94"], and finally SCH: C.CH, CO, Et (239°), the ether of methyl-thiazyl-acetic acid [121"] (Steude, A. 261, 36). The ether melting at 94° is converted by warming with water into the compound CH, CO.S.CH, CO.CH, CO, Et (155° at 15 mm.), whence H, SO, forms an acid C, II, SO, [168°].

THIO ACETIC ACID C. H. SO i.e. CH., CO.SH. Mol. w. 76. (93°). S.G. 1º 1·074. Prepared by distilling acetic acid with P.S. (Kekulé, A. 90, 311; Ulrich, A. 109, 272; Kekulé a. Linnemann, A. 123, 273). Obtained also from AcCl and KSH (Jacquemin a, Vosselmann, J. 1859, 354), by heating lead acetate with Na,S.O., (Fröhde, Z. 1866, 543), and by the action of KSH on an alcoholic solution of PhSAc (Kekulé, Z. [2] 3, 196). Colourless liquid, turning yellow on keeping. Smells like acetic acid and H.S. Not solid at -17°. M. sol. warm water, v. sol. alcohol and ether. Violently attacked by fuming HNO. PCl. yields AcCl. PSCl., and HCl. Its neutral solutions give pps. with AgNO. and HgCl., which quickly turn black. Molten ZnCl., forms CMciS.; CMc [225°], which may be crystallised from hot alcohol (Bongartz, B. 19, 2182). HCl passed into a mixture of thio-acetic acid and benzoic aldehyde forms (CH., CO.S.), CHPh [148°], crystallising from hot ether in slender needles.

Salts. -KA'. Crystals, v. sol. water and alcohol. -NaA' haq. - BaA', 2 aaq. - SrA', 2 aq. - CaA', 2 aq. - PbA', Silky needles (from hot water or alcohol). Quickly decomposes, with separation of PbS.

Methyl ether MeA'. (96°). Formed by heating AcBr with Me₂S at 100° (Cahours, Bl. 25, 562; Wallach a. Bleibtren, B. 12, 1062). Formed also from AcCl and Pb(SMe)₂ (Obermeyer, B. 20, 2920).

Ethyl ether Eth. (116° i.V.). Formet from AcCl and NaSEt (Saytzeff, Z. [2] 4, 642; Beckmann, J. pr. [2] 17, 461). Formed also from PhOAc and NaSEt (Seiffert, J. pr. [2] 31, 468). Colourless liquid, with alliaceous odour. Oxidised by AgMnO, to acetic acid and ethane sulphonic acid.

n-Propyl ether PrA'. (136°).

Isopropyl ether PrA'. (126°).

Isobutyl ether CH₂PrA'. (149°).

Anhydride v. Acetyl sulphide.

Thio-acetic acid CH₂CS.OH.

Amide v. Thioacetamide.

Anitide CH_xCS.NHPh. [75°]. Formed from CH_xCCl:NPh and H_zS (Leo, B. 10, 2134). Prepared by heating acctanilide with P.S. at 100° (Hofmann, B. 11, 339; Jacobsen, B. 19, 1071). Yellowish needles (from water). So, NaOHAq and reppd, by acids. On oxidation with alkaline K_xFeCy_o it yields ethenyl-amidophenyl mercaptan. MeI forms C,H_xNSMeI or (CH_xCS.NPhMe)HI [139°), which yields an aqueous solution from which AgNO_x at once

ppts. AgI, and which is converted by AgCl into ppts. AgI, and which is converted by AgCl into C.H.NSMeCl, whence (C.H.NSMeCl), PtCl, may be got (Bernthsen, A. 192, 56). NaOEt forms CH. C(SMe):NPh, whence Mel yields the ether CH. C(SMe):NPh (245°) (Wallach a. Bleibtreu, B. 12, 1061; 13, 529), which is decomposed by Mel at 100° into methyl thioacetate and methyl-aniline. NaOEt and EtBayield the corresponding CH. C(SEt):NPh, a heavy oil, insol. alkalis, split up by warm HClAq into thioacetic ether and aniline. 'Ethyl-iso-thioacetanilide' yields (C.H.H.NS).H.PtCl. (C10H18NS),H,PtCl6.

Methyl anilide CH, CS.NMePh. [59° (290°). Formed from AcNMePh and P₂S, (Wallach, B. 13, 528). Monoclinic tables, v. sol.

o-Toluide CH, CS.NHC, H, [68°]. Yields CH, C(SEt):NC, H, Me (262°), an oil which reacts

with bases forming amidines and EtSH.
p-Toluide [132°]. Yields oily
CH, C(SEt):NC,H, (273°) (Wallach a. Wüsten, B. 16, 147).

Xylidide CH, CS.NHC, H, Me. [80°] (G.); [95°] (Jacobsen). Formed by heating acetyl-xylidine with P,S, on the water-bath (Gudeman,

B. 21, 2551). V-Cunidide CH₃.CS.NHC,H₂Me₃.

Prisms (Jacobson a. Elley, B. 22, 907).

(a) Naphthalide CH₃.CS.NHC₁₀Π₁. [96°].

Tables. Formed from naphthyl-acetamidine and CS₂ (Bernthsen a. Trompetter, B. 11, 1760).

(3)-Naphthalide. [146]. Needles or plates (Jacobsen, B. 21, 2627). Oxidised by K, FeCy.

to C, H, S CMe [81°].

Tri-thio-ortho-acetic acid CH₃.C(SH)₃.

Ethyl ether CH₃.C(SEt)₃. Formed from mercaptan, CHCl₃, and N₁₁OH at 100° (Laves, B. 25, 854). Brownish liquid. Ox KMnO, and H.SO, to the trisulphone. Oxidised by

Benzyl ether CH₃.C(SC,H₃)₃. [46°]. Formed from benzyl mercaptan, CHCl₂, and (2 p.c.) NaOHAq (Laves). Crystals, v. sol. CHCl₃, m. sol. alcohol.

THIO-ACETIC ALDEHYDE. On passing H.S into an aqueous solution of aldehyde, crude thioacetic aldehyde separates as an oil, which solidifies at -8° , and then melts at -2° . This oil [V.D. 60 (H = 1)] is a mixture of thioacetic aldehyde and its polymerides, and may be represented, in a state of vapour, as $C_2H_4S + C_0H_{12}S_3$ (Pinner, B. 4, 258; Klinger, B. 9, 1893; 10, 1877; 11, 1023). On distillation, or on passing HCl through the liquid, it is converted into the polymeric tri-thio-tri-acetic aldehyde.

Tri-thio-tri-acetic aldebyde C.H.S., Mol. w. 180. [46°]. V.D. 89.7 (calc. 90) (Hotmann, B. 3, 589; Z. [2] 6, 699). Formed by passing H.S into an acid solution of aldebyde (Klinger; of. Weidenbusch, 4. 66, 152; Crafts, C. R.54, 1279). Formed also from parallelyde and H₂S. White needles, sol. alcohol and ether. Smells like garlic. AgNO₂ added to its alcoholic solution forms crystalline C₈H₁₂S₃2AgNO₂. Chlorine forms ethylidene chloride (Pinner, A. 179, 21). KMnO₄ oxidises it to CH₂CH(SO₄H), and oxysulphides, including C₄H₁₂S₂O₅ [217°], which crystallises from hot water in needles (Guareschi, A. 222, 301). Zinc permanganate values of M. S.O. which deep at weather the control of the control produces CaH12SaO, which does not melt below

245°, C,H₁₂S,O, [112°-116°], and C.H.S.O. [228°-231°] (cf. Baumann, B. 26, 2074). (a)-Tri-thio-tri-acetic aldehyde C.H. S. i.c. CHMe S.CHMe S. [102°]. (247°). V.D. 6 (air = 1). Formed by the long-continued action of H.S on a mixture of equal parts of water, conc. HClAq'andaldehyde. Long prisms (from acetone). Reduced by HI to Et₂S₂. Oxidised by KMnO₄ to C₄H₁₂S₂O₄ [284°] (S. 1 at 100°; '116 at 20°), and C₄H₁₂S₂O₄ or C₂H₄ SO₂C₂H₄ SO₂. which softens at 340° and is converted by MeI into C_uH₁₈S₁O_a [302°]. Yields crystalline C_aH₁₂S₂AgNO₃ and C_aH₁₂S₂AgNO₃.

 (β) -Tri-thio-tri-acetic aldehyde $C_*H_{12}S_*$. [126°]. (247°). V.D. 6·0. Formed by the action of AcCl or H.SO, on its (a)- isomeride. Prepared by passing H.S into a mixture of aldehyde (1 pt.) and alcohol previously saturated with HCl (3 pts.) (Baumann a. Fromm, B. 22, 2600; 26,2074). Long needles (from alcohol). Oxidised by KMnO, to the same sulphones as the (a)isomeride. Reacts with MeI, yielding SMe₃I. Distillation with Cu forms \(\psi\)-butylene.

Ostination with Cut forms q-butylene. Forms crystalline C₄H₁₂S₄AgNO₂ and C₄H₁₂S₃AgNO₂.

(γ)-Tri-thio-acetic aldehyde C₄H₁₂S₂, [76°].

(242°). Formed, together with C₅H₁₂NS₃, by boiling thialdine sulphocyanide with water (Marckwald, B. 19, 1827; 20, 2817). Needles (from alcohol), insol. water, v. sol. ether and CS. Volatile with steam. Sol. conc. H.SO. and reppd. by water. When mixed with EtI (4 pts.) and left for some weeks it suddenly (4 pts.) and left for some weeks it studently changes to a crystalline mass of the (β)-isoneride. C₄H₁,S₅3AgNO₃. Plates, v. sol. water. Yields Ag₂S on boiling with alcohol.

'Di - thialdehyde thiocarbimide' C₅H_pNS₂. [138°]. Formed as above. Needles, n. sol. ether. Yields C₅H_pNS₂AgNO₂ v. sol.

nh. sol. ether. Hens Ostanovasor water, and (C₃H₂NS₃).PtCl₂.

Di-thio-acetic orthoadehyde. Ethyl ether CH₃.CH(SEt)₂. Formed by passing HCl into a mixture of acetic aldehyde and EtSH (Baumann, B. 18, 884). Mobile oil. THIOACETIC ANHYDRIDE v. ACETYL SUL-

THIO-ACETONE *CH, CS.CH, A product of the action of H,S on acetone, and formed also when CMe₂(SEt)₂ is heated above 160' (Baumann a. Fromm, B. 22, 2592). Volatile oil, with very persistent and disagreeable smell. Unstable.

Duplo-thioacetone C₆H₁₂S₂ i.e. S<CMe₂>S. V.D. 5.08 (calc. 5.11). (184° cor.). Formed by heating acetone with P.S. at 125° (Wislicenus, Z. [2] 5, 324; Autenrieth, B. 20, 375). Formed also by heating tri-thio-tri-acetone at 200° for some time (Fromm a. Baumann, B. 22, 1043). Oil. Its alcoholic solution gives a white pp. with HgCl₂. Reduced by sodium-amalgam to isopropyl mercaptan (Spring, Bl. [2] 40, 69). Oxidised by a 5 p.c. solution of KMnO, to the disulphone SO₂ CMe₂ SO₂ [220°-225°].

Tri-thic-tri-acetone U₂H₁₈S₂ i.e.

S<CMe. S CMe. [24°]. (130° at 15 mm.). Formed, together with C13H28S4 [171°], by passing H,S into a cooled mixture of acetone and cone. HClAq (Fromm a. Baumann, B. 22, 1037, 2597). Needles (from alcohol); insol. water, v. sol. alcohol and ether. Boils, with much decomposition, at 225°-230°. Gives a white pp. with HgCl2 and a yellow pp. with lead acetate. Potassium permanganate and H₂SO₄ yield the trisulphone SO₂ CMe₂ SO₂ CMe₂ [302°] and

SCMe₂·SO₂CMe₂ [208°].

Duplo-di-thio-acetone (Me₂CS₂)₂. (c. 243°). Formed from acetone and yellow ammonium sulphide in the cold (Willgerodt, B. 20, 2467). Dimetric crystals, a:c=1: 868, insol. water. Partially decomposed on distillation.

Di-thio-orthacetone. Di-ethylether CMe (SEt)2. Acetone-cthyl-mercaptol. (191°). Formed by passing dry HCl into a mixture of acetone (1 pt.) and mercaptan (2 pts.) (Baumann, B. 18, 887). Liquid.

Di-phenyl ether CMe, (SPh),; v. Dr-PHENYL-PROPYLIDENE DISULPHIDE.

THIOACETONURAMIC ACID v. ACETONYL

THIOCARBAMATE

THIO - ACETOPHENONE C.H.CS.CII, [119.5°]. Formed by the action of alcoholic ammonium sulphide on acetophenone (Engler, B. 11, 930). Colourless leaflets or needles, insol. water, sl. sol. alcohol, v. sol. ether. May be sublimed.

THIO-ACETYL-TOLUIDINE v. Toluide of

THIO-ACETIC ACID.

THIO-ALLOPHANIC ACID. Ethyl ether C.H.aN.SO. i.e. NH.CO.NH.CO.SEt. [180]. Formed by heating urea with Cl.CO.SEt at 80°-90° (Peitzsch a. Salomon, J. pr. [2] 7,477). Pearly needles (from water), v. sl. sol. cold water and alcohol. Aqueous NH, at 100° forms biuret and mercaptan. Boiling baryta-water gives allophanic acid and mercaptan. Aniline yields di-phenyl-biuret and mercaptan.

Isoamyl ether NH_CO.NH.CO.SC.H.,.. [176]. Needles (Schöne, J. pr. [2] 32, 251). AcCl yields an acetyl derivative [859]. Phenyl ether [2189] (Gattermann, A.

244, 43).

Isothio-allophanic ether NH2.CS.NH.CO2Et. [170°-175°]. Formed by the action of thio-urea on COCl.CO.Et (Peitzsch, B. 7, 896). Prisms (from alcohol).

Di-thio-allophanic ether NH, CS.NH.CO.SEt. Formed from KSCy, alcohol, and HCl (Blankenhorn, J. pr. [2] 16, 358). Pearly prisms, insol. cold water, sol. hot ether. Alcoholic NII, at 150° forms thio-urea. Baryta-water yields

mercaptan, CO., and thio-urea.

DI-THIO-AMMELIDE C₃H₁N₁S₂ i.e.

C₃N₄(NH₂)(SH)₂. S. 3 at 100°. Formed by boiling pseudosulphocyanogen C₃HN₅S₂ with KSH or ammonium sulphide solution (Jamieson, A. 59, 339; Ponomareff, J. R. 8, 222). Small needles, nearly insol. cold water, alcohol and ether, v. sol. aqueous ammonium sulphocyanide. Acid in re-

aqueous ammonum sulphocyanide. Acid in reaction, decomposing carbonates.

Reactions.—1. Yields cyanuric acid when heated with HClAq.—2. NH,Aq forms melamine C,H,N, by heating in a Scaled tube.

Salts.—NaHA"1\frac{1}{3}aq. Tables.—KHA"2aq.

White prisms, v. e. sol. water and alcohol.—
MgH_A"_6aq.—CaH_A"_2aq.—BaH_A'"_5aq.—BaH_A'"_5aq. Monoclinic crystals, sl. sol. cold

water.—SrH,A",4aq.—AgHA". Flocculent pp. insol. water.

insol. water.

Methyl ether C₃N₄(NH₂)(SMe), [2007].

Formed by heating C₃N₄(SMe), with alcoholic NH₄ for five hours at 100° (Hofmann, B. 18, 2756). Trimetric tables, v. al. sol. water, v. sol. alcohol. Boiling cone. HClAq forms MeSH, cyanuric acid. and NH₄.—B'HAuCl₄. Needles.

Ethyl ether EfA". [112°]. Formed by heating tri-thio-cyarpine ether with alcohol NH₄ at 180° (Klason, J. fr. [2] 33, 298). Trimetric prisms. Converted by acids into ammelide.

Isoamyl ether (0₂H_{11),2}A". [82°].

Di-thio-methyl ammelide di-methyl ether Cy₂(NHMe)(SMe), [175°]. Formed by heating Cy₃(SMe), with aqueous NMeH₄ (Hofmann, B. 18, 2761). Needles or prisms (from dilute alcohol).

dilute alcohol)

THIO-AMMELINE C.H.N.S i.e.

C(SII) N.C(NII₂) N. S. 77 at 100° (K.)

Formed by adding HCl to an aqueous solution of dievan-diamide and ammonium sulphocyanide or devan-duame and am some supprocyanic pat 100° (Rathke, B. 18, 3106; 20, 1059; 23, 1675). Formed also from C₂N₄(NH₂)₂Cl and KSH (Klason, J. pr. [2] 33, 296) and by heating \(\psi\$-sulphocyanogen with cone \text{NHAq at 100°} (Ponomareff, C. R. 80, 1384). Needles, sl. sol. hot water, v. sol. acids and alkalis. Yields a canary-yellow pp. on boiling with ammoniacal CuSO,. Cone. HClAq at 130° yields cyanuric acid, H₂S, and NH₂. Ethylene bromide forms crystalline C₃H₁N₃SHBr. Conc. NH₂Aq at 200° forms melamine. Boiling NaOHAq yields ammeline. Ammoniacal silver nitrate ppts. C₂H₁N₂SAg and C₄H₂N₃SAg₂. Bromine added to a solution of thio-ammeline in HBrAq forms S₂(C₃N₃(NH₂)₂)₂, which dissolves in alkalis, and is split up by boiling with acids into ammeline, thio-ammeline,

Salts. B'IINO. Needles. B'H2SO.3aq.
B'H2C.O.aq. Needles, v. sl. sol. cold water.
Methyl ether MeA'. [268°]. Formed by heating tri-methyl tri-thiocyanurate for five hours with conc. alcoholic NH, at 160° (Hofmann,

B. 18, 2757). Tables (from water).—B',H,PtCl,. Ethyl ether EtA'. [165°]. Isoamyl ether C,H,A'. [178°]. Reference.—TRI-PHENYL-THIO-AMMELINE. THIO-ANILINE v. DI-AMIDO-DI-PHENYL SUL-

THIOANISOIC ACID (so called) C10H14SO4. Got by boiling anethol with HNO, (S.G. 1.1), distilling the product and shaking the fraction 215°. 245° with cone. NaHSO,Aq and some alcohol (Städeler a. Wächter, A. 116, 163). Crystalline (containing 2aq), v. e. sol. water, alcohol, and eiher.—NH,A'aq.—NaA' aq. S. 15 in the cold.—BA', 2aq.—MgA', 5ad.—AgA'. Plates, m. sol. water.

THIOBENZAMIDE v. Amide of THIOBENZOIC

(a)-THIO-BENZOIC ACID CaH, CO.SH. Mol.

w. 138. [c. 24°].

Formation.-1. From BzCl and alcoholic K.S (Engelhardt a. Latschinoff, Z. [2] 4, 353). 2. By boiling EtOBz, PhOBz, and Bz.O with alcoholic KSH.

Properties .- Yellow oil or white crystalline mass with unpleasant smell, volatile with steam. Decomposed by distillation. V. sol. alcohol and

ether. Its solutions, when exposed to air, deposit crystals of Bz₂S₂. Nitric acid also oxidises it to benzoyl disulphide. A neutral solution

it to benzoyi disulphide. A neutral solution gives with CuSO₄ a greenish-yellow pp., turning bright red; the pp. then containing Bz₂S₂.

Salts.—KA'. Large prisms (from alcohol), v. sol. water.—NaA'.—BaA'₂ zaq. Laminæ (from alcohol).—PbA'₂.—AgA'. v Yellowisho white pp.

Methyl ether C_cJ₂.COSMe. (232°).

Formed from Pb(SMe)₂ and EzCl (Obermeyer, B. 2020).

20, 2922).

20, 2922).

Ethyl ether Eth'. (243°). Formed by the action of BzCl on Pb(SEt), in presence of ether (Tütscheff, Petersb. Acad. Bull. 5, 295), and got also by bolling AgA' and Etl, and from PhOBz and NaSEt (Seiffert, J. pr. [2] 31, 471). Oil, with unpleasant smell, sol. alcohol and ether. Belling alcoholis VOM. Boiling alcoholic KOH forms KOBz and KSEt. Alcoholic KSH yields KSBz and KSEt. Oxidised by AgMnO, to benzoic and ethane sulphonic acids

(Beckmann, J. pr. [2] 17, 464).

Isoamyl ether C₃H₁A'. (271°).

Phenyl ether PhS.B2'. [56°]. Formed from phenyl mercaptan and BzCl Schiller a. Otto, B. 9, 1635). Needles (from benzene)

Di-nitro-phenyl ether C_sH₃(NO₂)₂A'.

[118°]. Formed from (a)-chloro-m-di-nitro-benzene, alcoholic KSH, and BzCl (Willgerodt, B. 18, 328). Needles (from alcohol).

Benzyl ether C,H,A'. [39·5°]. Formed from benzyl mercaptan and BzCl (Otto a. Lüders, B. 13, 1286). Triclinic crystals, yielding

PhCH. SO.H on oxidation. p. Tolyl ether C,H,A'. [75°] (S. a. O.).

Annydride v. BENZOYL SULPHIDE.

(B)-Thic-benzoic acid CaH5.CS.OH. Formed by boiling thiobenzoic aldehyde with nitric acid (S.G. 13) (Fleischer, A. 140, 234). Needles (containing ½aq), sol. alcohol and benzene. More sol. hot water than benzoic acid. When heated strongly it blackens without melting .- BaA'24aq.

Small nodules, v. sol. water and ppd. by alcohol.

Amide C. H. CS. NH. Thiobenzamide. [116°]. Formed by passing H2S into an alcoholic solution of benzonitrile containing a little NH, and heating on a water-bath (Cahours, C. R. 27, 329; Bernthsen, B. 10, 1241; A. 192, 49; Gabriel a. Heymann, B. 23, 157). Formed also by heating benzylamine (2 mols.) with S (1 mol.) at 180° (Wallach, A. 259, 304). Long needles (from hot water). Decomposed by HgO, yielding HgS and benzonitrile. Sodium-amalgam acting on its alcoholic solution forms amorphous thiobenzoic aldehyde, benzonitrile, benzylamine, and benzoic aldehyde. Iodine added to its alcoholic solution reacts with formation of di-benzenyl-azo-sulphim

 $C_{e}H_{s}.C \underset{N}{\overset{N.S}{>}} C.C_{e}H_{s}, \text{ crystallising} \quad \text{in long}$

colourless needles [90°] converted by boiling H_SO, into a base C₁,H₁,N₂ [71°], which yields B'_2,H_2,PtCl₄ (Hofmann, B. 2, 645; B. 25, 1587; Wanstrat, B. 6, 335). Zinc and HCl reduce thiobenzamide in alcoholic solution to benzylamine. Hydroxylamine forms C₆H₅.C(NOH).NH₂. Ethylene bromide at 100° forms the compound C.H. (S.C(NH)C.H.),2HBr [233°] decomposed by boiling water into C,H₁(SBz)₂ (Gabriel a. Heymann, B. 24, 783). Chloral (1 mol.) forms, on warming, a compound C,H₂Cl,NSO or C,H₂Cl,NS

silky plates [104°], sl. sol. water, v. sol. alcohol (Spica, G. 16, 182).

Anilide C.H., CS.NHPhor C.H., C(SH):NPh. Thiobensanilide. [102°]. Formed by the action of P.S. (1 pt.) on benzanilide (2 pts.), and by heating phenyl-benzamidine or s-di-phenyl-benzamidine CPh(NPh)(NPhH) with H.S or with CS₂ (Bernthsen, B. 11, 503; A. 192, 31). Formed also by passing H₂S into a solution of C₄H₄.CCl:NPh in benzene (Leo, B. 10, 2133), and from benzophenone oxim and P2S, (Dodge, A. 264, 184). Obtained by heating benzyl-aniline 264, 184). Obtained by heating benzyl-aniline (1 mol.) with S (2 at.) at 220° as long as H₂S escapes (Wallach, A. 259, 301). Thin prisms (from EtOAc), nearly insol. boiling water, v. sol. alcohol and ether. V. sol. KOHAq. Converted into benzanilide by heating with dry PbO or with alcoholic potash at 150°. Yields benzenyl-o-amido-phenyl-mercaptan on dry distillation, on baction with S and alcoholic returnest in alkaling heating with S, and also on treatment in alkaline

solution with K₂FeCy₆ (Jacobsen, B. 19, 1068). Hydroxylamine yields C₆H₂.C(NOH).NHPn. o-Toluide C₆H₃.CS.NHC₆H₄Me [1:2]. [86°]. Formed by melting BZNHC₆H₄Me with P₂S₅. (Stieglitz, B. 22, 3160). Yellow, six-sided prisms (from benzene). Hydroxylamine in alcohol forms, on heating, C.H. C(NOH).NHC,H, [147°], crys-

tallising in needles.

p-Toluide. [129°]. Formed in like manner (Miller, B. 22, 2405), and also by the action of H.S on C₆H.,CCl:NC,H, (Leo, B. 10, 2134; Pfitzinger a. Gattermann, B. 22, 1065), and by heating p-tolyl-benzamidine with CS₂ (Bernthsen a. Trompetter, B. 11, 1759). Long yellow needles, insol. water, v. sol. alcohol, ether, and

Xylide C, H, CS.NHC, H, Mo. [90°]. Formed by heating the benzoyl derivative of (4,2,1)-xylidine with P_2S_3 (Gudeman, B. 21, 2552). Small needles (from alcohol). Oxidised by

 K_sFeCy_s to oily $C_sH_2Me_2 < N > CPh$.

Di-phenyl-amide C,H,CS.NPh, [151]. Triclinic crystals (Bernthsen, A. 192, 37).

(a) Naphthallide v. vol. iii. p. 474.

Di-thio-benzoic Acid C₆H₂.CS.SH. Formed by adding an alcoholic solution of K₅S to C₆H₂.CCl₄ (Engelhardt a. Latschinoff, Z. [2], 4,455; Klinger, B. 15, 862). Heavy, red oil, v. sol. alcohol and ether. Its dilute ethereal solution is crimson. Resinifies when exposed to air. —PbA'₂. Thin orange-red needles (from alcohol or xylene).—HgA'₂. Golden plates (from alcohol).—AgA'. Brown pp., insol. water and benzene. References. — Oxy-THIO-BENZOIO ACID and

AMIDO-THIO-BENZAMIDE.

(a)-THIO-BENZOIC ALDEHYDE CaHs. CHS. Bensylidene sulphide. Formed by passing H.S into an alcoholic solution of benzoic aldehyde (Laurent, A. Ch. [3] 1, 292; Klinger, B. 9, 1895; 15, 863; Böttinger, B. 12, 1056), or of hydrobenzamide (Cahours, C. R. 25, 457). White amorphous powder, softening at 85°, decomposed at a higher temperature. Insol. water and cold alcohol, v. e. sol. benzene and chloroform. Does not combine with KHSO, or HCy. Potash-fusion yields benzyl mercaptan. heating with copper it forms Cus and s-di-phenylethylene. Alcoholic KSH on heating forms Ph.CS.SK and di-benzyl disulphide. Thioglysollic soid forms C.H. CH(S.CH, CO,H), [124°]

(Bongartz, B. 21, 479).

(β)-Thio-benzoic aldehyde (C_cH₁.CHS)_x.

[225°]. Formed from the (a) isomeride by treatment with AcCl, EtI, or a little iodine in benzene (Klinger, B. 10, 1877). Prepared by penzene (Klinger, B. 10, 1877). Prepared by passing H_S into a mixture of benzoic aldehyde and alcoholic HCl (Baumann a. Fromm, B. 22, 2604). Needles. Crystallises from benzene as (C.H.-S), C.H., and gives off its benzene at 130°-140°. V. sol. hot HOAc. m. sol. alcohol. On heating with copper-powder it yields CuS and di-phenyl-ethylene. di-phenyl-ethylene. An oily compound (C,H,S),H,S is formed, together with benzyl disulphide and di-thio-benzoic acid, by the action of alcoholic KSH on benzylidene chloride (Klinger, B. 15, 864). This compound yields benzoic acid on treatment with dilute HNO,

(γ)-Thio-benzoic aldehyde C₆H₅CHS. [167°]. Occurs in the benzene mother-liquor in the preparation of the (B) - isomeride (B. a. F.). Small pointed needles, much more sol. benzene and chloroform than the (β) -modification, sl. sol. alcohol and ether. Its crystals do not contain benzene of crystallisation. By adding iodine to its solution in benzene it is changed to the

(β)- isomeride.

Thio-benzoic orthaldehyde C₆H₃.CH(SII).

Methyl ether C, H, CH(SMe)2. Formed by passing HCl into a mixture of benzoic aldehyde and MeSH (Bongartz, B. 21, 487). Oil. Oxidised by KMO, to C₆H, CH(SO₂CH₈), [163°].

Ethyl ether C₆H₅, CH(SEt), Oil (Bau-

mann, B. 18, 885).

p-Bromophenylether CuH.,CH(SCuH,Br). [80°]. Silky needles (Bau-

mann, B. 18, 885).

Reference .- NITRO-THIO-BENZOIC ALDEHYDE. THIO-BENZOPHENONE C.H. CS.C.H.

Formed by heating CSCl2 (5g.) with benzene (25 g.) and AlCl_a (9 g.) (Bergreen, B. 21, 337). Reddish-brown oil, v. sol. ether, benzene, and hot alcohol. Decomposed by distillation. acts with hydroxylamine, forming Ph2C:NOII and with phenyl-hydrazine, with production of CPh2:N2HPh.

Thio - benzophenone (CSPh₂)_z [146·5°]. Formed from CCl₂Ph₂ and K₂S (Engler, B. 11, 922). Small white needles. Converted by CrO₄ and HOAc into benzophenone. Does not react with hydroxylamine or phenyl-hydrazine.

THIO-BENZOYL-(a)-NAPHTHYLAMINE v.

THIO-SELL PARTY OF CPH. H.S. i.e. THIOBENZPINACONE C. H.S. i.e. CPh. H.S. S. CPh. H. CPh,(SH).CPh,(SH) or CPh,H.S.S.CPh,H. [151°]. Formed from benzophenone by the action of alcoholic ammonium sulphide (Engler, B. 11, 922) or P.S. (Japp a. Roschen, C. J. 49, 479), and, together with thiobenzophenone, by the action of KSH on C_aH_a.CCl_xC_aH_a (Behr, B. 5, 970). Formed also by the action of alcoholic KSH on (C_eH₃) CHCl, and of P₂S₃ on di-phenyl-carbinol. Slender needles (from alcohol), v. sol. CS. In alcoholic solution it is converted by finely-divided copper into tetra-phenyl - ethane CHPh. CHPh.

THIO-BIURET C.H.N.OS. Formed by boiling carbimido-urea ('amidodicyanic acid') with ammonium sulphide (Wunderlich, B. 19, 452). Needles (containing aq). Sol. hot water and alkalis, v. sl. sol. ether. Gives a white pp Vol. IV.

with copper salts. By ammoniacal AgNO, it is converted back into carbimido-urea.

THIO-BUTTRIC ACID C.H.SO i.e. CH₃CH₂CH₂CO.SH. (180°). Formed by distilling butyric acid with P₂S₃ (Ulrich, 4. 109, 280). Liquid with disgusting smell, v. sl. sol. water, v. sol. glochol₂-PbA'₂. Small crystals (from hot water).

(from hot water).

Thio-isobutyric acid. Methyl other
C₃H₁₀SO i.e. Pr.CO.SMe. (c. 142°). V.D. 57°5.

(Obermeyer, B. 20, 2022). Oil.

THIO-ISOBUTYRIC ALDEHYDE PrCHS. (70°-90°). A product of the action of S on isobutyric aldehyde at 180° (Barbaglia, G. 18,

(a)-THIO-CARBAMIC ACID NH..CO.SH. This acid, set free by adding acids to a solution of its ammonium salt, splits up at once into COS and ammonia. The ammonium salt COS and ammonia. The ammonium sair NH_CO.SNH₄ is prepared by passing gaseous COS into alcoholic NII₄ (larthelot, J. 1868, 160) or into NII₄Aq at 0° (Schmidt, B. 10, 191; Kretzschmar, J. pr. [2] 7, 474). It forms colourless crystals, v. c. sol. water, m. sol. alcohol, insol. ether. The dry salt becomes pollow in air, forming ammonium sulphocyanide. The dry salt forms thio-urea when heated in a sealed tube at 135°. Thio-urea is also formed when Pb(OH)2 is added to its cold aqueous solution. HgO forms, in the cold, ammonium cyanate (Fleischer, B. 9, 438). Water at 100° forms NH₄SH and (NH₄)HCO₃. FcCl₃ gives a red liquid, and finally a red pp. (Mulder, **2**. 168, 228).

Methyl ether NIL.CO.SMe. Formed, together with a small quantity of the (B)isomeride, by adding HCl to a solution of potassium sulphocyanide in boiling McOH (Blankenhorn, J. pr. [2] 16, 375). Monoclinic prisms (from ether). Decomposed by alcoholic NH₂ into MeSH and urea. Aniline at 100° forms

into MeSH and urea. Amuno MeSH, s-di-phenyl-urea and NH₃.

NH CO.SEt. [102°] (Pinner, 102°) B. 14, 1083); [108°] (F.). Formed in like manner (B.) and also by passing NH, into Cl.CO.SEt (Salomon, J. pr. [2] 7, 256) and by the action of EtBr on NII, CO.SNH, (Fleischer, B. 9, 991). Plates, v. sol. hot water, alcohol, and ether. Decomposed at 150° into mercaptan and cyanuric acid. P₂O₅ converts it into ethyl sulphocyanide.

Isoamyl ether CO(NH₂).SC₅H₁₁. [107°]. From CO(SC₅H₁₁)Cl and NH₂ (Schöne, J. pr. [2] 32, 247). Glittering plates (from ether). Sol. hot water, but decomposed by boiling water.

Gives amorphous pps., insol. water, alcohol, and ether with AgNO₃, HgCl₂ and PtCl₄.

Reactions.—Alcoholic NH, forms urea and amyl mercaptan.—2. Alcoholic KOH forms K₂CO₃, NH₃ and amyl mercaptan.—3. Heated with aniline it forms NH₃, HSC₃H₁₁, and diphenyl-urca.

(B) Thio-carbamic acid NH2.CS.OH.

Methyl ether NH, CS.OMe. [48°] . Formed by the action of alcoholic NH, on MeO.CS.SMe or on MeO.CS.SEt (Salomon, J. pr. [2] 8, 115).

Ethylether NH, CS.OEt. Xanthogenamids.

[38°]. Formed by the action of NH, on zantho-genic ether EtS.CS.OEt, on MeS.CS.OEt, and on (EtO.CS),S, (Debus, A. 72, 1; 75, 121; 82, 258; Chancel, J. 1851, 513; Salomon a. Maintz, J. pr. [2] 8, 114). Monoclinic prisms, al. sol. water, miscible with alcohol and ether. Decomposed on distillation into mercaptan and eyanic acid. Boiling KOHAq resolves it into syante acid. Boiling Koriaq resolves it into alcohol and potassium sulphocyanide. P.O. forms ethyl sulphocyanide (Correl, J. pr. [2] 10, 34). Nitrous acid passed into water containing xanthogenamide in solution forms crystalline C.H., N.SO. CuSO, followed by HCIAq ppts. C.H., NOSCuCl as a white crystalline powder, nearly insol. water, sol. hot alcohol. Compounds of CuCl with 2, 3, and 4 mols. of xanthogenamide may be obtained. KI added to a boiling alcoholic solution of (C₃H,NOS)₂CuCl forms crystals of (C₃H,NOS)₂CuI and (C₄H,NOS)₂CuI. Compounds (C₃H,NOS)₂3GaSCy and C.H. NOSCuSCy may also be prepared (Debus). Isovaleric aldehyde in presence of HCl and alcohol forms C,H,,CH(NH.CS.OEt),[108°] (Bischoff, B. 7, 1083). B - Iodo propionia acid forms NH, CO.S.CH,CH,CO.H [147-5°], which yields CaA', 3aq, BaA', 2aq, and Ag,A" (Langlet, B, 24, 3849). \$-Iodopropionic acid and Ac,O yield sinapano propionio acid CO S CH2 CH2 [159°], v. sol. hot water, converted by HgO into the mercaptide of β -thiolactic acid.

Isobwyl ether NILCS.OCH,Pr. [36°].
Tables (from alcohol or ether) (Mylius, B. 5, 976; Blankenhorn, J. pr. [2] 16, 380).
Isoamyl ether NILCS.OC,II, Oil (Johnson, C. J. 5, 242).

(Johnson, C. J. 5, 242).

Di'shio-carbamic acid NH...CS.SH. Mol. w.

93. The ammonium salt NH...CS.SNH, is formed by passing NH, (from 150 pts. NH,Cl) into 95 p.c. alcohol (600 pts.) containing CS. (96 pts.) (Mulder a. Bettink, J. pr. 103, 178; cf. Zeiso, A. 48, 95; Debus, A. 73, 26). It is also formed by heating (NH,) CS,. On gradually adding HClAq to a cooled cone, solution of the ammonium salt the free acid separates as colourless needles, v. sol. water, alcohol, and ether; acid in reaction. An alcoholic solution of the acid gradually decomposes into CS, and the NH, salt. An aqueous solution of the acid decomposes on heating into H.S and HCyS. The di-thio-carbamates also split at 100° into H.S. and sulphocyanides. An alcoholic solution of lodine decomposes NH_CS.SNH, forming EtNCS and EiNH, (Hofmann, Z. [2] 5, 671). Ammonic di-thio-carbamate treated with HGl and solution of I gives crystals of the bisulphide (CSNH). Where I was a long to the bisulphide (CSNH). S₂(CS.NH₂)₂ (Klason, J. pr. [2] 36, 62). FeCl, added to a solution of the NH₄ salt gives a black pp. turned white by excess. AgNO, gives a yellow pp., turning black. A solution of aldehyde forms carbothialdine ?IH, CS, SN(C,H,),. Benzoic aldehyde, isovaleric aldehyde, and acrolein form analogous bodies.

Salts.—NH.A'. Deliquescent lemon-yellow prisms. On heating with KOHAq it forms K₂S, KSCy, and NH.—CuA'₂. Yellow powder, insol. water.—PbA'₂. White pp., blackening on boiling with water.—ZnA'₂; white pp.

Ethyl ether NH.CS.SEt. Mol. w. 121.

[42°]. Formed by passing H.S under pressure into ethyl sulphocyanide at 100° (Jeanjean, J. 1866, 501; Salomon a. Conrad, J. pr. [2] 10, 29). Trimetric crystals (from ether), insol. water, v. e. sol. alcohol. Alcoholic NH, or KOHAq in the

cold forms mercaptan and ammonium sulphocyanide.

Isopropyl ether NH. CS.SPr. [97].
Trimetric plates (Gerlich, A. 178, 82).
Acetyl derivative of the ethyl ether
NHAc.CS.SEt. [123]. Formed by heating thio-acetic acid with ethyl sulphocyanide (Chanlaroff, B. 15, 1987). Yellow needles (from alcohol), v. sol. hot water. Decomposed by distilla-tion into thio-acetic acid and ethyl sulphocyanide. Boiling baryta-water forms mercaptan and acetic acid. Hot dilute HClAq forms NH..CS.SEt.

Isothiocarbamic ether v. DI-ETHYL-(a)-THIO-CARBONATE. A mide.

THIO-CARBAMIDE v. THIO-UREA.

THIOCARBAMYL SULPHIDE C,H,N2S, i.e. (NH₂CS)₂S (?) Very unstable oil, got by adding HCl to its ammonium salt. Quickly decomposes into CS₂, sulphur, H₂S, and ammonium sulphocyanide. The ammonium salt C.H.₂(NH₁), N.S.₃ is a product of the action of CS. on alcoholic NH₂ in the cold (Zeise, B. J. 4, 98; Hlasiwetz a. Kachler, A. 166, 137). It forms colourless prisms, v. sol. water, m. sol. alcohol, sl. sol. ether. The moist salt slowly decomposes into H.S and ammonium sulphocyanide. The cupric salt CuC, II, N, S, is canary-yellow.

Thiocarbamyl disulphide C.H.N.S (NH_CS) S₂. Formed by the action of Cl on a solution of the ammonium salt of the preceding body, and on ammonium di-thio-carbamate (Debus, A. 73, 27). Perrly plates, v. sol. hot alcohol, insol. water. Decomposed by boiling water into CS, ammonium sulphocyanide,

THIOCARBIMIDES. Mustard oils. Compounds RN:CS. Essential oil of mustard is allyl thiocarbimide. They are formed by the action of CSCl₂ on primary amines (Rathke, A. 167, 218), and by the action of aqueous HgCl₂ on the dithiocarbamates RNH.CS.SNH₂R obtained by heating primary amines with CS, and alcohol or ether (Hofmann, B. 1, 171; 2, 452; 7, 811; 8, 106; Rudneff, J. R. 10, 188). Methyl sulphocyanide is partially converted into methyl thocarbimide by heating at 180°. Allyl sulphocyanide changes to the mustard oil on boiling. Thiocarbinides are also got by distilling alkyl cyanates with P₂S₃ (Miohael a. Palmer, Am. 6, 258). The thiocarbinides are pungentials. They are reduced by Zn and HClAq to amines and CH₂S, whereas sulphocyanides yield HCy, mercaptans, and other products. Amines convert thiocarbimides into thio-ureas; thus aniline combines with phenyl thiocarbimide, aniline combines with phenyl thiocarbimide, forming s-di-phenyl-thio-urea. Alcoholic potash, or alcohol at 100° forms thio-carbamic ethers NIH.CS.OF& (Hofmann, B. 2, 117; Schiff, B. 9, 1316). Water at 200°, or HClAq at 100°, forms amine, CO₂, and H.S, while with sulphocyanides it yields Et₂S, CO₂, and NH₃. Conc. H₂SO₄ forms amine and COS. HNO, forms amine and CO, whereas with the isomeric sulphocyanides it forms a sulphonic acid. Hydroxylamine unites with thiocarbimides, forming oxy-thio-ureas NIHR.CO.NH.OH. (Tieman, R. oxy-thio-ureas NHR.CO.NH.OH (Tiemann, B. 22, 1939). Chlorine unites with PhN:CS, forming unstable (PhNCS)2Cl2 whence boiling water

forms (PhNCS),0 [118°], crystallising in yellow needles (Helmers, B. 20, 786).

THIOCARBIMIDO-ACETIC ACID C,H,NSO, i.e. CH₄(N:CS).CO₄H. Formed by boiling thichydantoin with HClAq (Volhard, J. pr. [2] 9, 6), and by boiling isoamyl sulphocyano-acetate with and by bolling isosamy supprocyano-acetate with fuming HClAq (Classeon, B. 10, 1952; Heintz, A. 136, 232). Trimetric plates, v. e. sol. hot water. Oxidised by HNO, to H.SO, and oxalic acid. Weak acid.—BaA', aq. Four-sided prisms, sl. sol. cold water. Benzoic aldehyde and NaOHAq (1 mol.) react, forming the compound CHPh:C(CO₂Na).S.CO.NII₂, which crystallises with 1½ aq and is converted by HCl into CO.S NH.CO>C:CHPh [242°] (Andreasch, M. 10, 73).

THIOCARBIMIDO-BENZOIC ACID v. m-AMIDO-BENZOIC ACID.

THIOCARBONIC ACID.

Thiocarbonates v. vol. i. p. 703. The thiocarbonic ethers that have not been treated of in former articles are described below.

Methyl thiocarbonates v, vol. iii. p. 399.

Methyl iso-dithiocarbonate CO(SMe), (169°). Formed by warming methyl sulphocyanide with H₂SO₄ (Schmitt a. Glutz, B. 1. 166).
Ethyl thiocarbonates v. vol. ii. p. 520.
Ethylene thiocarbonates v. vol. ii. p. 493.

di-ethyl di-thio-di-carbonate C.H. (S.CO.Et). Formed by heating C.H. Br. with KS.CO.Et in alcohol (Welde, J. pr. [2] 15, 52). Thick oil, converted by alcoholic potash into C₂H₄(SH)₂ and KO.CO.Et.

Isobutyl di-thio-carbonic acid CH., Pr.O.CS. II. Salts.-NaA'. Formed from C,H,ONa and CS., Yellowish white needles, v. e. sol. water and alcohol.—KA'. Needles (from alcohol), S.G. 12 1:371 (Clarke, B. 11, 1505). Chlorine gas passed into its aqueous solution forms oily (CH₂PrO.CS)₂S₂ (Mylius, B. 5, 976).

Ethyl ether Eth'. (228°).

Isobutyl ether CH.Pr.O.CS.SCH.Pr. (249°). S.G. 12 1009 (Mylius, B. 5, 975).

Isoamyl ether CH₂l'1 (265°-270°) (Mylius).
Isoamyl di-thio-carbonic soid CH, Pr.O.CS.SC, H,...

C.H.,.O.CS.SH. Oil, with unpleasant smell. Salts.-KA'. Formed from fusel oil, KOH, and CS₂ (Balard, A. Ch. [3] 12, 307; Erdmann, J. pr. 31, 4; Desains, A. Ch. [3] 20, 505; Johnson, C. J. 5, 142). Gives a lemon-yellow pp. with CuSO₄.—PbA'₂. Plates. Iodine forms oily

(C,H,10.CS),S,... Di-isoamyl s-di-thio-carbonate CO(SC,H,1),... (281°) (Schmitt a. Glutz).

Cetyl di-thiocarbonate v. vol. i. p. 728. Iso-butyl-tri-thio-carbonic acid C₄H_aS.CS₂H. Formed from C, H, SNa and CS2 (Mylius, B. 6, 816). The Na salt crystallises in yellow needles, v. sol. alcohol and ether.

Isobutyl ether (C.H.S),CS. (287°). Got by heating aqueous K.CS, with isobutyl iodide.

Yellow oil with faint odour.
Di-isoamyl-tri-thiocarbonate Di-isoamyl-tri-thiocarbonate (C,H,S)₂CS. (247°). S.G. 88 (Husemann, A. 126, 297). Oil,

with unpleasant smell.

Di-allyl tri-thio-carbonate (C,H_sS)₂CS. (170°-175°). S.G. 94. Formed from allyl lodide and Na₂CS, in the cold (Husemann, A.

126, 269). Pungent yellow oil, with offensive odour.

THIOCARBONYL - ACETOACETIC ETHER CS:CAc.CO.Et. [156°-162°]. Formed from thio-carbonyl chloride and acctoacetic ether (Bergreen, B. 21, 347). Yellow needles, sl. sol, ether

THIO CARBONYL DI AMIDO DI BENZOIO

ACID v. m-AMIDO-BRYZOIG ACID.
THIOCARBONYL BENZOYL - ACETIC ETHER CS:CBz.CO₂Et. [164°]. Formed from CSCl, and benzoylacetic ether (Bergreen, B. 21, Yellow needles, sol. alcohol-chloroform. THIO CARBONYL CHLORIDE b. Sulpho-

Thio-carbonyl tetrachloride v. Pen-chloro-

chloride of CARBON.

METRYL-MERCAPTAN.

THIO . CARBONYL . ETHYL . o . AMIDO. PHENOL C,H, NEt CS. [112°]. 300°). Formed from ethyl-o-amido-phenol and CSCl₂ (Seidel, J. pr. [2] 42, 449, 457). Insol. water and dilitic NaOHAq, m. sol. cold alcohol. HClAq at 170° forms ethyl-amido phenol, CO,

and H2S. PCl, yields CH CO CCJ. THIO - CARBONYL - METHYL - AMIDO-PHENOL $C_0H_1 < N_0^{MO} > CS$. [128°]. (above 300°). Formed by the action of CSCl, on methylo-amido-phenol (Seidel, J. pr. [2] 42, 452). Needles, insol. water, sl. sol. cold alcohol.

THIO CARBONYL - DI - (β) - NAPHTHYL-THIO - UREA $C_{19}II$, $N < \stackrel{CS}{C(NC_{10}II)} > S$. [152°]. Formed from di-(B) - naphthyl-thio-ures and CSCl₂ in benzene (Freund a. Wolf, B. 25, 1466). Stellate groups of needles, m. sol. hot benzene. Melts at 152' with evolution of gas, forming a solid melting at 224°

THIO-CARBONYL-DI-p-TOLYL-THIO-UREA C,H,N:C \left\(\frac{N(C,H,)}{S}\right\)CS. [109°]. Formed from di-p-tolyl-thio-urea [172°] and CSCl2 in ether (Freund a. Wolf, B. 25, 1465). Yellowish needles, v. sol. hot alcohol and ether. Converted by HgO

into carbonyl-di-tolyl-thio-urea [112°].
THIOCHRONIC ACID C, H, S, O, C_o(OH)(SO_oH)(SO_oH)₀. Formed by adding tetra-chloro-quinone to a cone. solution of K_sSO_o (Hesse, A. 114, 313; Graebe, A. 146, 40). Yellow trimetric prisms, v. sol. hot water, insol. alcohol. Coloured brownish-red by FeCl, Reduces AgNO, Converted into hydroquinone disulphonic acid by heating with water at 135', or by boiling with

Euthiochronic acid C.H.S.O. i.e. Cu(OH)2O2(SO2H)2. Di-oxy-quinone disulphonic acid. Formed by boiling thiochronic acid with KOHAq. Deliquescent yellow heedles, v. sol. water and alcohol. Reduced by tin and HClAq to C_aH_aS₂O₁₀, which yields Na₂A" 2aq and K₂A" 2aq, which are re-oxidised in aqueous solution by air to euthiochronates.—Na, A'aq (dried tion by air to cutinocuronates.—rat, a "aq qureu at 150").—K,A'"2aq. Minute lemon yellow prisms, v. sol. water.—K,HA'"aq. Small orangered four-sided prisms.—Ba,A'"4aq. Ochreyellow pp.—Ag,A'': a morphous pp.

(a) THIO - CINNAMIC ACID C,H,80 i.e.
C,H,CH:CH.CO.SH. Formed from cinnamoyl

chloride and Pb(SEt), the resulting oily ether

being boiled with alcoholic KSH (Engelhardt, Z.

[2] 4, 359).—KA'. Crystallins. (β)-Thio-cinnamic acid. Amide C₀H,S.NH₂.
 [112°]. Formed by passing H₂S into a solution

of cinnamic nitrile in alcoholic NH₄ (Rossum, Z. 1866, 362; Krüss, B. 17, 1768). Cplden plates.

(a) THIO-CINNAMIC ALDERYDE (C, H, S), 167°]. Formed by passing H,S into oil of

cinnamon dissolved in alcoholic HCl (Baumann a Fromm, B. 24, 1452). Crystalline, v. e. sol. a Fromm, B. 24, 1452). benzene, sl. sol. alcohol.

(β)-Thio-cinnamic aldehyde (C,H,S), [213]. Formed at the same time as the (a)-isomeride. Prisms, v. sl. sol. cold benzene and alcohol.

Thio - cinnamic orthaldehyde. Phenyl ether C. H.CH:CH.CH(SPh). [81°]. Formed by passing dry HCl into a mixture of cinnamic aldehyde and phenyl mercaptan (Baumann, B. 18, 885). Needles (from ligroin).

p-Bromo-phenyl ether CHPh:CH.CH(S.C₈H,Br)₂. [107°]. Needles (from sleehel or ether)

alcohol or ether).

Glycollyl ether CHPh:CH.CH(S.CH., CO, H), [143°]. Formed from cinnamic aldehyde and thioglycollic acid (Bongartz, B. 21, 481). Plates (from water). Zinc-dust in alkaline solution converts it into CHPh:CH.CH, S.CH, CO.H [77°], crystallising from dilute alcohol in plates.

TRI.THIO-CITRIC ETHER C,H,O(CO.SEt)3. Formed from tri-phenyl citrate and NaSEt in presence of ether (Seiffert, J. pr. [2] 31, 470). Oil, smelling like mercaptan.

THIO-COUMARIN C. II.

Formed by heating equal parts of coumarin and P.S. at 120°; the yield is 50 p.c. Also by heating o-coumaric acid with P.S. Long yellow needles, v. sol. alcohol, ether, and benzene; insol. water. Sublimable. By heating with aqueous alcoholic KOH it is reconverted into coumarin. Unlike coumarin it readily reacts with hydroxylamine and with phenyl-hydrazine (Tiemann, B. 19, 1661).

THIO-CRESOL v. TOLYL MERCAPTAN.
THIO-CROCONIC ACID C.H.O.S, probably

SC < C(OH), CO < Formed by saturating a warmsolution of potassium croconate treated with 2 mols. of HCl, with II_sS.—BaA" 2aq: brownish-yellow amorphous pp., v. sol. dilute HCl, which after some time changes to reddish - brown crystals with violet reflex, incol. dilute HCl (Nietzki a. Benkiser, B. 19, 299).

THIO-CUMINIC ACID. Amide C₁₀H₁₆NS 6.6. C₃H₁, C₅H₄, CS.NH₂. Formed by passing H₂S and the latest control of the contro

into a solution of cuminic witrile in alcoholic NH, (Czumpelik, B. 2, 185). Needles, v. sol. hot alcohol. Converted in alcoholic solution by iodine into C₂₂H₂₂N₂S [45°] crystallising in prisms (Wanstrat, B. 6, 322).

THIODICYANDIAMIDINE v. GUANYL THIO-

THIOCYANIC ACID v. SULPHOCYANIC ACID. THIOCYANO- v. SULPHOCYANO-.

DI-THIO CYANURIC ACID Cy3(SH)2(OH) aq. Preparation .- An alcoholic solution of KCyS is mixed with the calculated quantity of HCl, filtered from KCl, and evaporated at 40°. The residue is extracted with strong NH,Aq and

BaCl, is added to the filtrate. The barium salt

gradually separates in globular crystals (Klason, J. pr. [2] 33, 121). Yield, very small.

Properties.—White scales (from hot water).
Sol. NaOHAq. A solution of the potassium salt gives pps. with AgNO, HgCl, and Pb(OAc),

Reactions .- 1. Conc. HCl at 130° gives cyanuric acid and H₂S.—2. Cold KMnO₄Aq and hot HNO₂Aq form cyanuric acid.—3. *Iodine* forms

(HOC₃), S, as a white crystalline powder.

Salts.—KH₂A'''. Silvery mass of microscopic prisms.—BaHA'''2aq.

Tri-thio-cyanuric acid Cy₃(SH)₃. Formed by warming powdered C,N,Cl₃ (1 mol.) with concurrence WEH (4 mol.) aqueous KSH (4 mols.) (\hat{H} ofmann, \hat{B} . 18, 2196; Klason, J. pr. [2] 33, 116). Minute prisms, when ppd, from dilute solutions; amorphous, from conc. solutions. Nearly insol. hot water, alcohol and ether. Not decomposed at 200°. FeCl, gives no colour in solutions of the acid, but in conc. solutions of the K salt it gives a white pp. and a yellow solution.

Reactions. -1. HClAq at 130° gives cyanuric acid and H.S. -2. Alkaline KMnO₄ at 20° gives cyanuric acid. -3. Warm IINO₄ forms cyanuric acid. -4. At 360° it gives off CS₂ and some

HUyS and leaves melem $C_6H_6N_{10}$.

Salts.— $K_3A'''3aq$.— K_3H_A''' , 6aq.—Na H_2A''' .

Crystals, v. sol. wator.—BaHA'''3aq. Yellow crystals, ppd. by addition of BaCl2 and NH_Aq.—
BaH_A''',2aq. Prisms,m. sol. water.—SrHA'''5aq.

aH₄A"'₂2aq. Prisins, in. sol. water. -CaHA"'5aq. Prisins, in. sol. water. Methyl ether Mc₄A"'. [189°]. heating methyl sulphocyanide with a few drops of HClAq at 100° (flofmann, B. 13, 1351; 18, 2197, 2755, 2774; 19, 2065). Hexagonal crystals. An alcoholic solution of ethylamine at 100° forms Cy₈(NHEt)(SMe)₂ [114⁹] while at 140⁹ it yields Cy₄(NHEt)₂SMe [84⁹]. Alcoholic NH, forms, in like manner, Cy₈(NH.)(SMe), and Cy₈(NH.)₂SMe. Ethyl ether Ft, A.". [27⁹]. (350⁹). Formed from Cy₂Cl₃ and NaSEt. Colourless tablets (from HOAc) appropriate healthclick NH = 1500⁶ in 1900.

HOAc) converted by alcoholic NH, at 180° into Cy₃(NH₂)(SEt)₂ [112°] (crystallising in trimetric forms; a.b.c = 669:1:301, v. sol. ether), accompanied by Cy₃(NH₂)₂(SEt)₂ [165°], which is insol.

cther (Klason, J. pr. [2] 33, 208).

Anylether (C,H₁₁)₃A'''. Oil. Yields
Cy₂(NH₂)(SC₃H₁₁)₂ [82°] and Cy₃(NH₂)₂SC₃H₁₁ [1780].

Phenylether Ph3A". [97°]. Prisms (from HOAc).

p-Tolyl ether (C,H,),A". [114°].
THIO-DI-ETHYL-ANILINE v. TETRA-ETHYL-DI-AMIDO-DI-PHENYL SULPHIDE.

C.H. CH:CEt THIO-ETHYL-COUMARIN

[94°]. Formed by heating (a)-ethyl-coumarin with P.S. at 120° (Aldringen, B. 24, 8462). Yellowish-red plates, sol. alcohol. May be sublimed.

THIO-ETHYLENE GLYCOL v. ETHYLENE

THIO FORMIC ACID H.CO.SH (?) [120°]. Formed by the action of H.S on lead formate (Wöhler, A. 91, 125; Limpricht, A. 97, 361), but not from P.S. and formic acid (Hurst, A. 126, 68). E.mall transparent crystals (from alcohol) with alliaceous odour, insol. water. May be sublimed. According to Nicol (Pr. E. 10, 425) a solution of thioformic soid, got from

PbA', and H2S, rapidly decomposes, yielding formic acid.

Salts .- H.CC.SK. Formed from CHCl, and alcoholic K2S (Nicol, T. E. 29, 531). Needles. sol. water and alcohol, nearly insol. dilute alco-AgNO, added to its aqueous solution forms a white pp., turning black on standing. HNO, yields S and formic acid. HgO also gives formic

•acid.—(H.CO.S).Pb.

Anilide H.CS.NHPh. Thioformanilide. [137°]. Formed from dry phenyl carbamine and H_2S (Hofmann, B. 10, 1095, 1238). Formed also by passing dry H.S over di-phenyl-formamidine NPh:CH.NHPh at 150° (Bernthsen, A. 192, 35). Prepared by warming formamidine (5 pts.) with P.S. (3 pts.), the yield being 60 p.c. of the theoretical (Hofmann, B. 11, 338). Thin plates (from water), partially decomposed on distilla-tion into H.S and phenyl carbamine. Its solution tastes bitter. Decomposed by hot KOHAq into aniline, H₂S, and formic acid. Heated in a sealed tube at 180° it yields C₁H₁₂N_{.S} [140'] v. sol. alcohol (Nicol, B. 15, 211). NaOEt and EtBr yield oily CH(SEt):NPh (c. 235°) (Wallach a.

Wüsten, B. 16, 145).

o-Toluide H.CS.NHC,H, [96°]. Got by heating formyl-toluide with P₂S₃ (Senier, C. J. 47, 762).

p-Toluide. Yellow needles.

Xylide HCS.NHC, H, Me. [105°]. Small needles (from alcohol) (Gudeman, B. 21, 2549).
Thio-orthoformic acid. Ethyl ether

CH(SEt), Formed by boiling chloroform with aqueous NaSEt (Gabriel, B. 10, 186; Claesson, J. pr. [2] 15, 174). Oif, with nasty smell, partly decomposed on boiling. Oxidised by HNO₃ to ethane sulphonic acid. Fuming HClAq yields

formic acid and mercaptan

Benzyl ether CH(SC,H,), [98°]. Formed from NaSC,H, and chloroform (Dennstedt, B.

11, 2265). White crystals.

Phenyl ether CH(SPh)₃. [39·5°]. Trimetric tables. Oxidised by potassium permanganate to PhS.CH(SO₂Ph)₂ [176°] (Laves, B. 23,

1416; 25, 347).
Reference.—Chloroformic acid.

THIO-FORMIC ALDEHYDES

Thio-formic paraldehyde (CH₂S)₃. Methylene sulphide. Mol. w. 138. [216°]. V.D. 5°08 (obs.).

Formation.—1. By heating Na S with methylene iodide (Husemann, A. 126, 293). - 2. By reducing CS₂ with Zn and HClAq (Girard, A. 100, **306**).—8. By the action of H₂S on formic aldehyde or trioxymethylene.

Preparation.—By saturating a mixture of formic aldehyde (2 vols.) and conc. HClAq (4 vols.) with H₂S (Baumann, B. 23, 67).

Properties .- Prisms, smelling like onions. Insol. cold water, sl. sol. alcohol and ether, m. Sol. accord water, Sl. sol. accord and ether, In. sol. benzene and CS. May be sublimed. Oxidised by KMnO, to a trisulphone and also C.H.S.O. crystallising in colourless needles.—Forms: C.H.S.2ARNO. C.H.S.ARNO. ARNO. ARRO. ARRO.

Thio-formic orthaldehyde. Ethyl ether CH₃(SEt)₂. (184°) (C.); acetic, benzoic, cinnamic, o-oxy-benzoic, and o₂ (180°) (F.). S.G. ¹² ·987. Formed from CH₂, m., and p-nitro-benzoic aldehydes melt at 108°, and NaSEt (Claesson, J. pr. [2] 16, 176). Liquid 124°, 146°, 148°, 123°, 130°, and 162° respec-(184°) (C.);

with unpleasant smell. Oxidised by HNO, to ethane sulphonic acid. KMnO, and H₂SO₄ yield CH₂(SO₂O₂H₃)₂ (Fromm, A. 253, 155). Thio-formic metaldehyde (CH₂S)₃. [176°]. Formed, as a white amorphous substance, on

warming an aqueous or alcoholic solution of hexamethyle e-amino saturated with H₂S (Wohl, B. 19, 2344). Insol. most solvents. Decomposed when heated above its melting-point

Di-thio-formic paraldehyde (C₃H₃S₂O), aq. Dithioglyceric aldehyde. [82°]. (180°-185°). Formed by passing H.S into a solution obtained by electrolysis of dilute glycerin (Renard, A. Ch. [5] 17, 307). Amorphous waxy mass, sol. warm water, insol. alcohol and other

(a)-THIO-FURFURALDEHYDE [128]. Formed, together with the (β)-isomeride, by passing H.S into a solution of furfuraldehyde (10 g.) in alcohol (100 c.c.) and HClAq (20 c.c.) at -5° (Baumann a. Fromm, B. 24, 3593). Crystals, v. e. sol. alcohol and chloroform, insol. water.

(β)-Thio-farfuraldehyde (C,H,SO), [229°]. Needles, v. sl. sol. alcohol, v. sol. chloroform.

Thio-furfuraldehyde (C.II.SO), [n = 20 to 24]. Mol. w. (by Raoult's method) 2182. Formed by mixing an alcoholic solution of furfuraldehyde with alcoholic ammonium sulphide (Cahours, A. 69,85; B.a.F.). White crystalline powder, softens at 80° and is melted at 91°. Thiofurfuraldehyde is decomposed by warm aniline, yielding furfuraldehyde and H.S (Schiff, B. 19, 2153). THIO-GLYCERIN v. GLYCERIN.

THIO-GLYCOL v. ETHYLENE MERCAPTAR. THIO-GLYCOLLIC ACID CH_(SH).CO2H.

Sulphydro-acetic acid.

Formation.—1. By reducing the compound CISO...CHCl.COCl with tin and HClAq (Siemens, B. 6, 659).—2. By adding CH.Cl.CO.H (1 mol.) to cone. KSHAq (2 mols.) (Claesson, A. 187, 113).—3. By the action of H.S on glyoxylic acid in presence of Ag₂O (Böttinger, A. 198, 215).—4. By boiling thiohydanton with barytawater (Andreasch, B. 12, 1385).—5. Together with HSCy, by the decomposition of rhodanic acid C₂H₂NS₂O with baryta-water (Ginsberg a. Bondzynski, B. 19, 113).

Properties .- Oil, miscible with water, alcohol, and other. Decomposes when quickly heated. Very dilute FeCl₃ gives a fugitive indigo-blue colour, changed by a few drops of NH₃Aq to dark red and then to violet. Excess of FeCl, oxidises it to di-sulphido-di-acetic acid S₂(CH_xCO₂H)₂, which is also readily formed by atmospheric oxidation of the alkaline solution. A solution of the K salt added to CuSO, gives a bluish-black pp. reduced by further addition of the K salt to the white cuprous salt Cu2(S.CH2.CO2H)2. HCl passed through a mixture of thioglycollic acid and acetoacetic ether gives rise to crystalline CO_EL.CH_CMe(S.CII_CO_H)_ [96°] (Bongartz, B. 21, 485). Acetyl-propionic acid forms, in like manner, CO_H.CH_2.CH_2.CMe(S.CM_2.CO_H)_a 1514]. Aldehydes react, forming the compound CliH(S.CH_xCO_xH)_x, compounds which are produced either on standing, on warming, or on treatment with ZnCl_xor dry HCl (Bongartz, B.19, 1981; 21, 479). Such compounds obtained by using acetic, benzoic, cinnamic, o-oxy-benzoic, and o-,

tively. Thioglycollic acid reacts with ketones in presence of ZnCl, or HCl, forming acids CRR'(S.CH, CO, H)2: such compounds obtained from acetone, acetophenone, and benzophenone

from hectone, acctophenone, and benzophenone melt at 135°, 139°, and 164° respectively.

Salts.—KHA"aq (from water).—KHA"
(from alcohol). Decomposes KCO₃, forming H₄(SK).CO₃K.—BaA" 34q; crystalline pp.—BaH₂A"₂; gummy.—CdA".—Hg(SCH₂CO₃H).

Reedles or flat prisms, v. sol. hot water and alcohol.—H₂C(S.CH₂CO₂),BaH₂. Minute crystals.—Hg₃M₂C(O₄),AlH₃.—Hg₃Mh₄A"₂.—HgA"₂.—HgA"₃.—Bi(HA")₃. [c. 33°].

Yellow pp.—Cu₃H₂A''₂. White pp.—Cu₃BaA''₂.—Ag₂A''.—Ag₂(NH₄)A''(NO₃).—Ag₂HgA''₂.

Ethyl ether EtA'. Formed by boiling

Ethyl ether EtA'. Formed by boiling thioglycollic acid with alcohol and a little thioglycollic acid with alcohol and a little H₂SO₄ (Claesson, A. 187, 116). Oil with nasty smell. Slowly decomposed by boiling into H₂S and S(CH₂CO₂Et)₂. Alcoholic HgCl₂ ppts. ClHg.S.CH₂CO₂Et, converted by excess of the ether into Hg(S.CE₂CO₂Et)₂ (Wislicenus, A.

146, 145).

Ethyl derivative CH. (SEt). CO.H. Formed by mixing CH. Cl. CO.Et with NaSEt and alcohol (Claesson, B. 8, 120). Liquid, v. sol. alcohol and ether, m. sol. water. Decomposed by heat, but may be distilled with steam. -by heat, but may be distilled with steam. KA'.—BaA'.2—CaA'.2—MgA'.2 aq. —ZnA'.2 aq. —CdA', aq. [85°].—CoA'.2 aq. [90°].—NiA'.2 aq. —CuA'.2 aq. —AgA'aq. Crystalline pp. Ethyl ether of the ethyl derivative CH_(SEt).CO.Et. (188°). S.G. 2 1-0169. Oil. Converted by Etl at 120° into crystalline CH (SET).

CH_(SEt_I).CO_Et.

Ethyl ether of the isoamyl derivative CH₂(SC₅H₁₁).CO₂Et. (230°). S.G. \$ 9797. Oil.

Phenyl derivative v. PHENYL-THIO-GLY-

COLLIC ACID.

Benzyl derivative CH_Ph.S.CH_CO_H. [59°]. Formed from CH_Cl.CO_H and benzyl mercaptan (Gabriel, B. 12, 1641). Flat tables. Yields Eth' (275°-290°) and the amide CH₂Ph.S.CH₄.CONH₄ [97°] crystallising in flat plates.

Phenyl-phenyl derivative

C.H.Ph.S.CH. CO.H. [170°]. Crystals.

Amide CH.(SH).CO.NH... A product of the passage of H.S through an alcoholic solution of chloro-acetamide containing a little NH₃ (Schulze, Z. 1865, 73). Groups of small prisms.

Ethyl derivative of the amide
CH₁(SEt).CONH₂ (4⁴). Formed from

CH₄(SEt).CONH₂. [44°]. Formed from CH₄(SEt).CO,Et and ammonia. Thin prisms. Reference.—NITROSO-THIO-GLYCOLLIC ACID.

THIO-GLYCOLLICORTHALDEHYDE. Ethul derivative of the ether CH_(SEO.CH(OEt), (169°). Formed from CH_Cl.CH(OEt), and NaSEt (Autenrieth, B. 24, 162). Volatile in steam.

Phenyl derivative of the ethyl ether CH₂(SPh).CH(OEt)₂. (273°). Got in like manner.

THIO-HYDANTOIC ACID C.H. N.SO. i.e. NH, CS.NH.CH, CO, H or NH. C(NH).S.CH. CO.H. Formed by heating sodium chloro-acetate in aqueous solution with thio-urea (Maly, A. 189, 380). Crystalline powder, sl. sol. water, v. sol. acids and alkalis. Decomposed by heat. Converted into thio-

hydantoin by warming with Na.CO.Ac or

HClaq. THIOHYDANTOIN C.H.N.BO i.e.

CS < NH.CH₂ or C < NH.CH₂.

Formation .- 1. By heating this-ures with chloro-acetic acid or chloro-acetamide (Volhard, A. 166, 383; Mulder, B. 8, 1264; Maly, A. 168, A. 100, 505; Mutters B. 0, 1204; Mary, A. 105, 133; B. 10, 1853; Claesson, B. 10, 1352).—2. By heating thioglycollic acid (2 mols.) with cyanamide (1 mol.) in aqueous solution (Andreasch, B. 13, 1421; M. 1, 442).

Preparation .- Thio-urea (50 g.) dissolved in water (500 c.c.) is mixed with chloro-acetic acid (62 g.) in water (50 c.c.), heated to 90°, cooled, and mixed with the calculated quantity of NaOH

(Andreasch, M. 8, 414).

Properties .- Long needles (from hot water). insol. alcohol and ether. Decomposes about 200°. Since it cannot be desulphurised by HgO, Liebermann (A. 207, 132) suggests that it does

not contain the group CS.

Reactions.—1. Chlorine passed into its cooled reactions.—I. Chaorine passed into its cooled solution in HClAq forms thio-oxy-hydantoin (Kramps, B. 13, 788).—2. Br forms di-bromothio-hydantoin.—3. KClO₃ and HCl yield C₃H₃KN₂SO₃, crystallising in monoclinic tables, S₁. 17 at 22°; 23°3 at 100°, converted by nitrous acid into SO₃H.CH₂.CO₂H, and by baryta-water into sulpho-acetic acid and urea (Andreasch, B. 13, 1423; M. 4, 131). -- 4. Baryta-water forms thioglycollic acid and dicyandiamide. - 5. Boiling HClAq forms thiocarbimido-acetic acid.

Salts.—Ag.C.H.N.SO.—B'.H.SO. Plate -B'HNO. B'HCl.—B'H.C.O. aq. Prisins.-B'₂H₂PtCl₆. -B'C₆H₂N₃O₅. Minute yellow needles.

References. -Di-Bromo- and Nitroso-thio-

HYDANTOÏN.

DI-THIO-HYDROQUINONE CaH4(SH)2. [98°]. Formed by reducing benzene p-disulphonic chloride with tin and HClAq (Körner a. Mon-Formed also from G. 6, 142). selise, (C, H, (NH2))2S2 by diazotisation, treatment with potassium xanthate, and saponification of the product with alcoholic potash (Leuckart, J. pr. [2] 41, 205). Six-sided plates, slowly oxidised by

THIO-ISATYDE v. ISATYDE.

THIO-LACTIC ACID CH,.CH(SH).CO,H.

a-Sulphydro-propionic acid.

Formation. -1. From a-chloro-propionic acid and KHS (Schacht, A. 129, 1; Lovén, J. pr. [2] 29, 368). -2. By the action of H2S on silver achloro-propionate or silver pyruvate (Böttinger, A. 188, 320; B. 9, 404, 804, 1061; 11, 1561; 18,

486).

Preparation.—By saturating a solution of adding conc. HClAq pyruvic acid with H,S, and adding conc. HClAq

and zinc (Lovén).

Properties. —Syrup, miscible with water, alcohol, and ether. May be distilled in vacuo. Its odour is unpleasant. FeCl, gives a transient indigo colour, and then oxidises it to sulphido-dipropionic acid. CuSO, gives a violet solution; a smaller quantity of CuSO, ppts, the cuprous salt. Cobalt acetate and air gives a brown colour. '

Salts.—BaA', (at 130°). Gummy mass.— Hg(S.CHMe.CO,H), — Hg(S.CHMe.CO,K), zaq. Hg(S.CHMe.CO),Ba 2]aq. — AgS.CHMe.CO,H.

-Bi(S.CHMe.CO.H). - Pt(S.CHMe.CO.H). CuS.CHMe.CO.H. Yellow pp. -PbC.H.O.S.

Ethyl ether Eth'. Oil. Yields
CuS.CHMe.CO.Et as a yellowish powder.

THIO-DILACTYLIC ACID v. SULPHIDO-DI-

PROPIONIC ACID.

THIO-MALIC ACID C.H. SO. Formed from brome-succinic acid and aqueous KSH at 110³ (Carius, A. 129, 6). Deliquescent mass, oxidised. by dilute HNO, to sulpho-succinic acid.—BaA".
—Ag_A". Bulky pp., readily blackening.

THIO-MESITOL v. Таг-метиуь-рнемуь мег-

CAPTAN. THIO-DI-METHYL-ANILINE METHYL-DI-AMIDO-DI-PHENYL SULPHIDE.

THIO-METHYL-COUMARILIC ETHER C₁₂H₁₂SO₂ i.e. C₆H₄ < CMe SC.CO.SEt.

Formed from methyl-coumarilic ether and P.S. (Hantzsch, B. 19, 2400). Yellow needles (from alcohol), v. sol. ether.

THIO-(a)-METHYL-COUMARIN C, II, SO i.e. C.H. CH; CMe. [122°]. Formed by heating (a)-methyl-coumarin with P2S3 at 120° (Aldringen, B. 24, 3460). Yellow needles, insol. water, v. sol. alcohol. Converted by alcoholic potash into (a)-methyl-coumarin.

THÍO-METHYL-DI-PHENYL-AMINE v. METHYL-IMIDO-DI-PHENYL SULPHIDE.

THIO-METHYL-URACIL C₅H₆N₂SO CS NH.CMe CH (?). S. .054 at 21°. Formed by the action of alcoholic potash on the needles which separate after some days from a solution of thio-urea (1 mol.) and acetoacetic ether (1 mol.) in alcohol to which a little HCl has been added (Nencki a. Sieber, J. pr. [2] 25, 72; List, A. 236, 1; Behrend, B. 19, 219). Plates, v. sl. sol. ether. Decomposed at 280°.

Reactions.-1. The K salt reacts with EtI Reactions.—1. The K salt reacts with EH forming C,H,N,SOMe [220°], which yields C,H,A,gN,SO.—2. Chloro-acetic ether forms C,H,N,SO(CH,CO,Et) [143°], which yields C,H,N,SO(CH,CO,Et) [143°], which yields C,H,N,SO(CH,CO,ET) [140°].—2. Br forms methyl-uracil, and finally di-oxy-methyl-uracil. Cl acts in like manner, forming C_H_cCl_2N_2O_3. -3. On warming with lead hydrate in strongly alkaline solution it is converted into methyl-uracil. Account Hollag at 150°, cone. NH₂Aq at 150°, and Account Hollag at 150°, and Account Hollagan Hollag

- (C₃H₃N₂SO)₂H₃ - C₃H₄N₂N₃SO - C₄H₄Cl₃N₂SO - C₄H₄N₂N₃SO 2aq - C₅H₄N₂KSO 3aq - C₅H₄N₂KSO 3aq - THIONAMIC ACID. H. Rose (I'. 33, 235;

42, 415) found that SO2 and NH, combined in equal volumes, when dry NH, was mixed with excess of dry SO, to form a yellowish white solid, which quickly decomposed in solution, or moist air, giving (NH₄)₂SO₄ and ammonium salts of other sulphur oxyacids. Rose concluded that the substance was SO₂NH₃ from the fact that it was formed by combining equal volumes of the two gases; if this empirical formula is accepted the compound may be 90, NH, H or SO.OH.NH, When dry SO2 was mixed with excess of dry When dry SO₂ was mixed with eacens of all NH₂, Rose found that 1 vol. SO₂ combined with 2 vols. NH₂; the product—an amorphous, white solid—may be SO₂.NH₂.NH₄ or SO.ONH₄.NH₂.

M. M. P. M.

THIONAMIDE. By passing NH, into cooled S.Cl., Schiff (A. 102, 111) obtained a white solid which was decomposed by warm water to (NH.), SO, Aq. The solid contained NH.(Cl.; Schiff regarded it as a mixture of this salt with SO(NH.).; he did not attempt to separate the supposed thionamide from NH.Cl.

M. M. P. M. (a)-THIO-NAPHTHOIC ACID.

Amide CuH, CS.NII. [126°]. Formed from (a)-naphthoic nitrile and alcoholic ammonium sulphide at 30°-353 (Hofmann, B. 1, 40; Bamberger, B. 21, 54). Crystals, v. sol. alcohol.

Tetrahydride of the amide

CH_CH_>C₀H_xCS.NH. Formed by digesting a solution of tetrahydride of (a)-naphthonitrile in alcoholic ammonia saturated with H₂S for some days at 30°-40° (Bamberger a. Bordt, B. 22. 629). Dark-yellow oil.

(β)-Thio-narhthoic acid. Amide C₁₀H_{1.}CSNH_{2.} ['49°]. Formed from (\$\beta\$)-naph-thonitrile and ammonium sulphide at 35°-40° (Bamberger a. Bockmann, B. 20, 1115). Noedles, v. sol. alcohol. Dissolves in hot water, being slowly converted into the nitrile.

THIO-NAPHTHOL v. NAPHTHYL MERCAPTAN. THIO-DI-NAPHTHYL-AMINE v. IMIDO-DI-

NAPHTHYL SULPHIDE. THIONATES. Salts of the tilionic acids (q. v., p. 698). Four series of thionates are known; a fifth probably exists: M2820 = dithionates; M.S.O. - trithionates; M.S.O. - tetrathionates; M.S.O. pentathionates; and probably M.S.O. hexathionates. The thionates are formed by the action of alkalis on the liquid obtained by passing H.S into saturated SO, Aq; also by the oxidation of sulphites, thiosulphates, and mixtures of these, and in other reactions (cf. Thionic acids, p. 698). For general qualitative reactions of thionates and thiosulphates v. Debus (C. J. 53, 298).

DITHIONATES, M.S.O., MuS.O., and Mus.(S.O.), (Hyposulphates.) The alkali salts are formed by the interaction of a dilute solution of I in KIAq and dilute NaHSO, Aq (Spring a. Bourgeois, Bl. [2] 46, 151; Sokoloff a. Mattscheffski, B. 14, 2058); also by the reaction of KMnO, Aq on thiosulphates in acetic acid solution, or on sulphites or trithionates (Hönig a. Zatzek, M. 4, 738; Fordos a. Gélis, J. Ph. [3] 36, 113). The Ba salt is formed by passing SO₂ into water holding MnO₂ in suspension, filtering, and adding BaOAq (for more details v. DITHIONIC ACID, p. 698); most of the other dithionates are obtained by the interaction of BaS,O,Aq and sulphates; several have been prepared by digesting H.S.O.Aq with metallic hydroxides. The difficulties are sol. water; the salts of the alkali and alkaline earth metals are not readily decomposed either in solution or as solids; solutions of most of the other salts are decomposed by heat, giving off SO₂ (v. Klüss, A. 246, 179, 284; Geuther, A. 226, 232).

Dithionates give off SO, when heated to redness, leaving normal sulphates; thus M.S.O. = SO₂ + M₂SO₄; this reaction is characteristic; so also is the reaction of H.SO.Aq or HClAq with boiling solutions of dithionates, whereby H,SO,Aq is formed and SO, is given off, without separation of S.

Ammonium dithionate (NH_a)₂S₂O₆. Obtained by decomposing the Ba salt in solution by (NH_d)_SO₄Aq, filtering and crystallising. S.G. 1.704 (Topsoë, C. C. 4, 76). Klüss (A. 246, 179, 284) gives formula 2Am₂S₂O₆, aq, and says the salt crystallises in monoclinic needles. Very sol. water; insol. alcohol. Aquedus solution may be boiled without change. Forms double salts with AmCl (Fock a. Klüss, B. 24, 3017); also with the dithionates of Al, Cd, Co, Cu, Fe,

Mn, Ni, and Zn (K., l.c.).

Barium dithionate BåS₂O₈, 2aq. Formed by passing SO₂ into water at c₄0° holding coarselypassing SO₂ into water at the order of the mode, is dissolved (MnO₂ in suspension, till the MnO₂ is dissolved (MnO₂ + SO₂ + Aq = MnSO₂Aq; and also MnO₂ + 2SO₂ + Aq = MnS₂O₄Aq, filtering if necessary, adding BaOAq to alkaline reaction (MnS₂O₄Aq + BaO₂H₂Aq = BaS₂O₄Aq + MnO₂H₂), [Min2.04.4] + Ba0.H.2.41 = Da5.3.0.4.4 + Min2.12.1, filtering from MnO.H., evaporating, and recrystallising from water (cf. Stas, Chem. Proport. 117). White prisms; S. 24.75 at 18°, 90.9 at 100°, 100°6 at 102° = b.p. of saturated solution; insolalcohol. The crystals effloresce in air, losing 2H₂O; a hydrate with 4H₂O is obtained by slow evaporation (v. Heeren, P. 7, 55; Gay-Lussac, A. Ch. [2] 10, 312; Baker, C. N. 36, 203; cf. Spring a. Bourgeois, Bl. [2] 46, 151. For crys-Spring a. Boürgeois, Bl. [2] 46, 151. For crystalline form v. Senarmont, J. 1857. 142; Rammelsberg, P. 58, 295; von Lang, W. A. B. 45 [2] 27). Schiff (A. 105, 239) described double salts with MgS.O₆ and Na.S.₂O₆ (cf. Kraut, A. 118, 96); Bodländer (Chem. Zeit. 14, 1140) described a double salt with Rb.S.Q₆; and Klüss (4. 246, 179, 284) double salts with Ag.S.O₆ and Tl2S2O6.

Many of the other dithionates are prepared

from the Ba salt.

Potassium dithionate K.S.O. Prepared from a solution of the Ba salt by adding an equivalent quantity of K.SO. in solution, warming, filtering, and evaporating; also by boiling ing, filtering, and evaporating; also by boiling K_xSO_xAq with MnO_x filtering, and separating from K_xSO_x by fractional crystallisation (K_xSO_x) is much less sol. water than K_xS_xO_x). White, hexagonal crystals; unchanged in air; decrepitates when heated and then gives off SO_x and leaves K_xSO_x; S.G. 2.277 (Topsoë, Bl. [2] 19, 246). The crystals rotate the plane of polarisation of light an augmons solution is entically tion of light; an aqueous solution is optically

tion of light; an aqueous solution is optically inactive (Pape, P. 139, 221). S. c. 6 at ordinary temperature, c. 66 at 100°; insol. alcohol (Heeren, P. 7, 55).

Solium dithionate Na, S.O., 2aq. Prepared similarly to the K salt. Also formed, according to Bunte (B. 7, 646), by heating Na.Et.S.O. for some time at 100° (Et.S. distils off). Large, lustrous, rhombic prisms; unchanged in air, B.G. 2:175 at 11° (Baker, C. N. 36, 203). S. 47·6 at 16°; 90 9 at 100°; insol. alcohol. Solution is slowly reduced by sodium-amalgam to Na.SO.AQ (Spring, B. 7, 1161). Kraut (A. 117, 97) described a hydrate with 6H.O.

Dithionates of the following metals have

Dithionates of the following metals have Dithionates of the following metals have also been described (the figures indicate the references): Al (1) (3); Be (3); Bi (3); Cd (1) (2) (4); Ca (1) (4) (5); Cr (3); Co (1) (2) (3) (4); Cu (3); Fe (1) (3) (4); Fb (1) (4) (5); Li (2) (4); Mg (1) (4) (5); Mn (4); Hg (1) (2) (3); Ni (2) (4) (5); Rb (6); Ag (1) (2) (4) (5); Sr (2) (4); Tl (3); Sn (8); U (3); Zn (1) (2) (4).

[1] Heeren, P. 7, 72, 171; (2) Rammelsberg,

P. 58, 298; (3) Klüss, A. 246, 179, 284; (4) Tor. Piccard, J. pr. 86, 456.
TRITHIONATES M¹₂S₂O₆ and M¹¹S₂O₆. The

TRITHIONATES M'-S,O, and M'-S,O. The alkali salts are formed by digesting cono.

MHSO,Aq with S at 50°-60° (6MHSO,Aq+2S-2M,S,O,Aq+M,S,O,Aq+3H,O)(Pelouze,A.Ch.

[3] 79, 85); also by heating dilute MHSO,Aq, or keeping the solution for a long time in a closed tube (Saint-Pierre, C. R. 62, 632); by passing SO, into M,SAO,Aq (2M,S,O,Aq+8SO,-2M,SO,Aq+S,O,A passing SO₂ into $M_2S_2O_3Aq$ ($2M_2S_2O_3Aq + 3SO_2 = 2M_2S_2O_4Aq + S)$; by passing SO₂ into M_2SAq (Chancel a. Diacon, J. pr. 90, 35; Rathkg, J. pr. 95, 11); by the interaction of I and a mixture of M_2SO_3 and M_2SO_3 in solution ($M_2SO_3Aq + M_2S_2O_3Aq + I_2 = M_2S_2O_4Aq + 2MIAQ$) (Spring, B. 7, 1157); by the interaction of boiling water on $AgKS_2O_3$ or $HgNa_2(S_2O_3)_2$, whereby $K_2S_2O_4Aq$ or $N_2S_2O_3Aq$ is formed, along with AgS_2O_3 or $HgS_2S_2O_3Aq$ is formed, along with AgS_2O_3 or $HgS_2S_2O_3Aq$ is formed, along with AgS_2O_3 or $HgS_2S_2O_3Aq$ is formed, along with R₂S₂O_aAq or Na₂S₂O_aAq is formed, along with Ag₂S or HgS (Spring, L.c.); by reacting on M₂SO₂Aq with S₂Cl₂ (Spring, B. 6, 1108); by decomposing M₂S₂O₂Aq by a non-oxidising acid, e.g. by H₂SO₄ (Spring a. Levy, Bull. de l'Acad. roy, de Belge, 42, 108); by heating (NH₂)₂SO₄ with P₂S₃, Spring (B. 7, 1158) obtained a little (NH₂)₂SO₆, along with much (NH₂)₂SO₆ some NH, polysulphides, and P compounds; K2S3O6 is also obtained from Wackenroder's solution.

The trithionates are soluble in water; they very readily decompose; heated with water they give off SO, deposit S, and form sulphates in solution. Addition of excess of CuSO,Aq to solution of a trithionate causes ppn. of CuS and

evolution of SO, (Spring, B. 6, 1108).

SELENOTRITHIONATES M.SeS.O. are described dithio-triselenates under Selenates (p. 434). Potassium trithionate K2S3O8. A conc. solution of K2S2O3 is formed by dissolving the salt in 8 pts. water and 1 pt. alcohol till the alcohol separates from the aqueous solution; SO₂ is passed into this solution at 25°-30°, solid K₂S₂O₃ being added from time to time, till the liquid is yellow and smells of SO₂; the crystals that separate are dissolved in water at 60°-70°. the solution is filtered from S, mixed with eight times its volume of 84 p.c. alcohol, warmed gently, and allowed to crystallise (Plessy, A. Ch. [3] 20, 162; for other methods of preparation v. Langlois, A. Ch. [2] 79, 77; Rathke, J. 1864. 164; Chancel a. Diacon, C. R. 56, 710). White rhombic needles (Baker, C. N. 36, 203). Very sol. water, insol. alcohol. Aqueous solution gives K₂SO₄Aq, SO₂, and S when heated. Debus (C. J. 53, 313) found that K₂S₃O₆Aq slowly changes at the ordinary temperature, giving K,30,Aq, states at the ordinary temperature, giving K,30,Aq, K,28,O,Aq, and K,53,0,Aq without separation of S. According to C. a. D. (l.c.), K,5,O,Aq interacts with K,5,Aq to give only K,5,O,Aq; with H,S the products are K,SO,Aq, K,28,O,Aq, and S (Debus, C. J. 53, 329). Sodium-amalgam reacts (Readily, producing KNaS₂O₃ and KNaSO₃ (Spring, B.7, 1161).

The other trithionates that have been iso-

The other trumonates that have been isolated are those of Ba (Kessler, P. 74, 253); Pb (K., l.c.; Chancel a. Diacon, O. R. 56, 710); Na (K., l.c.; Rathke, J. fr. 95, 13; Villiers, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); Rather, C. R. 106, 1356); and Zn (Fordos a. Gélis, A. Ch. 1312); and Rather, C. R. 106, 1356); and Rather, Ra

TETRATHIONATES M',S,O, and M''S,O,.
The alkali salts are formed by triturating M,S,O, with I, adding a little water and pouring into

atcohol (von Klobukoff, B. 18, 1869; Eliasberg, B. 19, 322; Fock a. Klüss, B. 23, 2429); the Pb salt is formed by the prolonged interaction of I and PbS_O, also by the interaction of H_SO_Aq and a mixture of PbS_O, with PbO₂ (Chancel a. Diacon, J. pr. 90, 55); tetrathionates are also formed, according to Spring a. Levy (Bull. de l'Acad. roy. de Belge, 42, 108), by the interaction of thiosulphates and ferrous or cuprous salts, KMO_Aq, hypochlorites, or KClO₃ dissolved in H_SO_Aq. K_S_O₄ is obtained by neutralising Wackenroder's solution by KC_H_O₂ (v. Debus, G. J. 53, 278; cf. Curtius a. Henkel, J. pr. [2] 37, 137). The tetrathionates are c. sol. water, but insol. alcohol; aqueous solutions are generally decomposed on evaporation.

Potassium tetrathionate K.S.O., Formed by adding I, little by little, to cone. K.S.O., Aq till a permanent reddish-brown colour is produced, dissolving the crystals that separate in warm water, filtering from S, adding alcohol till the pp. that forms is re-dissolved, and allowing to crystallise (Kessler, P. 74, 253). Spontaneous decomposition of cone. K.S.O., Aq gives K.S.O., and S (Debus, C. J. 53, 311). Perfectly dry K.S.O., ac ne be kept unchanged in a dry atmosphere; but in ordinary air, after a time, SO., is formed; an aqueous solution of K.S.O., Slowly changes to K.S.O., Aq., K.S.O., Aq., K.S.O., Aq., and SO., (D., l.c.). BrAq reacts to form H.SO., Aq. S, and KBr; but if the BrAq is added very gradually the S that is formed combines with residual K.S.O., to form K.S.O., Aq., and H.S is then passed in, K.S.O., and S are formed, and the S combines with unchanged K.S.O., to form K.S.O., (D., l.c.). Sodium-amalgam forms KNaS.O., Aq (Spring, B. 7, 1161).

The other tetrathionates that have been isolated are those of Ba (Lewes, C. J. 39, 69; Fordos a. Gólis, A. Ch. [3] 32, 66; Curtius a. Henkel, J. pr. [2] 37, 137); Cd (Kessler, P. 74, 253); Gu (Chancel a. Diacon, C. R. 55, 510); Fe (F. a. G.); Pb (K.; C. a. D.); Na (K.; von Klobukoff, B. 18, 1869); Sr (K.); and Zn (F.

PENTATHIONATES M',S,O, and M''S,O,. Wackenroder, in 1845 (A. 60, 189), asserted that the liquid formed by passing H,S into SO,2Aq contained pentathionic acid H,S,O,; other chemists confirmed his results, and prepared a few salts of the acid (v. Lenoir, A. 62, 253; Fordos a. Gélis, A. Ch. 13] 22, 66; Kessler, P. 74, 257; Ludwig, Ar. Ph. [2] 85, 9; Chancel a. Diacon, C. R. 56, 710. At a later time the existence of pentathionates was denied, chiefly by Spring (B. 12, 2254; 13, 924; 15, 2618), but upheld by Kessler (B. 13, 424; v. also Takatmatsu a. Smith, B. 13, 1076). In 1881 Lewes (C. J. 89, 68) seemed to have isolated BaS,O, and K,S,O, but Spring failed to confirm his results. Shaw, however (C. J. 43, 357), repeated Lewes's experiments, and obtained K,S,O. In 1888 Debus (C. J. 53, 278) made an elaborate investigation of Wackenroder's solution, and prepared K,S,O, therefrom. Curtius a. Henkel (J. pr. [2] 37, 187) assert that Wackenroder's solution contains acid tetrathionates, in which the ratio of S to Ba is greater than 48:Ba, and that these have been mistaken for pentathionates. But Debus's experiments seem to have settled

the dispute in favour of the existence of pentathionates. Ammoniacal AgNO₂Aq gives very distinct brown colouration, followed by a black pp, with pentathionates; this reaction distinguishes them from salts of other 8 oxyacids (v. Debus, Lc., p. 297).

Lc., p. 297),

Potassium pentathionate 2K₂S₂O₆, 3aq.

Debus (C. J. 53, 294) prepared this salt from Wackenroder's solution (v. p. 699) by adding the salt of the salt from the sal 16:66 g. KC.H.O. previously fused) to 43 c.c. of the solution of S.G. 1343; the KC.H.O. was dissolved in as little water as possible acidulated with a few drops of acetic acid; the solution was placed in a large flat dish in a current of air until the liquid had evaporated; the crystalline residue (weighing 26 g.) was repeatedly pressed between filter-paper, and then dissolved in 50 c.c. water + 1 c.c. H.SO., at 40°; the minute quantity of S that separated (c. '005 g.) was filtered off, and the filtrate was allowed to crystallise in a flat dish. The crystals that separated (18.75 g.) were a mixture of K.S.O. and K2S3O4; they were dried by placing them on blotting paper, and the crystals of pentathionate were picked out (5.75 g. were obtained), crystallised twice from water acidulated with a little H.SO,Aq, and dried over H.SO. The crystals H_SO,Aq, and dried over H_SO. The crystals of pentathionate form four-sided rhombic plates, or six-sided star-like plates; those of tetra-thionate form six-sided prisms, with pyramids only on one end, and with the side on which only of one char, and with the sale of which they rest much developed. Lewes (C. J. 39, 75) described three salts: K₂S₂O_a, K₂S₂O_a, H₂O, and K₂S₃O_a, 2H₂O; Debus's salt was 2K₂S₂O_a, 3H₂O. According to Fock a. Klüss (B. 23, 2428), this is the only salt that exists (cf. D., l.c., p. 297). The salt can also be obtained by passing H.S into

Crystals of $2K_sS_0O_a$ 3H_O begin to decompose, when kept in a stoppered bottle, after a month or so, giving eventually a yellow, pulpy mass of $K_sS_0O_a$, S, and water; the decomposition is caused by water in the interstices of the crystals. By powdering finely, washing with dilute alcohol, and placing over H_sS_0 , Debus (l.c. p. 295) kept the salt unchanged for two or three years. $2K_sS_0O_a$ 3H_O dissolves in c. 2 parts water, forming a clear, neutral solution, which soon decomposes with separation of S and formation of $K_sS_0O_a$ 4Q (D., l.c., p. 311); addition of a drop of dilute KOHAq to the solution causes separation of S (p. 291); $H_sS_0O_a$ 4 produces $K_sS_0O_a$ 4 and $K_sS_0O_a$ 4 are formed in the solution (p. 328); SO_2 produces $K_sS_0O_a$ 4 and $K_sS_0O_a$ 4Q (p. 332); the salt is insoluble in alcohol.

K.S.O.Aq acidulated with H.SO.Aq (D., l.c., p.

Barium pentathionate BaS_aO_a . 3aq; obtained by Lewes (C. J. 39, 68) by partially neutralising Wackenroder's solution by BaOAq, crystallising over H_aSO_a , pouring off from BaS_aO_a , and again crystallising.

Copper pentathionate CuS, O., 4ac; obtained by Debus (i.e., p. 300) in blue, prismatic crystals, by adding Cu(C,H,O,),Aq to Wackenroder's solution and allowing to evaporate. Debus probably obtained zinc pentathionate, but not in a pure state (i.e. p. 290)

in a pure state (l.c., p. 299).

HEXATHIONATES. By adding KC,H,O,Aq
to the mother-liquor from K,S,O, and K,S,O,
(v. supra), evaporating in a current of air, dis-

solving in water with a little H.SO.Aq, allowing to evaporate in portions, and collecting the crystals separately, Debus (C. J. 53,301) obtained a salt in which the ratio of S to O was almost 68:60, as required by potassium hexathionate.

os:oo, as required by points tarm necessariance.

M. M. P. M.

THIONESSAL v. Tetra-phenyl-menophene.

THIONIC ACIDS. The acids H.S.O., where

z=2, 3, 4, 5, and probably 6, are generally called thionic acids, and are distinguished as di-, tri-, &c., thionic acid. The acids are known only in aqueous solutions: most of these solutions readily oxidise to H_SO_Aq. Dithionic acid is produced by the action of certain oxidisers on H_SO_Aq; dithionates are formed by oxidising sulphites and thiosulphates; trithionates are formed when mixtures of sulphites and thiosulphates are oxidised, also when SO, Aq interacts with alkali thiosulphates; tetrathionates result by the action of certain oxidisers on thiosulphates. These processes may be represented diagrammatically as follows (the actual re-actions are much more complex):

(1) 2H₂SO₃Aq + O = H₂S₂O₆Aq + H₂O; (2) 2M₂SO₃Aq + O = M₂S₂O₆Aq + M₂O; M₂S₂O₃Aq₂ + 3O = M₂S₂O₆Aq; (3) M₂S₂O₃Aq + M₂S₂O₃Aq + O = M₂S₂O₆Aq;

(4) M₂SO₂Aq + M₂SO₄Aq + SSO₂Aq = 2M₂S₂O₆Aq + S; 2M₂S₂O₄Aq + SO₂Aq = 2M₂S₂O₆Aq + S; (4) 2M₂S₂O₄Aq + O = M₂S₁O₆Aq + M₂O₅. After passing H₂S for a long time into nearly saturated H₂SO,Aq, the solution contains H₂S₂O₆, much H₂S₄O₆, H₂S₅O₆, and probably H₂S₆O₆, along with H₂SO₄, dissolved solloidal S, and a little S in suspension. This solution is known as Wackenroder's solution (Wackenroder, A. 60, 180 [1845]). It has been examined by many chemists; a very thorough investigation was made by Debus in 1888 (C. J. 53, 278; where references will be found to other memoirs). The solution examined by Debus was prepared by passing a slow current of H2S into 480 c.c. nearly saturated SO2Aq at a little above 0° for two hours, keeping in a stoppered bottle for forty-eight hours at the ordinary temperature, passing in H₂S for two hours, after forty-eight hours again passing in H₂S, and repeating these treatments until the liquid no longer smelled of SO, after standing for a couple of hours at the ordinary temperature (about two weeks were required before the action was completed). liquid thus obtained contains a large quantity of S, partly as a hard brittle solid, partly as a soft and gummy mass, and partly in suspension in minute particles which pass through filter paper; the liquid remains milky after filtration, and does not become clear on standing for two or three weeks (regarding the variety of S its solution, v. Sulphur, Allotropic forms of, p. 608). Debus (l.c., p. 348) thinks that the product of the direct interaction of SO, Aq and duct of the direct interaction of SC₂Aq and H₂SA₂A₁B₃C₄Aq); that part of this H₂S₁O₄ reacts with excess of SO₂Aq fo form H₂S₂O₄Aq and H₂S₂O₄Aq (PH₂S₂O₄Aq + H₂SO₄Aq + H₂ H. S.O.Aq forms H.S.O.Aq (? H.S.O.Aq + H.S.O.Aq = H.S.O.Aq + H.SO.Aq) (D., Lc., p. 838); that the H.S reacts with H.S.O.Aq to form H.O and S, part of the S combining, as it is formed, with H.S.O.Aq to form

H.S.O.Aq, H.S.O.Aq and H.S.O.Aq, and part

remaining in solution as colloidal S. If H₂S is passed into Wackenroder's solution, more H₂S₂O₂ is formed; and if the passage of H₂S is continued until all reaction ceases the thionic acids are decomposed, and the final product or S = 2 H₂O₂ = 1. products are S and H₂O, so that the equation SO₂Aq + 2H₂SAq = 3S + 2H₂OAq correctly represents the interaction of SO₂Aq with H₂SAq so far as the final products are concerned (v. D., l.c., p. 351).

Solutions of the thionic acids more or less rapidly decompose, the final products being H,SO,Aq, SO,Aq, and S; oxidisers such as Cl or HNO,Aq—in some cases air is sufficient convert them into H,SO,Aq; reducers, such as Na amalgam, produce H2S2O3Aq, sometimes also H₃SO₃Aq, and in some cases H₂SAq. None of the acids has been isolated apart from water; salts of all are known (v. Thionates, p. 695). The acids are all dibasic.

Regarding the constitution of the thionic acids v. Mendeléeff, B. 3, 870; Michaelis, A. 170,

31; Spring, D. 6, 1108; Debus, C. J. 53, 351.

DITHONIC ACID IL S.O. Aq. (Hyposulphuric acid.) A solution of this acid is formed by suspending coarsely-powdered MnO₂ in water, and passing in SO₂ while the liquid is kept at c. 0°; filtering, adding BaOAq to alkalino reaction, and filtering from BaSO, and MnO,H2; evaporating, crystallising out BaS, Og. 2aq, and decomposing this salt in solution by the equivalent quantity of H_SO, Aq ; filtering from BaSO, and evaporating in vacuo till a liquid of S.G. 1.347 is obtained (MnO₂ + 2SO₂Aq = MnS₂O₄Aq; MnO₂ + SO₂Aq = MnSO₄Aq) (Spring a. Bourgeois, Bl. [2] 46, 151). If evaporation is continued beyond this concentration, H.SO, Aq and SO, are formed; the same decomposition occurs when H.S.O.Aq is evaporated by heat. H.S.O.Aq is reduced by Zn and HClAq to H.SO.Aq at 0° (Otto, A. 147, 187); it is oxidised to H.SO.Aq by Cl, HNO₂, KClO₃ and HCl &c.; it slowly oxidises in air (cf. DITHIONATES, p. 695). Thomsen (Th. 2, 259) gives the following heats of Set (11.2, 2.3) gives the browning factor of formation of $H_{S_0}O_1^2Aq := [S^2,O^3,Aq] = 211,080$; $\{2SO^2,O_1Aq\} = 68,920$; $\{2SO^2,O_1Aq\} = 53,520$; for the heat of oxidation of $H_1S_1O_1Aq$ to H_2SO_1Aq he gives $(S_2O_5\Lambda q + O = 2SO_3\Lambda q) \quad [S^2O^3\Lambda q, O]$ = 78.710.

TRITHIONIO ACID H.S.O.Aq. A dilute solution of this acid is formed by decomposing K.S.O.Aq by the equivalent quantity of HClO.Aq or H.S.F.Aq, and filtering from KClO or K.S.F. (Langlois, C. R. 10, 461; 62, 812; Kessler, P. 74, 250). The dilute solution cannot be evaporated, even in vacuo, without partial decomposition, with formation of SO₂ and S; when heated it rapidly changes to H.SO,Aq, SO₂ and S. The dilute solution is colourless and odourless, and has a sour and bitter taste (cf. Tarthionates, p. 696). The K salt, from which the acid solution is obtained, may be prepared by dissolving K₂S₂O₂ in water containing one-eighth part of alcohol, adding the containing one-eighth part of alcohol, adding the salt till the alcohol separates from the aqueous solution, passing in SO,, with addition from time to time of a little K.S.O., temperature being kept at 25°-30°, till the liquid is yellow and smells of SO, setting aside till crystals separate, and re-crystallising from warm water (filtering from separated S) (Pleasy, A. Oh. [3] 11, 183). TETRATHIONIC ACID H.S.O.Aq. PbS.O.Aq is decomposed by the equivalent quantity of H.SO.Aq (not by H.S., which reacts with H.S.O.), and the filtrate from PbSO. is concentrated on the water bath, and then in vacuo over H.SO, (Fordos a. Gelis, C. R. 115, 920). PbS O may be prepared by pouring a solution of 2 pts. Na, S O, 5H, O in much warm water into a dilute warm solution of 3 pts. lead acetate, and thoroughly washing the ppd. PbS2O, with warm water, adding water enough to partially dissolve the PbS₂O₂, then adding 1 pt. I, and letting stand for some days, with frequent shaking, filtering from PbI₂, evaporating and crystallising (2PbS₂O₂+2I+Aq=PbS₂O₃Aq + PbI₂).

H₂S₂O₈Aq is colourless and odourless; it has

a sour taste. Dilute H2S4O6Aq may be boiled without change, but the conc. solution decomposes to H.,SO,Aq, SO., and S. Dilute HClAq or H,SO,Aq does not interact with cold H,S,O,Aq; H₂SO₄Aq does not interact with cold H₂S₁O₄Āq; on warming H₂S is given off; HNO₂Āq or Cl rapidly oxidises II₂S₁O₄Aq to H₂S₂O₄Aq or Cl rapidly oxidises II₂S₂O₄Aq to H₂S₂O₄Aq or Cl retarrationates, p. 696). Thomsen (Th. 2 262) gives the following data for II.F.:—[S',O,Aq] = 192,430; [2SO²S₂O,Aq] = 50,270; [2SO²Aq,O] = 53,490. Pentathitonic acid H₂S₂O₂Aq, and Hexathinonic acid H₂S₂O₂Aq. These acids very probably exist in Wackguroder's solution (v. supra., 698), as salts of H₂S₂O₃, and probably also of H₂S₂O₃, have been obtained from that solution; solutions of the acids have not been isolated

solutions of the acids have not been isolated (v. Pentathionates, p. 697, and Hexathionates,

697). THIONINE. The group $S \longrightarrow C_uH_u(NII_J)$. N. P. M. THIONINE. The group $S \longrightarrow C_uH_u(NII_J)$. N. THIONINE.

i.e. $C_uH_u(NH_u) < \sum_{N}^{S} > C_uH_u:NH$ (Bernthsen a. Goske, B. 20, 931).

 $\textbf{THIONOL} \ C_{12} H_7 NSO_2 \ \textit{i.e.} \underbrace{S}_{C_6 H_3 (OII).N} C_6 H_3 > 0.$ Formed by heating imido-di-phenyl sulphide with dilute H₂SO₂ at 150°-160° (Bernthsen, A. 230, 188). Brownish-red powder, which acquires green lustre on rubbing. Insol. cold water, sol. acids and alkalis, forming a violet solution. Yields di-oxy-imido-diphenyl sulphide (q. v.) on reduc-tion.—B'2H2SO4. Green needles.—B'BaO (dried at Plates with green lustre.-B'Ag O'(dried at 100°). Brown amorphous pp. .

THIONOLINE v. OXY-AMIDO-IMIDO-DIPHENYL SILPHIDE.

THIONURIC ACID C.H. N.SO. i.e.

CO NH.CO CH.NH.SO, H. Formed by the

simultaneous action of NH, and SO, on alloxan in aqueous solution (Liebig a. Wöhler, A. 26, 268, 314, 331). Formed also by warming nitrosobarbituric acid with ammonium sulphite (Baeyer, A. 127, 210). Crystalline mass of needles, v. sol. water. Decomposed by boiling water into uranil and H₂SO₂. Reduces ammoniacal AgNO₃ to a mirror.—(NH₃A"aq. Four-sided tables, al. sol. cold water. At 200° it yields (NH₃)₂SO₄ and zanthinine (Finck, A. 132, 298).—(NH₃HA". White needles.—CaA". Prisms.—PbA"aq.

THIONYL-m-AMIDO-BENZOIS ACID

SO:N.O.H..CO.H. Mathyl ether MeA'. [57°]. (212° at 100 mm.). Formed from methyl m-amido-benzoate

and SOCl, (Michaelis, A. 274, 250). Yellow crystalline mass, v. sol. ether and benzene.

Ethyl ether EtA'. Oil. THIONYL-DIAMIDO-DI-PHENYL-ETHYL-ENE C.H.(C.H.N.SO).. [2022]. Formed from di-amido-stilbene and SOCl. (Michaelis, A. 274, 265). Red needles, m. sol. benzene and CHCl., THIONYL-AMIDO-PHENOL. Ethyl de-

rivative C. H. (OEt). N:SO. [82°]. (220° at 200 mm.). Fortyed from p-amido-phenetol and SOCl. (Michaelis, A. 274, 246). Light-yellow needles, v. sol. ether. Slowly decomposed by water.

THIONYL-AMYLAMINE SO:NC,H₁₁. (87° at 60 mm.). Formed from amylamine (103°) in ether and SOCl₂ (Michaelis, A. 274, 191). Oil, decomposed by water.

THIONYL-ANILINE C.H.N.SO. (200°), S.G. 15 1.236. Formed from aniline in benzene solution and SOCl. (Michaelis, B.23, 3480; 24,745). Liquid with peculiar odour, sol. alcohol. Converted by alkalis into aniline and sulphite. Chlorine forms tri-chloro aniline [78°]. Conc. HClAq also forms aniline and SO₂. The compound C₆H₁Br₈N:SO [750] is the superior and the compound C₈H₂Br₈N:SO [750] is the superior and superior aniline and SO₂. [75°] is formed from tri-bromo-aniline in benzene and SOCl₂. The compounds [1,2]C₃H₁Cl.N.SO [-8], [1:3] C₆H₂Cl.N.SO (233°) and [1:4] C₆H₂Cl.N.SO [36°] (237°) are formed in like manner. o., m., and p. Thionyl-bromo-anilines melt at 4°, 32°, and 61° respectively (Michaelis, 4.274, 201). This problem of the composition of the compositi A. 274, 221). Thienyl-tetra-bromo-aniline melts Thionyl-p-iodo-aniline [54°] and [4:2:1] at 78°. C.H. I. N:SO [74°] are also crystalline.

ference.-Nitro-thionyl-aniling THIONYL BROMIDE SOBr. v. Sulphub oxy-

BROMIDES, p. 617.
THIONYL-ISOBUTYLAMINE C.H.NSO i.e. CHMe₂.CH₂.N:SO. (116°). Formed from SOCl₂ and isobutylamine in other (Michaelis, A. 274,

191). Liquid, with pleasant smell.
THIONYL CHLORIDE SOCI, v. SULPHUR

OXYCHLORIDES, p. 617. THIONYL-CUMIDINE C.H.Pr.N:SO. (158°). Got from SOCI, and the cumidine obtained from isopropyl-benzene by nitration and reduction (Michaelis, A. 274, 239). Oil, not decomposed by boiling water.

Thionyl-\psi-cumidine CaH_Mea.N:SO. [-10°].

(246°). Oil, v. sol. alcohol and ether.

THIONYL ETHYLAMINE EtN:SO. Formed by adding SOCI, to an ethereal solution of ethylamine cooled below 0° (Michaelis, B. 24, 756).

.C.H.Me.N:SO. Volatile with THIONYL-MESIDINE [-11°]. (241°). S.G. ¹⁴ 1·121. steam (Michaelis, A. 274, 240).

THIONYL-METHYLAMINE MeN:SO. (59°). Liquid (Michaelis, A. 274, 187).

THIONYL-METHYL ANILINE

SO(C.H. NHMe)₂. [154°]. Formed from SOCl, and methyl-aniline in ethereal solution in preand methyl-amment extension as the sence of AlCl. (Michaelis a. Godohaux, B. 23, 3019). Colourless needles, v.* sol. alcohol. Yields a nitrosamine SO(C_bH., NMe.NO), [171°].

THIONYL-(a)-NAPHTHYLAMINE C₁₆H. N:SO. [33°]. (226° at 100 mm.). Formed from (a)-naphthylamine in benzene and SOCI. (Michaelis, A. 274, 253). Reddish yellow needles, slowly converted by water into naphthylamine. sulphite.

Thionyl-(β)-naphthylamine [53°]. Needles. The thionyl derivative of bromo-(\$\beta\$)-naphthyl-

amine [63°] melts at 118°.

THIONYL-o-NITRO-ANILINE C₆H₄N₂SO₃ i.e. C₆H₄(NO₂).N:SO. [62°], the m-compound melts at 63°, while the p-isomeride melts at 70° (Michaelis, A. 274, 225).

THIONYL-NITRO-MESIDINE "C.H10N2SO3 i.e. C. HMe. (NO.). N:SO. [77°]. Got from nitro-mesidine [74°] (Michaelis, A. £74, 241). Light yellow needles, v. e. sol. benzene.

Thionyl-di-nitro-mesidine. [127°]. Formed

from di-nitro-mesidine [193°

THIONYL-NITRO-NAPHTHYLAMINE C₁₀H₆(NO₂).N:SO. Nitro-naphthylamines [191°] and [119°] yield thionyl derivatives melting at 89° and 135° respectively (Michaelis, A. 274, 258).

THIONYL-NITRO-TOLUIDINE C,H,N,SO, 4.e. C.H.Me(NO.).N:SO. The compounds from (2,1,4)-nitro-toluidine [75°] and (3,1,4)-nitro-toluidine [114°] melt at 44° and 39° respectively (Michaelis, A. 274, 232).

DI.THIONYL-PHENYLENE-DIAMINE

C_aH₄(N:SO)₂. The m- and p- compounds melt at 44° and 116° respectively (Michaelis, A. 274, 261).

THIONYL-PHENYLETHYL-AMINE
PhCH₂CH₂N:SO. (172° at 25 mm.). Liquid,

decomposed by water into SO, and base. SO, passed into its othereal solution forms amorphous PhCH, CH, NH. SO,H, whence benzoic aldehyde yields PhCH, CH, N(SO,H). CHPh.OH [114] (Michaelis, B. 26, 2167).

THIONYL-PHENYL-HYDRAZINE v. Action

of SOCl₂ on Phenyl.-Hydrazine.
THIONYL-PHENYL-PROPYLAMINE

CH2Ph.CH2.CH2.N:SO. Formed from phenylpropylamine hydrochloride and SOCl2 (Michaelis a. Jacobi, B. 26, 2161). SO₂ passed into its ethereal solution forms the amorphous compound NH(SO₂H).C₂H_aPh, which reacts with benzoic aldehyde forming SO₂H.N(CHPh.OH).C₂H_aPh (106°).

THIONYL-PROPYLAMINE PrN; SO. (104°). Smells like bleaching-powder (Michaelis, A. 274,

190).
THIONYL-TOLUIDINE C.H.Me.N.SO.

Formed from toluidine and SOCI, The o-compound is liquid (184° at 100 mm.). The m-compound is liquid (220°). The p- isomeride [7°] pound is liquid (220'). The p-isomerate [1] (c. 224°) may be crystallised by cooling (Michaelis a. Herz, B. 23, 3482; 24, 753; A. 274, 231). The thionyl derivatives of (3,1,4)- and (5,1,2)-bromo-toluidines melt at 47° and 50° respectively.

bromo-toluidines melt at 47° and 50° respectively.

THIO-ORCIN C_aH_aMe(SH)₂. [35°]. Formed
by reducing C_aH_aMe(SO_aCl), with tin and HClAq
(Gabriel, B. 12, 1640).—PbO,H_aS₂.

THIONYL-XYLIDINE C_aH_aMe_aN:SO. The
(1,2,4)- compound [-9°] (131° at 20 mm.),
(13,4)- compound (238°), and (1,4,2)- isomeride
[-8°] (119° in vacuo) are all oily (Michaelis, A.
274, 287). Thionyl-fluoro-xylidine (144° at 45 mm.) is also an oil.

THIO-OXALIC ACID. Ethylether C.H., SO, i.e. CO.Et. CO.SEt. (217° cor.). S.G. 2 1-145. Formed by the action of Cl.CO.CO.Et. on mercaptan (Morley a. Saint, C. J. 43, 400). Colourless liquid with faint odour like garlic. Colouriess inquite with a late of the composed by KOHAq into mercaptan, alcohol, and oxalate. Alcoholic KOH (1 mol.) forms EtSH and CO_Et.CO_K. Water slowly decomposes it, forming oxalic acid, alcohol, and mer-

aptan. Dry NH, forms mercaptan and CO,Et.CONH.

(β)-Thio-oxalic acid NH₂CS.CO₂H. The salt C₂H,KNSO₂ is formed by the action of cold conc. KOHAq on the ethers. It crystallises in needles, v. sol. water and decomposed by evaporating. The free acid is unstable.

Tating. The free acid is unstable.

Amide of the methyl ether.

NH_CS.CO_Me. [86°]. Formed by passing dry
H_S into Cy.CO_Me (Weddige, J. pr. [2] 7, 79;
9, 133; 10, 193). Light-yellow crystals, sol.

water, alcohol, and ether.

Amide of the ethyl ether NH_CS.CO_Eta-Mol. w. 133. [64°]. Formed in like manner. Lemon-yellow crystals. Re-converted by boiling with alcohol and Pb(OH), into cyanoformic ether. Methylamine and ethylamine form the crystalline compounds CO(NHMe).CS.NH2 and CO(NHEt).CS.NH2 respectively.

Amide of the isobutyl ether

NH₂.CS.CO₂C₄H₉. [58°]. Lemon-yellow crystals, sl. sol. water.

Di-amide CO(NH2).CS.NH2. Formed from CO, Et. CS. NH., and alcoholic ammonia (Weddige, J. pr. [2] 9, 137). Lemon-yellow needles (from alcohol), sl. sol. water.

Di-thio-oxalic acid. Amide CS(NH2).CS(NH2). Hydrogen rubeanide. Mol. w. 120. Formed, together with yellow Cy.CS.NH2, by combination of cyanogen with H.S (Wöhler, P. 3, 177; Völckel, A. 38, 315). Formed also by passing cyanogen into an alcoholic solution of NaSH and ppg. by HCl (Wollner, *J. pr.* [2] 29, 129; Ephraim, *B.* 22, 2305). Prepared by passing H2S into an ammoniacal solution of CuSO, which has been decolourised by KCy (Formanck, B. 22, 2655). Small yellowish-red crystals, sl. sol. water, sol. alcohol and ether. Dilute KOHAq forms oxalic acid, conc. KOHAq forms KCy and KCyS. Boiling HClAq forms oxalic acid. MeI and MeOH at 150° form SMe, I. Alcoholic hydroxylamine hydrochloride (2 mols.) forms $C_2(NH_2)_2(NOH)_2$ and H_2S . Benzoic aldehytic, acting on a boiling solution, forms a compound [209°] which is apparently

CHPh<S>C.C≤S>CHPh (Ephraim, B. 24,

1027) PbC₂H₂N₂S₂: orange pp. (Wallach, B. 13, 528). Yields PbS on boiling with water.

Anilide CS(NHPh).CS(NHPh). Formed from oxanilide by successive treatment with PCl, and H2S (Wallach, B. 13, 527). Golden plates.

Di-methyl-di-amide D1. methyl. d2. amrae CS(NHMe). CS(NHMe). [140°]. Formed from thiocyanic acid, alcohol, and methylamine (Wallach, 4. 262, 360). Yellow crystals, sl. sol. alcohol. Converted by NaOEt and propyl chloride into C(NMe)(SC₂H₁).C(NMe)(SC₂H₂) (170°-175°).

Di-ethyl-di-amide CS(NHEt).CS(NHEt). [58°]. Formed in like manner. Yellowish-red crystals, insol. water. Converted by NaOEt and Etl into C(NEt)(SEt).C(NEt)(SEt) (126°-129°).

Di-amyl-di-amids

CS(NHC,H₁₀).CS(NHC,H₁₀). [60°]. Formed from thiocysnic acid, alcohol, and amylamine (Wallach, A. 262, 362). Red prisms.

Di-bensyl-diamide CS(NHCH,Ph).CS(NHCH,Ph). [115°]. Formed

from thiocyanic acid, alcohol, and benzylamine. Yellowish-red crystals, al. sol. warm alcohol. Hexa-thio-ortho-oxalic acid. Ethyl ether

C.(SEt). Formed from C.Cl. and NaSEt (Classon, J. pr. [2] 15, 212). Heavy oil. THIO-OXY- v. SULPHYDRO-.

THIO-PARABANIC ACID. Methyl derivative v. METHYL-THIG-PARABANIC ACID. Allyl derivative C.H.N.SO, i.e.

 $_{\text{CS}}$ $\stackrel{\text{NH.CO}}{\stackrel{\text{CO}}{\sim}}$ $\stackrel{\text{CO}}{\sim}$ Oxalyl - thio - sinaminc. [90°]. Formed by warming the dicyanide of allyl-thio-urea with dilute H₂SO₄ (Maly, Z. 1869, 260). Lemon-yellow needles, m. sol. cold water.

THIOPHENE C,H,S i.e. SCH;CII cor.). V.D. 3-0 (calc. 2-9). S.G. 22 1-062; \$1-0884; \$\frac{1}{2}\$1-0705 (R. Schiff, B. 18, 1601). S.V. 84-9. \$R_{\infty}\$ 41-4 (Nasini a. Scala, G. 17, 70). H.C.p. 670,900 (Berthelot a. Matignon, C. R. 111, 1200). 10; Bl. [3] 4, 252). H.F. -14900. Critical temperature 317° (Pawlewski, B. 21, 2141). Critical pressure 47.7 atmospheres. Occurs in coal-tar benzens to the extent of about 5 p.c.

(V. Meyer, B. 16, 1471).

Formation .- 1. In small quantity by passing acetylene through boiling sulphur (V. Meyer a. Sandmeyer, B. 16, 2176).—2. By heating succinic anhydride with P.S.,—3. By heating sodium succinate with P.S., the yield being 50 p.c. of the theoretical amount (Volhard a. Erdmann, B. 18, 460). It is not beauty the heating 18, 454). It is not formed by heating s-di-bromo-succinic acid with P2S3 or P2S3 (Ossipoff, J. R. 20, 245). -4. By heating crythrite with P.S. (Paul a. Tafel, B. 18, 688). -5. From its (α)-carboxylic acid, which is obtained by heating mucic acid with BaS (Paul a. Tafel, B. 18, 456).-6. In small quantities by passing Et2S through a red-hot tube (Meyer, B. 18, 217) .- 7. In small quantities by passing ethylene, coal-gas, or ligroin-vapour over heated iron pyrites. -8. In small quantities by heating P2S3 with crotonic acid, with n-butyric acid, with paraldehyde, or with ether (Meyer).

Isolation .- 20 pts. commercial 'pure ' benzene is shaken for four hours with 1 pt. of H.SO. The acid is diluted with two or three times its weight of water and treated at once with steam. Nearly pure thiophene passes over. Yield, about 3, p.c. by volume of the H₂SO, used (Schulze, B. 18, 497).

Properties.—Liquid with faint odour, not decomposed below 335°. Not solid at -20°. Greatly resembles benzene. Oxidised by HNO3 with great violence. On shaking with isatin and H₂SO, it yields a blue colouring matter (indophenine). Not affected by boiling with sodium. Benzene that contains thiophene gives a bright-blue colour to H.SO, containing nitrous a origin rouge corour to m. So, containing introdus acid. Thiophene (10 g.) shaken with alcohol (100 g.), cold saturated HgCl₂ solution (1,000 g.), and NaOAc (70 g.) dissolved in water (130 g.) forms a white pp. containing C₄H₂(HgCl)S₄, which containing the containing that the states of the containing that the states of the saturated lines are also below in white states. which crystallises from alcohol in white plates [188°], and C,H₂(HgCl),S, a white powder, insolateohol (Volhard, A. 267, 172). The compound C,H₃(HgCl)S is converted by AcCl into a thienyl worthyl between and by I into methyl ketone and by I into di-iedo-thiophene. Thiophene combines with CHPh, and with dibromo-di-(8)-naphthyl oxide (Liebermann, B. 26, 853).

Reactions.—1. Chloral and H₂SO₄ yield CCl₂CH(C₁H₂S)₂.—2. BzCl and AlCl₂ form thienyl phenyl ketone.—3. Phenyl-glyoxylio acid and H₂SO₄ form C₁₂H₂NSO₂, which dissolves in chloroform with crimson, and in H₂SO₄ with the chloroform with crimson, and in H₂SO₄ with purple colour.—4. Cl and Br yield chloro- and bromo- derivatives.—5. H.SO, forms a brown solution containing a sulphonic acid, and slowly decomposes the thiophene, forming H.S., SO, and an amorphous pp.—6. II₂SO, and KNO form a compound called 'nitroso-dithiophene'

HO.N C.H.S O (?), ppd. by water as a dark insoluble powder (Liebermann, B. 20, 8231) .-7. Passed with PCl, through a red-hot tube it 7. Passed with PCl₂ through a red-hot tube it forms C₁H₂S.PCl₂ (218°) which is decomposed by water into C₁H₂S.P(OH)₂ [70°] and is converted by Cl into C₁H₃S.POCl₂ (259°) and by water into C₁H₃S.PO(OH)₂ [159°] (Sachs, B. 25, 1514).—8. Diazobenzene chloride and AlCl₃ forms (\$\textit{\theta}\)-phenyl-thiophene [57°] (Möhlau a. Berger, B. 20.2001).

References .- AMIDO-, BROMO-, DI-BROMO-DI-NITRO-CHLORO-, TRI-CHLORO-NITRO-, IODO-, IODO-NITRO-, and NITRO- THIOPHENE.

THIOPHENE (a) CARBOXYLIC ACID

C,H,SO, i.e. SCH CH. Thiophene 'B'carboxylic acid. [126.5°]. (260° cor.). H.F. 85,400. H.C.p. 591,900 (Stohmann, J. pr. [2] 43, 12). Formed by adding sodium-amalgam to a mixture of Cl.Co.Et with (a)-iodothiophene, with di-iodo-thiophene, or with di-bromo-thiophene (Nahnsen, B. 17, 2192; 18, 2304; Bonz, B. 18, 1900). 2306). Formed also by heating mucic acid with BaS for 6 hours at 205°, the yield being 12 p.c. of the theoretical (Paal a. Tafel, B. 18, 456). Obtained by oxidation of (a)-ethyl-thiophene (Schleicher, B. 18, 3017), of (a)-propyl-thiophene (Ruffi, B. 20, 1740), of thienyl methyl ketose (Peter, B. 17, 2645; 18, 542), and of thienyl ethyl ketone (Ernst, B. 20, 518) with alkaline KMnO.

Properties .- Slender white needles (from water) or long flat needles (by sublimation), v. sol. hot water, sl. sol. cold, v. e. sol. alcohol and ether, m. sol. chloroform, sl. sol. ligroin. a blue colour on warming with isatin and H₂SO₄ (indophenine reaction). Yields thiophene on bistilling with lime. Yields a di-bromo-derivative [211].

uve [211].
Salts.—BaA', 2aq. Small crystals. S. 22·19
at 14·5·.—CaA', 3aq. S. 18·5 at 18·5°.—ZaA',
(dried). S. 14 at 15·.—PbA', (dried). 5 at 18·5°.

—AgA': plates or needles. S. ·195 at 11°.

Ethyl ether Eth'. (218° cor.). S.G. 22
1·115#. Liquid, smelling like benzoic ether.

(190° uncor.).

Chloride C.H.S.COCI. Liquid, smelling like benzoyl chloride.

A mide C.H.S.CONH₂. [174°] (Meyer, A. 236, 210). Prisms, m. sol. ether. Phenyl thio-C.H.S.CO.NH.CO.NHPh. forms carbimide [206°]

Anilide C.H.S.CONHPh. [140°]. Formed by the action of phenyl cyanate on thiophene in presence of AlCl. (Leuchart a. Schmidt, B. 18, 2340). Iridescent plates.

Amidoxim C.H.S.C(NOH).NH. [92].

Formed by the action of hydroxylamine on the

nitrile (Meyer, A. 236, 213). Long prisms (from benzene).

Nitrile (192°) (D.); (200° cor.) (Peter, B. 18, Fermed by distilling thienyl-glyoxylic acid with aqueous hydroxylamine (Douglas, B. 25, 1311).

Tetrahydride SCH(CO.H).CH. [51°]. H.F. 114,900. H.C.p. 700,400. Formed by reducing the acid, in alkaline solution, with sodiumamalgam (Ernst, B. 19, 3278; 20, 518). Plates or needles (from ligroin), v. e. sol. water and alcohol, v. sol. ether. Volutile with steam. or needles them agreem, the steam alcohol, v. sol. ether. Volutile with steam. Much decomposed on distillation. Reduces ammoniacal AgNO. Salts.—CaA', 3aq. Crystalline, sol. water.—AgA'. M. sol. water. Methyl ether MeA'. ether EtA'. Liquid. (c. 206°). Ethul

Thiophene (β)-carboxylic acid

S<CH:CH (γ)-Thiophenic acid. [136°]. S. 44 at 17°. Formed by the action of alkaline KMnO, on (β) -methyl-thiophene (Muhlert, B. 18, KMnO₄ on (β)-methyl-thiophene (Muhkert, B. 18, 3008) or (β)-ethyl-thiophene, the yield being about 8 p.c. (Damsky, B. 19, 3284). Needles (from water), sol. ether, votatile with steam. Gives the indophenine reaction.— CaA'₂ 3aq. S. (of CaA'₂) 7-92 at 14·5°.—BaA'₄ (dried). S. 11·54 at 17°.—AgA'. Needles or plates, v. sl. sol. Aq. Amide CiH₃S.CONH... [178°]. Converted by phenyl cyanate into CiH₃S.CO.NH.CO.NHPh. 1206°1.

1206°

Thiophene 'a'-carboxylic acid. (258° cor.). This is a mixture of the (α)- and (β)- acids. It is got by saponifying the mixed nitrile which is formed by distilling a mixture of potassium thiophene (a) and (β) sulphonates with KCy (V. Meyer, B. 16, 2174; 18, 2315; Bonz, B. 18, 2308). Formed also by oxidising a mixture of (a) -methyl-thiophene (2 pts.) and (3) methyl-thiophene (3 pts.) and by slow evaporation of an aqueous solution of the mixed thiophene carboxylic acids in the cold (Egli, B. 18, 548; V. Meyer, B. 19, 2891; A. 236, 221). Volatile with steam. Can be separated into the (2)and (β)- acids by crystallisation.
Thiophene dicarboxylic acid

SCC(CO,H):C(CQ,H). [270°]. Formed by oxidising the corresponding di-methyl-thiophene with alkaline KMnO, (Grünewald, B. 20, 2586). Formed also by oxidising (\$\beta\$)-methyl-thienfl methyl ketone (Gorlach, A. 267, 153). Long needles (from water), v. e. sol. ether. Not yolatile with steam. Resorcin at 200' forms a fluorescein which exhibits yellowish-green fluor-escence in alkaline solution.—PbA".—BaA". Crystals, sl. sol. cold water.—Ag.A". White pp. Methyl ether Mo.A". [59.5°]. Plates.

Thiophene dicarboxylic acid

s<c(CO,H):CH

Formation,—1. By oxidation by alkaline KMnO, of dl-methyl-thiophene from coal tar (Messinger, B. 18, 567), from (a)-ethyl-thienyl methyl ketone, from (a)-ethyl-thiophene (a)-carboxylic soid (Schleicher, B. 18, 3020), from methyl-thienyl methyl ketone (Demuth, B. 18, 8025), and from (a)-methyl-thiophene carboxylic acid (Levi, B. 19, 656).—2. By saponifying its nitrile, which may be got by fusing potassirm

thiophene disulphonate with KCy (Jackel, B. 19, 191).—8. By saponifying its ether which is got by the action of sodium-amalgam on a mixture of di-bromo-thiophene and ClCO.Et (Bonz. B. 18, 2306).

Properties.—Crystalline powder, v. sl. sol. cold water, sol. ether. Not melted at 300°. Does not give the fluorescein reaction.

Salts. — BaA" aq. Crystalline, v. sl. sol. cold water.— CaA" Baq.—Ag;A": white pp.

Methyl ether Mc,A". [145] (J.); [147]
(S.); [151] (D.). White needles from alcohol.

Ethyl ether Et,A". [47] (J.); [52] Ethyl ether ELA [21] [0],

(S.). Long needles (from alcohol).

Nitrite C.H.SCy. [92]. Crystals.

Tetrahydride S CH(CO,H).CH2
CH(CO,H).CH3

[1620

cor.]. Formed by reducing the acid in alkaline solution by sodium-amalgam (Ernst, B. 19, solution by sodium-amalgam (Ernst, B. 19, 3275). Plates, v. sol. water, sol. ether. Roduces hot ammoniacal AgNO, Hot conc. IL_SO, cvolves CO (1 mol.).—BaA"; scales.—Ag_A": white powder.—Ma_A". Oil.

Thiophene dicarboxylic acid

S<CH——Q.CO₂H. Formed by oxidation of

S<CH - C.CO the corresponding di-methyl-thiophene by alkaline KMnO, (Zelinsky, B. 20, 2022). Needles, sl. sol. cold water. Decomposes and partially Methyl ether Me, A". [36°].

Thiophene tri-carboxylic acid C.SH(CO.H), Formed by oxidation of di-methyl-thienyl methyl

ketone with KMnO₄ (Messinger, B. 18, 2302).

Methyl ether Me₄A". [118°] Plates, v. sol. alcohol and ether.

References .- Bromo- and Iodo- THIOPHENE CARBOXYLIC ACID and NITRO-THIOPHENIC ACID.

THIOPHENE GREEN C., H., N., S. The leucobase C, SII, CII (OH) (C, H, NMe.), is got by heating thiophenic aldehyde with di-methyl aniline, ZnCl., and a little alcohol at 100° (I.evi, B. 20, 513). It crystallises in needles [98°], 20, 513). It crystames in needes (vo.), and is readily oxidised to thiophene green C₁BH_xC(OH)(C₄H₁NMc₂)₂, which is an oil and forms the salts (C₂H₂N₂S)₂ZnCl₂2aq, B'H₂SO₄, B'₂3H₄C₂O₄2aq, and B'2C₄H₂N₂O₇, crystallising in scates with coppery lustre.

Leuco-thiophene green v. TETRA-METHYL-DI-AMIDO-DI-PHENYL-THIENYL-METHANE.

THIOPHENE (a)-SULPHINIC ACID C,H,S.SO,H. [67°]. Formed by the action of zinc-dust on an alcoholic solution of thiophene sulphonic chloride (Weitz, B. 17, 800). Needles, v. sol. water, alcohol, and ether. Gives the indophenine reaction.—BaA', 2aq. White plates, v. sol. water,—ZnA', 2aq. AgA'. Crystalline pp.
THIOPHENE 'a'-SULPHONIC ACID

C.II.S.SO.H. Formed by shaking thiophene (20 g.) dissolved in ligroin (2,000 c.c.) with H.SO. (300 c.c.) for 2 hours (V. Moyer a. Kreis, B. 16, 2172; Biedermann, B. 19, 1615). Deliquescent mass. Yields thiophene on distillation. It is doubtless a mixture of the (a) and (b) acids.

NaA'aq.—BaA', 3aq.—CaA', —PbA', aq. Very soluble powder.—AgA' 3aq. Plates (Weits, B. 17, 796).

Ethyl ether EtA'. Oil. Chloride C.H.S.SO.CL [28"]. (above 200"). Oil or colourless crystals.

Amide C.H.S.CONH. [142°] (Langer, B. | 17, 1568). Needles (from water).-C.H.S.CO.NHAg. Pearly scales.

Anilide C.H.S.CONHPh. [96°L

Thiophene (8)-sulphonic acid

s CH:CH CH:C.SO.H Formed by the action of sodium-amalgam on di-bromo-thiophene (β)sulphonic acid, which is got by sulphonation of di-bromo-thiophene (Langer, B. 17, 1567; 18, 558). Obtained in like manner from iode-thiophene sulphonic acid, and from tri-bromothiophene sulphonic acid (Rosenberg, B. 18, 1776). Crystalline solid, v. sol, water. Gives a blue colour with isatin and H.SO₄.—BaA'₂.

Chloride C,H₃S.SO₂Cl. [43°]. Plates, v. sol. ether, insol. ligroïn.

Amide C₄H₃S.SO₂NH₂. [148°]. Tables. Thiophene disulphonic acid C₄H₂S(SO₃H)₂.

Formed by reduction of di-bromo-thiophene '\$\beta'\$ - di-sulphonic acid by sodium - amalgam (Langer, B. 18, 554, 1114; Rosenberg, B. 18, 3030). Crystalline, v. sol. water. -- BaA" 2 aq.

30.00. Crystaline, v. soi. witter.—Dax. 2; ad. Chloride C,H.S(SO,D.)., [1409]. Scales. A mide C,H.S(SO,NH.).. [e. 280°]. Needles. Thiophene disulphonic acid C,H.S(SO,H).. Formed by reducing iodo-thiophene (aB)-disulphonic acid with sodium-amalgam (Langer, B. 18, 560).

Amide C,H2S(SONH2)2. [142°]. Plates.

Gives the indophenine reaction.

Thiophene disulphonic acid C₄H₂S(SO₄H)₂. Formed from lead thiophene sulphonate and fuming H₂SO₄ (Jackel, B. 19, 185, 1066). Crystalline, v. sol. water and alcohol.—K₂A"aq: prisms, v. sol. water .- Na A" 3aq. Needles, v. sol. water. -BaA" 3aq. Flat prisms, sl. sol. water.—Ruh" 4aq. Blue needles.—Ag,A".

Chloride C,H₂S(SO₂Cl)₂. [77.5°]. Needles

(from ether).

Amide C₄H₂S(SO₂NH₂)₂. [211·5]. References.—DI-BROMO-, IODO- and NITRO-

THIOPHENE BULPHONIC ACID.

THIOPHENIC ACID v. THIOPHENE CARB-OXYLIC ACID

THIOPHENIC ALDEHYDE C, H, S.CHQ. (198° cor.). S.G. 21 1:215. Formed by distilling (a)-thienyl-glyoxylic acid (Biedermann, B. 19, 637, 1853). Formed also by the action of all S on CHCl CH_CH_ (Hantzsch, B. 22, 2838). Oil, smelling like benzoic aldehyde. Oxidised

by air to thiophene (a)-carboxylic acid. Oxim C.H.S.CH(NOH). Thiophene synal-doxim. [128°]. Needles (from ether). Con-verted by NaOHAq into thiophene carboxylic nitrile (Hantzsch, B. 24, 47). Yields an acctyl-derivative [75°-80°]. NaOMe and MeI in MeOH yield C₄SH₃.CH<0 [120°], crystallising in tables; converted by dilute H2SO, into the aldehyde and (3)-methyl-hydroxylamine (Goldschmidt a. Zanoli, B. 25, 2588). Phenyl cyanate in ether forms C.SH.CH:NO.CO.NHPh [70°], crystallising in needles.

Oxim C₄H₂SCHNOH. Thiophene anti-aldoxim. Formed by the action of hydroxyl-amine hydrochloride, NaOHAq and Na₂CO₂ on the aldehyde (Goldschmidt a. Zanoli, B. 25, 2590). Converted by phenyl cyanate into C.SH., CH; NO.CO.NHPh [144°], whence N2OH

forms CaSHa.CH:N.NHPh [46°]. o-Tolyl cyanate forms C,H,S.CH:NO.CO.NH.C,H, [60°].

Phenyl hydrazide O,SH,CH:N,HPh.
[134:5°]. Needles (from alcohol).

THIOPHENIC IMIDO-ETHYL ETHER

C₁I₁,S₂C(OE₂):NH. The salt B'HCl is formed by the action of dry HCl on the nitrile of thiophene emboxylic acid (Douglas, B. 25, 1312). It is crystalline, and is converted by hydroxylamine into C₄H₃S.C(OEt):NOH [67°].
THIOPHENINE is AMIDO-THIOPHENE.

THIOPHENOL v. PHENYL MERCAPTAN.

THIOPHENURIC ACID C,H,NSO, [172°]. Exercted in the urine of rabbits after injection of sodium thiophene (a)-carboxylic acid (Jaffé a. Levi, B. 21, 3458). Prisms, resembling hippuric acid (from water), v. sl. sol. ether, v. sol. alcohol. Split up by boiling baryta-water into glycocoll and thiophene (a)-carboxylic acid. - BaA', 2aq.

Needles, v. sol. water.— CaA', raq.— AgA'.
THIO-PHENYL-ACETIC ACID. A Amide C_sH_s.CH_c.CS.NH_c [98°]. Formed by heating phenyl-acctamide (3 pts.) with P.S. (2 pts.), and also by allowing a solution of phenyl-acetonitrile in alcoholic ammonium sulphide to stand for some days (Bernthsen, B. 11, 503; A. 184, 292). Trimetric crystals (from alcohol), decomposed on distillation into H.S and C.H.CH.CH.CN.

Reactions.-1. Boiling NH, Aq forms phenylacetamide. - 2. HgO forms phenyl-acetonitrile. 3. Zn and HClAq form phenyl-ethyl-amine (Colombo a. Spica, B. 8, 821). — 4. Benzoic aldehyde forms oily C. II. N.S. (?) — 5. Sodiunamalgam forms Ph.CH. CH. NII. and a compound C, H2, NS, [108]. -6. Indine added to a hot alcoholic solution forms C₁₆H₁,N.3 [42°],—7. MeI forms (CH.Ph.C(NH).SMe)HI [139°], which gives rise to (C₉H₁₁NS) H₂PtCl₆ - 8. EtI forms (C₁₀H₁₁NS) HI [116°], which is v. e. sol. water, and yields, on treatment with NaOHAq, the free base CH.Ph.C(NII).SEt, which is an oil that quickly decomposes into mercaptan and phenyl-acetonitrile. The salts (C₁₀H₁₃NS)HCl [c. 120°], B'₂H₂PtCl₀ [below 130°], and B'HBr are crystalline.—9. Aniline forms the compound CH..Ph.C(NH.):NPh.

THIO'- PHENYL - ALLOPHANIC ACID v. PHENYL-THIO-ALLOPHANIC ACID.

THIO - DI - PHENYL - AMINE v. IMIDO-DI-PHENYL SULPHIDE.

THIO . PHENYL . CARBAMIC ACID v. PHENYL-THIO-CARBAMIC ACID.

THIO - DI - PHENYL KETONE v. THIO-RENZOPHENONS.

THIO - LA - PHENYL - METHYL - AMINE v.

METHYL-IMIDO-DI-PHENYL SULPHIDE.

DI-THIO-PHTHALIC ACID C. II. (CO.SH).
The salt K.A" is formed by dissolving KSH (2 mols.) in an alcoholic solution of phenyl phthalate (1 mol.). The free acid splits up at once into H.S and thiophthalic anhydride (Schreder, B. 7, 706).

(a) - Di - thio - isophthalic acid. The K salt, formed by the action of KSH on phenyl isophthalate, crystallises in yellow needles.

Ethyl ether Et₂A". Formed by adding water to the hydrochloride of C_cH₁(C(NH).SEt)₂ (Luckenbach, B. 17, 1435). Small needles.

(β) - Di - thio - isophthalic acid. Amids C_cH₁(CSNH₂)₂. [200°]. Formed by heating isophthalic nitrile with alcoholic ammonium

sulphide (L.). Needles, sol. hot alcohol. Reconverted into the nitrile by lead acetate. Boil-

ing KOHAq forms isophthalic acid.

THIO.PHTHALIC ANHYDRIDE C.H.SO. i.e. $C_eH_{\bullet} < \stackrel{CO}{CO} > S$. [114°]. (284°). Formed by the action of KSH on phthalyl chloride, or on phenyl phthalate (Graebe a. Zsehokke, B. 17, 1175). Formed also by the action of As.S. on phthalyl chloride (Rayman, Bl. [2] 47, 898). Plates, v. sol. hot alcohol, ether, and chloro-form, sl. sol. water. Volatile with steam. Sol. alkalis and converted by long, boiling with alkalis into phthalic acid. Ammonia forms phthalimide. Resorcin and H2SO, give a thiofluorescein, the alkaline solution of which is deep red with green

THIO-PHTHALIDE $C_0H_1 < CO > S$. Formed by heating C,H,Cy,CH2.SCy with conc. HClAq for 5 hours at 180° (Day a. Gabriel, B. Thin needles (from dilute alcohol).

THIO-PHTHALIMIDINE C.H.NS i.e.

C₄H₄C(NH) S or C₄H₄Cy.CH₂SH. [62°].

Formed by warming o-cyano-benzyl sulphocyanide with 'H₂SO₄ at 65° (Day a. Gabriel, B. 23, 2481). Formed also by adding KSHAq to o-cyano-benzyl chloride in alcohol. Needles, which darken in air, v. sol. alcohol and ether. Boiling NaOHAq forms thiophthalide. added to its alcoholic solution forms $C_{16}H_{16}S_{3}$, crystallising from nitrobenzene in needles with green lustre. - B'HCl. Needles. - B'2H2PtCle. Orange - yellow prisms. - B'HI. Needles. Picrate: slender needles.

THIOPHTHENE C,H,S, i.e. CH-C-CH-CH-CH-S.C.S.CH (225° cor.). Formed by distilling citric acid (1 pt.) with P.S. (2 pts.), adding NaOHAq, and distilling with steam (Biedermann a. Jacobson, B.19,2444). Oil, not solid at -10° . Gives the D. 19, 2344). On, not some at -10°. Gives the indephenine reaction. — BC₀H,N₂O₂, [133°]. Yellow needles, v. sol. alcohol and benzene. Reference.—TETRA-HORON-THIOPHTHEME. THIOPHYLLINE C,H₄N,O₂, [264°]. Occurs, in small quantity, in extract of tea (Kossel, B.

21, 2164). Crystals (containing aq), more sol. water and alcohol than theoleomine, v. sol. NH₃Aq. Forms salts with acids. On evaporation with chlorine-water it leaves a scarlet residue, turned violet by NH₃Aq.—C,H,AgN₃O₂.

Amorphous, converted by MeI into caffeine

C,H,MeN,O, [229°].
(a) - THIO-PROPIONIC ACID C,H,OS. Methyl ether CH₃.CH₂.CO.SMe. (120°). V.D. 51·23. Formed from propionyl chloride and lead mercaptide in the cold (Obermeyer, B. 20, 2922).

(8) Thio-propignic acid Et.CS.OH. salt NaA'aq formed by boiling propionitrile with alcoholic ammonium sulphide is crystalline

(Dupré, Bl. [2] 29, 304).

Amide EtC(NH).SH. [42°]. Formed by heating propionamide (5 mols.) with P₂S, (1 mol.) Formed by in benzene for a short time (Hubacher, A. 259, 229). Yellowish plates, v. e. sol. benzene. THIO-ISOPROPYL-COUMARIN C₁₂H₁₂SO i.e.

C.H. CH:C(C,H.,). [81°]. Formed by heating isopropyl-coumarin with P.S. at 120° (Aldringen,

B. 24, 3463). Reddish-yellow needles, sol. hot alcohol, al. sol. ether.

THIO - PRUSSIAMIC ACIDS. By heating ammonium sulphocyanide there is formed, besides thio-urea, dithiodiprussiamic acid C.H., N.S., a yellowish-white powder, sl. sol. hot water; thiodiprussiamic acid C_eH_sN₁₀S, amorphous, m. sol. hot water; and ammonium dithiotriprussiamate C₉H₁₃N₁₃S₂, which crystallises from water. The first acid gives no colour with FeCl₂, the two other bodies give a red colour. The lead salts of these acids dissolve in hot water.

THIOTETRAPYRIDINE, so called,

 $C_{20}H_{18}N_{1}S$ (?). [155°]. Formed by heating nicotine (1 pt.) with sulphur (6 pts.) at 150° till the mass is chrome-green (Cahours a. Etard, Bl. [2] 34, 452). Yellow prisms (from alcohol).—B'2HCl.— B'HHgCl₃.—B'H.PtCl₃: yellow amorphous pp.
THIO - PYROCATECHIN v. OXY-PHENYL

MERCAPTAN.

THIO-PYROMUCIC ACID. Amids

C₄H₃O.CS.NII₂. [127°]. Formed by passing H₂S into a solution of furfuronitrile in alcohol-ether (Douglas, B. 25, 1314). Yellowish crystals, sl. sol. cold water, v. sol. alcohol.

THIO-PYRUVIC ACID. The compound (C₃H₄O₂S)C₃H₄O₃ [87°] soparates as a powder when II.S is passed into pyruvic acid (Böttinger, A. 188, 325). It is v. e. sol. water and is converted by boiling HIAq into CH3.CH(SH).CO2H.

Boiling water forms H.S and thiopyruvic acid.
DI-THIO-RESORCIN C. H. (SH). Mol. w. 142. [27°]. (243°). Formed by reducing the sulphochloride C₆H₄(SO₂Cl)₂ with tin and HClAq (Patschke, J. pr. [3] 2, 418, Körner, G. 6, 140). Crystals, smelling like some geraniums. Pb(OAc)2 added to its alcoholic solution ppts. orange $C_4H_1S_2Pb$, whence McI forms $C_8H_4(SMe)_2$ (278°) (Obermeyer, B. 20, 2927).

THIO.RUFIC ACID C₁₀H₁₁S₃O₄. Formed by the action of CS₂ on a mixture of NaOEt and acetoacetic ether (Norton a. Oppenheim, B. 10, 701). Pearly orange scales, nearly insol. water. -NaA': brick-red needles. - CaA'2: red needles.

THIO SALICYLIC ACID RENZOIC ACID

THIOSINAMINE v. ALLYL-THIO-UREA.
THIO-SUCCINIC ACID. Anhyo Anhydride $C_2H_4^* < \stackrel{CO}{CS} > 0$. 'Sulphosuccinyl.' [31°]. (225°). Formed by adding succinyl chloride dissolved in benzene or CS₂ to an aqueous solution of Na₂S. Got also by distilling succinic acid (100 g.) with P₂S₃ (100 g.) (Auger, A. Ch. [6] 22, 333). White crystals. Its aqueous solution gives off H₂S on heating. Phenylhydrazine forms CO₂H.C₂H.C₂C(SH):N.NHPh [120°] and C₂H.(CO₁C(N₂HPh)) O [216°], which on distillation changes to succinyl-phenyl-hydrazine (155°]. Phenyl-hydrazine also produces C₂H.(CO.N.H.Ph)₂ [219°] (Zanetti, C. C. 1889, 668). Sodium-amalgam forms C₄H.NaSO₂, converted by phenyl-hydrazine acetate into Formed by adding succinyl chloride dissolved converted by phenyl-hydrazine acetate into CO,H.C.H.,CH:N,HPh [c. 175°].

Di - thio - succinic acid C,H. (CO.SH).

Di thio succinic acid C.H. (CO.SH). The salt K.A.", got by boiling succinyl-phenol with KSH in alcohol, crystallises in minute needles. needles, v. sol. water, alcohol, and ether (Weselsky, B. 2, 518). Its aqueous solution is decomposed by spontaneous evaporation. Acids split it up into H₂S and thiosuccinic anhydride (v. supra).

Ethyl ether C.H.(CO.SEt)... (271°). Formed from di-phenyl succinate (42 g.) and sodium mercaptide (30 g.) in dry ether in the cold (Seiffert, J. pr. [2] 81, 469). Oil, smelling of garlic.

THIO. SUCCINURIC ACID C₅H₈N₈SO₂. [211°]. Formed by heating succinic anhydride with thiourea at 140° (Pike, B. 6, 1105). Yellowish powder, insol. alcohol and ether, sl. sol. water and HOAc. Decomposed by alkalis into thiourea and succinic acid.

• (a) - DI - THIO - TEREPHTHALIC ACID C₁H₂S₂O₂i.e. C₂H₁(CO.SH)₂. Formed by the action of alcoholic KSH on di-phenyl terephthalate (Schreder, B. 7, 708). Amorphous, v. al. sol. alcohol.

(β) - Di - thio - terephthalic acid. Amido C_aH₁(CS.NH_.)₂. [263°]. Formed by heating terephthalic nitrile with alcoholic ammonium sulphide (Luckenbach, B. 17, 1430). Yellow amorphous powder, insol. alcohol. Boiling with lead acetate reproduces the nitrile.

lead acetate reproduces the nitrile.

THIOSTUPHATES. Salts of the hypothetical thiosulphuric acid H₂S₂O₃. These salts were called hyposulphites before the isolation of the true hyposulphites (M₂S₂O₄, p. 592). Na₂S₂O₅, 5aq is still, however, commonly known as sodium hyposulphite. Thiosulphates are formed by boiling normal alkali sulphites in solution with S; (M₂SO₂Aq + S = M₂SO₂Aq); caustic alkali solutions and milk of lime also give thiosulphates by boiling with S. Thiosulphates are produced by the action of air, SO₂, or K₂Cr₂O₄Aq on the alkali and alkaline earth polysulphides in solution (M₂S₂Aq + 3O = M₂S₂O₄Aq + 3S; 2M₂S₄Aq + 3SO₄Aq = 2M₂S₂O₄Aq + 9S;

solutions and milk of lime also give thiosulphates by boiling with S. Thiosulphates are produced by the action of air, SO., or K.Cr.O.Aq on the alkali and alkaline earth polysulphides in solution (M.S.Aq + 30 = M.S.O.Aq + 3S; 2M.S.Aq + 3SO.Aq = 2M.S.O.Aq + 9S; 2M.S.Aq + 4M.Cr.O.Aq + H.O = 5M.S.O.Aq + 4Cr.O.Aq + H.O = 5M.S.O.Aq + 4Cr.O.Aq + H.O = 5M.S.O.Aq + 4Cr.O.Aq + 1157) by heating (NH.).2SO. with P.S. got a large quantity of (NH.).2SO. along with (NH.).2SO. and Some (NH.).2SO. along with (NH.).2SO. and Compounds; and by the interaction of H.S and SO.NH.ONH, he obtained (NH.).S.O. A little H.S.O.Aq is said to be formed by the interaction of the said to be formed by the interaction of the said to be formed by the interaction of said to be formed by the interaction of said to be formed by the interaction of steam and molten.

S (Myers, A. 129, 351).

The alkali salts, also the Ca and Sr salts, are readily soluble in water; many of the others are insoluble or only slightly soluble; the insoluble salts are often obtained from solutions of the alkali salts by double decomposition. Thiosulphates are decomposed by heating strongly; alkali salts leave a mixture of sulphate and sulphide; other salts also give off H₂S and S. Aqueous solutions of thiosulphates evolve H₂S when boiled, forming sulphates, or sulphides if the metal of the thiosulphate is ppd. by H₂S.

Aqueous solutions of thiosulphates are decomposed by dilute mineral acids, with separation of S and evolution of SO. Salts of the acid used are formed, and H.S.O.Aq, which then decomposes to H.SO.Aq and S. This reaction has been studied by several chemists (v. Berthelot, C.R. 108, 971; Vaubel. B. 22, 1686, 2703; Vortmann, B. 22, 2307; Foussereau, C.R. 104, 1842). Colefax (C. J. 61, 176) in 1892 examined the interaction of Na.S.O.Aq and acids? he found that when the products of the change are not removed the interaction stops before all the Vol. IV.

H.S.O.Aq is decomposed. C. determined the effects on the velocity and the limit of the reaction of concentration, increasing the relative mass of the acid used, the nature of the acid, temperature, and the presence of SO. in the solution before acidification (reference to older memoirs are given by C.).

Thiosulphates are converted into tetrathionates by the action of 1; oxidisers such as HNOs. KClOs and HClAq, and KMnOsAq produce sulphates. Accordings to Hönig a. Zatzek (M. 4, 738), KMnOs, in solution in acetic acid produces dithionates.

For the general qualitative reactions of thiosulphates compared with those of thionates v. Debus (C. J. 53, 298).

SELENOTHIOSULPHATES M.SeSO, are described Thioselenates, under Selenates (p. 434).

Constitution of thiosulphates. The formula

Constitution of thiosulphates. The formula SO_xOM.SM is generally adopted for the normal thiosulphates of monovalent metals (Odling, C. N. 29, 153; cf. Schorlemmer, C. J. [2] 7, 254; Williamson, C. J. [2] 7, 259). Some chemists, considering the resemblances between thiosulphates and sulphites, have suggested the

formula SO (v. Blomstrand, Die Chemie

der Jetztzeit [Heidelberg, 1869], 258; Buchanan, B. 3, 485; Michaelis, G. O. [5th ed.] 1, 745). The formation of thiosulphates by boiling sulphites with S is readily represented by either formula. according as sulphites are regarded as SO. OM.M or SO.OM.OM. As the balance of evidence is in favour of the formula SO, OM.M, it is likely that the salts formed by adding S to the sulphites are SO_OM.SM. The production of (NII_),S_0, by the interaction of (NII_),SO_ and P_S, (Spring, B. 7, 1158) also confirms the formula SO_OM.SM, inasmuch as a thiosulphate is produced in this reaction from a sulphate (SO, ONH, ONH, giving SO₂ONH₄SNH₄). Spring's synthesis of H₂S₂O₃ from SO₃ and H₂S – for the actual reaction carried out, viz. formation of (NH,)2S,O, by first combining SO, and NH,, and then interacting with H,S, is equivalent to the synthesis of H₂S₂O₂ (v. S., l.c.) - is also in keeping with the formula SO, OM.SM. By warming EtBr with Na2S2O2Aq, Bunte (B. 7, 646) obtained the salt EtNaS,O. This salt is decomposed by dilute acids giving EtSH and SO.,OH.ONa; when heated it gives off Et, S, and SO, leaving Na, SO. These reactions indicate that EtNaS, O, is SO, Na, EtS; hence the formula of Na,S,O, is probably SO,Na.NaS. One of the Na atoms in Na,S,O, is then probably in direct union with an atom of S; and as EtNaS,O, easily gives SO.OH.ONa, along with EtSH, it is likely that the formula of this salt is SO₂ONa.SEt, and hence that the formula for Na₂S₂O₃ is SO₂ONa.SNa. The formula SO₂.OH.SH makes possible the existence of two isomeric salts MM'S₂O₂, viz. SO₂.OM.SM' and SO_2 .OM'.SM; two such salts are known where M = Na and M' = K. (v. Potassium thiosulphate, p. 706).

Ammonium thiosulphate (NH₄)₂S₂O₂. Obtained by the interaction of (NH₄)₂CO₂ and CaS₂O₂Aq, filtering and evaporating (Rammelsberg, P. 56, 298); white, rhombic, deliquescent leaflets, crystallising with xH₂O. Fock a. Klüss (B. 22, 3099; 23, 534) obtained the anhydrous

salt by reacting on SO₂Aq with (NH₄)₂S₂, evaporating at a low temperature and finally over H.SO., and thoroughly drying between filter paper (cf. Arppe, A. 96, 118). The anhydrous salt is not deliquescent (F. a. K.). anhydrous salt is not deliquescent (F. a. K.). Double salts are described by F. a. K. (l.c.; also B. 23, 1753): (1) with CdS₂O₃; (2) with MgS₂O₃; (3) with K,S₂O₉, the salt obtained was SO₂.OK.SNH₄. F. a. K. could not obtain SO₂.ONH₄.SK; (4) with Cu₂S₂O₂ and Cu₂I₄, also with Cu₂I₄ and NH₄I (Brun. C. R. 114, 667); (5) with PbS₂O₃ (Rammelsberg, P. 56, 308); (6) with HgS₂O₄ (R. J.c.).

Barium thiosulphate BaS₂O₂.aq. A white pp. obtained by mixing Ba(C,H₂O₂),Aq and NAS.Co.Ao, and completing non. by alcohol:

pp. obtained by mixing Ba(C₂I₃O₂)₂Aq and Na₂S₂O₃Aq, and completing ppn. by alcohol; loses all water at 170°, at red heat gives

BaS, BaSO, BaSO, and S (H. Rose, P. 21, 437;

Rammelsberg, P. 56, 295).

Double salts. (1) With CdS.O. (Fock a. Klüss, B. 23, 1753); (2) with Cu.S.O. (Cohen, C. J. 51, 38); (3) with PbS.O. (Rammelsberg, P. 56, 308).

P. bb, 308).

Cadmium thiosulphate CdS₂O₂. 2iq (F. a. K.,
B. 23, 534); double salts with (1) Na₂S₂O₃,
(2) K₂S₂O₃, (3) SrS₂O₃ (F. a. K., B. 23, 1753;
Vortmann a. Padberg, B. 22, 2637).

Calcium thiosulphate CaS₂O₃, 6aq. Formed
by mixing hot cone. solutions of CaCl., and

Na.S.O., evaporating under 60°, separating NaCl, which crystallises first, and allowing to cool (Kessler, P. 74, 282). Also obtained by heating CasO, and S with water, or by boiling milk of lime with S, passing in SO,, and crystallising below 60° (Herschel, N. Ed. P. J. 1, 8, 296; 2, 154). Forms large, clear, six-sided, triclinic prisms, that efforcese in air at 40°; S. 100 at 3° (H., l.c.). Conc. solution gives CaSO and S. 8° (H., l.c.). Conc. solution gives CaSO, and S by heating above 60°. Rammelsberg (P. 56, 308) describes a double salt with PbS.O.

Cobalt thiosulphate CoS₂O₂, 6aq (Rammelsberg, P. 56, 398; Fock a. Klüss, B. 22, 8310). A double salt with Na₂S₂O₂ is described by

Vortmann a. Padberg (B. 22, 2637).

Copper thiosulphates. According to von Hauer (W. A. B. 13, 443) an acid cuprous salt Cu.H.(S,O₂), is obtained, in microscopic, goldenyellow needles, by adding conc. CuSO, Aq to Na₂S₂O₃Aq till the liquid is deep yellow, and gently Na_{5,5,2}, and the figure is deep yearlow, and gently warming, washing the pp. with water and alcohol, and drying over H₂SO₄. Double salts of Ou₅SO₂: (1) with BaS₂O₂ (Cohen, C. J. 51, 38); (2) with K₂SO₄ (C., Lc.); Rammelsberg, P. 56, 321); (3) with Ag₂SO₂ (C., Lc.); (4) with Na₂SO₃ (Lenz, A. 40, 99; Siewert, J. 1866, 257; Kessel, Na₂SO₃ (C., Rammelsberg, P. 56, 257; Kessel, P. 56, 257; K B. 10, 1677, 2000; Schütte, J. pr. 70, 249; Vortmann, M. 9, 165)

Iron thiosulphate. The ferrous salt FeS.O. 5aq was obtained by Vortmann a. Padberg (B. 22, 2637) by rubbing BaS.O. with conc. FeSO Aq (the sales being present in the ratio of equal numbers of molecules), filtering from BaSO,, adding a mixture of alcohol and ether, and allowing the green, oily liquid that separated to stand for some days. Small green crystals; very sol. water; solution is decomposed by boiling, with separation of FeS. A double salt with Na,S,O, is described by V. a. P. (i.e.). For accounts of former attempts to prepare pure ferrous thiosulphate v. Fordos a. Gélis (J. Ph. [8] 4, 833); Berthelot (A. Ch.

[5] 2, 58); Vogel (J. pr. 8, 102); Koene (P. 63, 245, 431); Rammelsberg (P. 56, 306).
 No ferric thiosulphate has been isolated.

Lead thiosulphate PbS₁O₂. Obtained by adding Na₂S₂O₂Aq to Pb(NO₂)₂Aq, or Pb(C₂H₂O₂)₂Aq, and washing the pp. with cold water. A white solid; very sl. sol. water; sol. solutions of alkali thiosulphates (v. Pape, J. 1864, 57; Letts, O. J. [2] 8, 424). For reaction with PCl,—giving PbCl, HCl, SO, SOCl, POCl, and probably PSCl,—v. Buchanan (B. 8, 485). Rammelsberg (P. 56, 308) has described double salts with the thiosulphates of NH, Ba, Ca, K (v. also Spring, B. 7, 1157), and Na (v. also Vortmann a. Padberg, B. 22, 2637).

Lithium thiosulphate Li, S,O, Saq (v. Fock a.

Klüss, B. 22, 3096).

Magnesium thiosulphate MgS,O, 6aq. By passing SO, into MgSAq till colourless, boiling MgSO, in SO,Aq with S, or adding BaS,O,Aq to MgSO, Aq and filtering, a solution is obtained which on evaporation at a low temperature gives small, white, prismatic crystals of this salt. small, white, prismatic crystals of this salt. Loses 3H_O at 170°, and gives off SO₂ and S at red heat, leaving MgSO₄ and MgO (Herschel, N. Ed. P. J. 1, 8, 296; 2, 154; Rammelsberg, P. 56, 303; Fock a. Klüss, B. 22, 3310). Double salts (1) with (NH₄)₂S₂O₂, (2) with K₂S₂O₄ are described by R. (l.c.; v. also Kessler, P. 74, 256; also F. a. K., B. 23, 534).

Mangaess thiosulphate MpSO₂, 5aq.

thiosulphate MnS.O. baq. Manganese Formed similarly to FeS.O., 5aq (Vortmann a. Padberg, B. 22, 2637). A double salt with Na.S.O. is described by V. a. P. (l.c.).

Mercury thiosulphates. Neither the mer-curous nor the mercuric salt has been isolated. Addition of a thiosulphate to solution of a mercurous salt ppts. Hg. S; with a mercuric salt, a compound of HgS with the mercuric salt employed is said to be formed (Rammelsberg, P. 56, 314). Double salts of mercurous thiosulphate with (1) (NH,),S,O₂, (2) Cu,S,O₃, (3) Na,S,O₄ are described by Rammelsberg (*l.c.*); and a double salt of mercuric thiosulphate with K,S,O₂ by Vortmann a. Padberg (B. 24, 1351).

Nickel thiosulphate NiS₂O₃, 6aq (Rammelsberg, P. 56, 309; Fock a. Klüss, B. 22, 3310). For a double salt with Na₂S₂O₃ v. Vortmann

Padberg (B. 22, 2637).

Platinum thiosulphate. Not isolated; but Schottländer (A. 140, 200) describes a double

Potassium thiosulphate K₂S₂O₃. Obtained by boiling conc. K₂SO, with excess of S; or by adding hot K₂Cr₂O,Aq to hot K₂S₄Ag, little by

ittle, waiting after each addition till the separated Cr.O. is pure green in colour (2K,S,Aq, +4K,Cr,O,Aq + H,O = 5K,S,O,Aq + 2KOHAq + 4Cr,O.); (Döpping, A. 46, 172; Kessler, P. 74, 274). In either case the filtered solution is evaporated to the crystallising point, and the crystals of K₂S₂O₂.xH₂O are heated to c. 180°. By evaporating at 30°, thin, four-sided, deliquescent prisms are obtained of the hydrated sait 3K,S,O,.H,O (Rammelsberg, P. 56, 29¢; Kessler, Lo.; Fook a. Klüss, B. 22, 8096). This hydrate is very sol. water, but insol. alcohol; it loses all water at c. 180°; heated more strongly it decomposes to K₂S₃ and K₂SO₄ (R., l.c.). Other hydrates are described by D. a. P., l.c. (v. also Plessy, A. Ca. [8] 11, 182; F. a. K., Lo.). The final products of the action of SO, on K₂S₂O₂Aq are K₂S₂O₂Aq, K₂S₂O₂Aq, and K₂S₂O₃Aq (Debus, C. J. 53, 343). Double salts.—(1) with (NH₂)₂S₂O₃ (Fock a. Klüss, B. 23, 534); the salt obtained was

SO, OK.SNH, the isomeric salt SO, ONH, SK SO_{2.}OK.SNH₄, the isomeric salt SO_{2.}ONH_{4.S}K could not be isolated; (2) with Bi₂(S₂O₂)₂ (Carnot, C. R. 83, 338); (3) with CdS₂O₃ (F. a. K., B. 23, 534); (4) with Cu₂S₂O₄ (Cohen, C. J. 51, 38); (5) with HgCy₂ (F. a. K., B. 24, 1351); (6) with HgS₂O₄ (F. a. K., Lc.); (7) with PbS₂O₄ (Rammelsberg, P. 56, 308; Spring, B. 7, 1157); (8) with Ag₂S₂O₃ (Cohen, C. J. 51, 38; Schwicker, B. 22, 1928 describes KAySO₄ NH 1 (20) With N₂ S₂ S₂ 1928, describes KAgS₁O₂, NH₃). (9) With Na₂S₁O₃ two salts are obtained: (i.) SO₂OK.NaS. 2aq, by the interaction of Am₂S₃Aq and NaKSO₃. 2aq; (ii.) SO₂SK.ONa. 2aq, by the interaction of Am₂S₃Aq and KNaSO₂ (v. Sulphites, p. 587); the first salt melts at c. 57° and has S. = 213.7 at 15°, heated with EtBrit gives SO, OK.SEt; the second salt melts at c. 62° and has S, =105°3 at 15°, heated with EtBrit gives SO, ONa.SEt (Schwicker, B. 22, 1728).

Silver thiosulphate Ag,S,O. This salt has probably not been isolated pure. On adding dilute AgNO, Aq to K, S, O, Aq a white pp. is formed, and is dissolved on shaking; addition of more AgNO₃Aq produces a greyish, flocculent pp., which is a mixture of Ag.S.O, and Ag.S. By treating this pp. with NH₃Aq, filtering from Ag.S, exactly neutralising the filtrate by HNO₃Aq, and quickly drying the white flocculent pp. that formed between filter paper, Herschel (N. Ed. P. J. 1, 26, 398; 2, 154) obtained fairly pure Ag,S.O. A white powder; slightly soluble water; solution has a sweet taste; decomposes

readily to Ag₂S and H₂SO₄Aq.

Double salts. Ag₂O and Ag salts generally dissolve readily in solutions of alkali thiosulphates, forming double salts, either of the form 2AgMs,O₃,aq, or of the form Ag,M₄(S₂O₃), 2aq (Herschel, Lc.). (1) With (NH₄)₂S₂O₃; by adding excess of AgCl to (NH₄)₂S₂O₃Aq, and washing the white crystalline pp., 2Ag(NH₄)S₂O₃aq is obtained. Using less AgCl and ppg. the solution by alcohol produces Ag₄(NH₄)₄(S₂O₃), 2aq (H₄, Lc.). (2) With Na₂S₂O₃; addition of AgNO₃Aq, drop by drop, with constant shaking, to Na₂S₂O₃Aq, till a permanent pp. begins to form, followed by addition of alcohol, pps. Ag₂Na₄(S₂O₃), 2aq; the salt is washed with alcohol, and dried in vacuo (Lenz, A. 40, 94); when the mother-liquor from this salt is allowed phates, forming double salts, either of the form when the mother-liquor from this salt is allowed to evaporate 2AgNaS₂O₂, aq is deposited (Her-schel, L.c.; cf. Lenz, L.c.). The second of these salts is much less soluble in water than the saits is muon less soluble in water than the first; it dissolves in Na,S,O,Aq, with formation of Ag,Na,(S,O),.2aq. Both salts are decomposed by boiling their aqueous solutions, with formation of Ag,S. (3) With K,S,O,; two salts are known similar to the sodium salts. Schwicker (B. 22, 1788) describes the compound AgKS.O., NH., Herschel (l.c.) obtained double salts with CaS.O., and with SrS.O.

Sodium thiosulphate Na S.O. 5aq Formation.—1. By boiling Na, SO, Aq with S.—2. By passing SO, into solution of sodium polysulphides.—3. By the action of SO, on soda waste suspended in water, whereby CaS, O, Aq is formed; followed by addition of Na, SO, filtration from CaSO, and appropriate from CaSO, and evaporation.

Preparation.—Na, SO, xaq is dissolved in a little water, the solution is boiled with flowers of sulphur for a considerable time, and filtered; the clear, colourless liquid is evaporated to the crystallising point, and the crystals that separate are purified by recrystallisation from water.

Properties.—Large, white, monoclinic prisms; S.G. 1736 at 40° (Kopp. J. 8, 45; cf. Schiff, J. 12, 41; Smith, Am. J. Pharm. 53, 148). Melts 12, 41; Smith, Am. J. Pharm. 58, 148). Mets at 45° in the water of crystallisation (Kopp. J. 8, 45); at 48.5° (Tilden, C. J. 45, 268). The crystals are dehydrated by keeping in vacuo over H.SO, or by heating to 100°. S. 49.75 at 0°, 69.44 at 20°, 104.16 at 40°, 192.3 at 60° (Kremers, P. 99, 50). An aqueous solution of the salt is easily supersaturated; thus Schiff (A. 113, 350) dissolved 171 parts Na,S,O, 5aq (=108.9 parts Na.S.O.) in 100 parts water at 19.1°, and Kremers obtained a solution of 217.4 parts Na S,O, in 100 parts water at the ordinary temperature. According to Baumhauer (J. pr. 104, 148), a supersaturated solution may be cooled to \$10° without crystallising; addition of a crystal of the salt causes rapid crystallisation, with the evolution of much heat (cf. Parmentier a. Amat, C. R. 98, 735) Solution of Na S.O. 5aq in water is accompanied by the disappearance of much heat; Rudorff (B. 2, 68) says that 110 parts Na.S.O., 5aq dissolving in 100 parts water lower the temperature from 10.7° to -8°, i.e. through 18.7°. Schiff (A. 113, 350) gives the following data for S.G. and compositions of aqueous solutions of Na.S.O. 5aq:-

	P.c.	B.G. of	P.o.	P.c.
				16.564
				17.201
				17.888
				18.475
				19.113
				19.750
				20.387
				21.024
				21.661
			85	22.298
		1.2048	86	22.935
	7.645	1.2110	37	23.572
13	8.282	1.2172	38	24.209
. 14	8.919	1.2234	39	24.846
15	9.556	1.2297	40	25.484
16	10.193	1.2362	41	26.121
17	10.830	1 2427	12	26.758
18	11.476	1.2492		27 ·895
	12.105	1.2558		28.032
				28.669
				29.806
				29.948
				80.580
				81-218
25	15.927	1.2354	50	81.855
	Na.S.O. 5ac 1	Na,S.O., 5aq Na,S.O., 2 1-074 3 1-911 4 2-584 5 5-185 6 8-822 7 4-459 8 8 5-096 9 5-733 10 6-371 11 7-008 112 7-645 13 8-282 14 8-919 15 9-556 16 10-193 17 10-830 18 11-476 19 12-105 20 12-742 21 13-379 22 14-016 23 -14-658 24 15-290	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Na.S.O. 5aq Na.S.O. 201. Na.S.O. 8ad. Na.S.O. 8ad. Na.S.O. 8ad. Na.S.O. 1.1440 26 2 2 1-274 1.1449 27 3 3 1-911 1.1558 28 4 2.584 1.1617 29 5 5 3.185 1.1676 30 6 3.822 1.1738 31 7 4.459 1.1800 32 8 5-096 1.1862 93 9 5-733 1.1924 34 10 6-371 1.1986 35 11 7.008 1.2048 36 12 7.645 1.2110 37 13 8.262 1.2172 38 14 8.919 1.2234 39 15 9.556 1.2297 40 16 10 193 1.2362 41 17 10.830 1.2427 42 18 11.476 1.2429 43 19 12.105 1.2588 44 20 12.742 1.2624 45 21 13.379 1.2620 46 22 14.616 1.2566 47 .23 .44653 1.2828 48

Na₂S₂O₃. 5aq is insol. alcohol.

According to Jochum (C. C. 1985. 642), a trihydrated salt Na₂S₂O₂. Baq is obtained by adding alcohol to a saturated solution of the ordinary salt, removing the oily liquid that seps. rates, and adding to it 98 p.c. alcohol. According to Parmentier a. Amat (C. R. 98, 785), Na, 8, 0, 5aq is obtained crystallised in needles, melting at c. 82°, by placing a supersaturated

solution of the ordinary salt in a freezing mixture in a closed vessel.

Reactions.—1. Heat decomposes Na.S.O.: the change begins at c. 220° with separation of S, at c. 400° Na,SO, and Na,S, are formed, and at a higher temperature more S is given off, and Na,SO, and Na,S remain.—2. Na,S,O,Aq inter-Na,S,O₆Aq; according to Villiers (C. R. 108, 402) some Na₂S₂O₆ is also formed. With a mix-Ado, to Ad ; seconding to viniers (c. R. 100, 402) some Na_S,O_a is also formed. With a mixture of Na_SO_a and Na_S,O_a in solution I produces NaIAq, Na_SO_aAq and Na_S,O_aAq (Colefax, C. J. 61, 198, 1083).—3. Na.S.O. is oxidised by potassium permanganate colution; in alkaline solutions the oxidation is complete to Na,SO,Aq according to Hönig a. Zatzek (M. 4, 738); Glaser (M. 6, 329) says that the oxidation is also complete in neutral solutions; Luckow (Fr. 32, 53) represents the oxidation, on boiling, either in neutral, acid, or alkaline solution as producing Na,SO₄ and Na,S₂O₅.—4. Acids interact with Na₂S₂O₅Aq, forming Na salts of the acids, and H.S.O.Aq, which then decomposes to H.SO.Aq and S; when the products are not removed from the solution the reaction stops before all the H₂S₂O₂ is decomposed (Colefax, C. J. 61, 176; and v. beginning of article THIOSULPHATES, p. 705).

Combinations.-1. With water (v. supra, Combinations.—1. With water (v. supra, Properties).—2. With various thiosulphates to form double salts. Double salts with CdS.O., CoS.O., FeS.O., PbS.O., MnS.O., NiS.O., Tl.S.O., and ZnS.O. are described by Vortmann a. Padberg (B. 22, 2637); Fock a. Klüss (B. 23, a. Padberg (B. 22, 2637); Fock a. Klüss (B. 23, 1763) also describe that with CdS_{1,0}. Rammelsberg (P. 56, 808) prepared salts with PbS_{2,0}. and Hg_{1,5}0, For a double salt with HgS_{2,0}. Schwicker (B. 22, 1728). For the double salts with K₁S_{2,0}, v. Potassium thiosulphate, double salts, No. (9) (p. 707), and for those with Ag_{2,0}, or an annual double salts, No. (9) (p. 707), and for those with Ag_{2,0}, or annual manual double salts, No. (9) (p. 707).

salts, No. (9) (p. 707), and for those with Ag.S.O., v. Silver thiosulphate, double salts, No. (2) (p. 707). Schottländer (A. 140, 200) describes a double salt 3Na.S.O.,PtS.O., 10aq.

Strontium thiosulphate SrS.O., 5aq. Prepared like the Ba salt (Herschel, N. Ed. P. J. 1, 26, 398; 2, 154; Kessler, P. 74, 274). Fock a. Klüss (B. 22, 3810) describe a salt SrS.O., aq.

Thallium thiosulphate Tl.S.O., A white, crystalline pp., formed by adding Na.S.O., A wite, crystalline pp., formed by adding Na.S.O., aq. thebberling, A. 184, 11). For a double salt with Na.S.O., v. Werther (J. pr. 92, 130); Vortmann a. Padberg (B. 22, 2637); also Jochum (C. C. 1885, 642).

Zine thiosulphate ZnS.O., Prepared by

(C. C. 1885, 642).

Zine thiosulphate ZnS,O., Prepared by double decomposition from ZnSO,Aq and BaS,O.Aq (v. Rammelsberg, P. 56, 295; Fordos a. Gélis, J. pr. 29, 291). For a compound with NH, v. B. (i.c.). For a double saft with Na,S.O. v. Vortmann a. Padberg (B. 22, 2637).

M. M. P. M.

THIOSULPHURIC ACID H.S.O.Aq. acid almost certainly exists in the liquid obtained by adding a gliute weak said to diluta Na.S.O.Aq. the soid and salt being mixed in equivalent quantities; the H.S.O.Aq acon begins to decompose to H.SO.Aq and S. Landolt (B. 16, 2958) has made an extensive investigation into the conditions and time of existence of H_iS_iO_s in solution. Thomsen (Th. 2, 256) gives the thermal data; [SO³Aq,S] = -9310; [SO²,S,Aq] = -1610.

For the salts of H2S2O, v. THIOSULPHATES. M. M. P. M. THIOTOLENE v. Methyl-thiophene. THIO-o-TOLUIC ACID. Amide C.H.Me.CS.NH. [88°]. Formed from o-toluic nitrile (Gabriel a. Heymann, B. 24, 786).

Thio-p-toluic acid. Amide. [168°]. Formed by passing H.S into an alcoholic solution of p-toluic nitrile (Paterzo a. Spica, B. 8, 441). Yellowish needles. Zinc and HClAq yield Zinc and HClAq yield C₆H₄Me.CH₂NH₄

THIO-TOLUÍDINE v. DI-AMIDO-DI-TOLYL SUL-

THIO-p-TOLYL-DI-PHENYL-DI-GUAN-IDINES v. DI-PHENYL-DI-GUANIDO-DI-TOLYL SUL-PHIDE and DI-PHENYL-DI-CARBIMIDO-TETBA-AMIDO-TETRA-TOLYL DISULPHIDE

THIO-TOLYL-DI-PHENYL-THIO-UREA v. DI-PHENYL-DI-THIOURAMIDO-DI-TOLYL SULPHIDE. THIO-URAMIDO-BARBITURIC ACID

 $C_bH_aN_aSO_a$ i.e. $NH_aC(NH).S.CH < CO.NH > CO.NH$ Formed by the action of thio-urea on an aqueous solution of chlore, brome, or di-brome-barbi-turic acid (Mulder, B. 12, 2309; Trzeinski, B. 16, 1057). Formed also by heating alloxan with thio-urea and alcoholic SO, at 100° (Nencki, B. 4, 722; 5, 451). Slender needles, insol. water, sol. hot HClAq. Converted by boiling KOHAq into thio-dialuric acid C,H₄N₂SO₄, 1½aq (?) which yields KA'aq. H₂SO₄ (½ pt.) at 150°-160° forms uro-sulphinic acid C₅H₄N₄SO₂.

THIO-URAMIDO-BENZENE p-SULPHONIC ACID. The salt NH, CS.NH.C, H, SO, K, formed by heating potassium sulphocyanide with amidobenzene p-sulphonic acid at 140°, crystallises from dilute alcohol in aggregates of thin needles (Pellizzari, A. 248, 156).

m-THIO-URAMIDO-BENZOIC ACID m-IHIU-URAMIDU-BERZUIG ACID
NH_CS.NH.C.H. [187°]. Formed from
m-amido-benzoic acid and potassium sulphocyanide (Arzruni, B. 4, 406). Formed also by
allowing a solution of m-cyanamido-benzoic
acid in colourless ammonium sulphide to stand for 24 hours (Traube, B. 15, 2118). Needles. Converted by ammoniacal AgNO, into muramido-benzoic acid. Not coloured by FeCl.

p-THIO UBAMIDO BENZYL-THIO UBEA
NH, OS.NH.C., H., OH., NH. CS.NH., p-w-di-thiuramido-toluene. [176°]. Formed by heating
p-amido-benzyl-amine hydrochloride (1 mol.) with potassium sulphocyanide (2 mols.) in aqueous solution (Amsel a. Hofmann, B. 19, 1289). White needles.

THIO-URAMIDO-BUTYRIC ACID. Anhy-NH:O S-CHEt [200°]. Formed from a-bromo-n-butyric acid and thio-urea (Andreasch, M. 8, 419). Needles, v. sol. hot water.
Thio-uramido-iso-butyric acid. Anhydride

NH:C NH.CO C,H,N,SO i.e. Formed from bromo-isobutyric acid and thio-urea (Andreasch, M. 8, 410). Plates, al. sol. water. Oxidised by HCl and KClO, to urea and a-sulpho-iso-butyric acid.

o-THIO-URAMIDO-CINNAMIC ACID NH_CS.NHC,H_CH:CH.CO_H. [286°-288°].
Got by heating the sulphocyanide of c-amidocinnamic acid C_H_(NH_HSCy)CH:CH.CO_H NH, CS.NH.O, H, CH:CH.CO, H.

(152°) at 115° (Rothschild, B. 23, 3342). V. sol. hot HOAc and NH,Aq.

a-Thio-y-uramido-cinnamic acid C, H, N, SO NH:C(NH2).S.C(CO2H):CHPh. Formed from benzoic aldehyde, thiohydantoin, and NaOHAq (Andreasch, M. 8. 421). Needles (from alcohol), decomposed by alkalis.
p-THIO.+URAMIDO-PROPIONIC ACID

NH:C(NH2).S.CH2.CH2.CO2H. Formed by heating \$\text{\$\text{biodo-propionic}}\$ acid with thio-urea and water and a little NaOH (Andreasch, \$M\$. 6, 831). Small pyramids (containing 2aq), sl. sol. cold water and cold alcohol. Decomposed by baryta into cyanamide and CH2(SH).CH2.CO2H. KClO. and HCl yield β-sulpho-propionic acid.
ωp-DI-THIO-URAMIDO-TOLUENE v. THIO-

URAMIDO-BENZYL-THIO-UREA.

DI-p-THIO-URAMIDO-DI-TOLYL-o-SUL-PHIDE [2:1:4] S(C₆H₂Me.NH.CS.NH₂)₂. Thiop-tolyl-di-thiurea. [121°]. Formed by evaporating to dryness an aqueous solution of di-pamido-di-tolyl sulphide, hydrochloride and ammonium sulphocyanide (Truhlar, B. 20, 669). White amorphous powder. Sol. alcohol and benzene, sl. sol. ether.

THIO-UREA CSN₂H₄ i.e. CS(NH₂), or HS.C(NH₂):NH. Mol. w. 76. [170°]. S. 9 in the cold (Volhard, *J. pr.* [2] 9, 13).

Formation.—1. By heating dry ammonium sulphocyanide for two hours at 170°, cooling to 100°, adding an equal weight of water at 80°, filtering, and allowing to crystallise (Emerson Reynolds, C. J. 22, 1; Claus, A. 179, 113; Smolka a. Friedreich, M. 10, 90).—2. By the action of tin and HCl, or of HI, on persulphocyanic acid C₂H₂N₂S₃ (Glutz, A. 154, 39).— 3. By passing dry H₂S into an ethereal solution of cyanamide (Baumann, B. 6, 1375).-4. By allowing a solution of cyanamide, mixed with yellow ammonium sulphide, to stand for a day (Baumann, B. 8, 26).—5. From cyanamide and thioacetic acid.—6. Together with urea by the action of ammonia on COS (Berthelot, C. R. 94, 1069).

Properties .- Silky trimetric needles, melting repetites.—Shay timetric needles, inclined at 170°. After one fusion it melts at 149° (Prätorius, J. pr. [2] 21, 141). V. sol. water, nearly insol. alcohol and ether. Tastes bitter, not coloured by FeCl₂. According to Armstrong (C. J. Proc. 3, 2), the molecule of this urea is

C.S.N.H.. Reactions.—1. Water at 140° forms ammonium sulphocyanide. Alcohol at 100° acts in like manner (Haller, Bl. [2] 45, 706). -2. An alcoholic solution of nitrous ether quickly conalcoholic solution of netrous ether quickly converts it into ammonium sulphocyanide. — 3. Prolonged heating at 170° also converts it into ammonium sulphocyanide. At 180° it slowly forms guanidine sulphocyanide and ammonium tri-thio-carbonate. Nitrous acid gives off nitrogen.—4. KOH at 100° slowly forms NH₂, KSH, KSCO₂, and a little KCyS. Alcoholic potash acts in like manner (Haller, C. R. 102, 974). H.SO, and HCl act in the same way .- 5. Aqueous H.So, and HCi act in the same way.—5. Aqueous KMnO₄ forms urea and other products (Maly, M. 11, 277).—6. Oxidising agents (e.g. H₂O₂, K₂Cr₂O₂, KNO₂, KMnO₄, and iodine) form S₂(C(NH₂):NH)₂, which has an insoluble nitrate (Storch, M. 11, 452).—7. Ammoniscal AgNO₂ forms urea and Ag₂S.—8. HgO, added to a cold aqueous solution, produces cyanamide.

PbO acts in like manner. At 100° the product is dicyandiamide (Hofmann, B. 2, 605).--Acetoacetie ether reacts forming an ether C,H,N,SO(OEt), which on saponification yields CS NH.CMe CH, v. sl. sol. water (Behrend, B. 19, 219).—10. CCl, COCl forms C,H,Cl,N,S,O, orystallising in slender needles, m. sol. alcohol, sl. sol. water, v. sl. sol. ether; converted by Br into CCl_xSO_xBr (McGowan, C. J. 49, 191; 51, 669; J. pr. [2] 36, 220). CCl_xSO_xCl added to an alcoholic solution of thio urea forms the chloride Cl.CSN H4, which is ppd. on adding ether, while the filtrate contains the compound (CSN₂H₄)₂(CCl₂.SO₂)₂ [125°], which is more sol. alcohol than water, and gives with Br a pp. of CCl, SO, Br. -11. CCl, SO, NH, in alcohol forms flat prisms of (CSN, H,) CCl, SO, H [139°], m. sol. mater and ether, v. sol. alcohol. converted by Br into CCl., SO, Br (M'Gowan, C. J. 51, 667; J. pr. [2] 36, 219).—12. Chloro-accions forms (NH,,CS,NH,CH,,CO,CH,)HCl [126°] (Pawlewski, B.* 21, 402).—13. ClCO, Et forms (NH,,CS,NH,CO,2Et)HCl [117°].—14. CH,Cl.OH gives C2H2N2S, a white amorphous powder, insol. water, nearly insol. all usual menstrua, reconverted into thio-urea by HClAq (von Hemmelmayr, M. 12, 89) .- 15. Di-bromo-succinic acid forms fumaric acid on heating (Nencki a. Sieber, J. pr. [2] 25, 74).—16. A hot cone solution of di-bromo-pyruvic acid forms 'sulphuvinuric acid' C.H. N. SO₂, which crystallises with 2aq, reduces Fehling solution to Cu,O in the cold, and to a copper mirror on warning, and yields the salts CaA'₂, MgA'₂, ZnA', HA'HCl, HA'HBr, and HA'HNO₂ aq (N. a. S.).—17. Bromo-pyruvic ether forms amido-thiazole carboxylic ether $S \leftarrow C(NH_2):N$ [173°] (Steude, A. 261, 30).— 18. Bromo-acctoacetic ether gives μ-amido-thiazyl-acetic ether SCH — C.CH CO.Et. C(NH₂):N. [94°], which yields an acid [c. 130°], split up on fusion into CO, and amido-methyl-thiazole (Steude). a - Chloro - acetoacetic ether forms C.NSMe(NH.).CO.Et [175°] (Zürcher, A. 250, 281).—19. Thio-urea heated with an alcoholic solution of chloro-acetic acid and phenyl-hydrazine forms C₀H₂N₂SO [175°] (Probst, J. pr. [2] 45, 416).—20. Fusion with (3)-iodopropionic acid and a little water forms C, H, N, SO, [176°], which crystallises from water in needles (containing 2aq), sl. sol. alcohol, insol. ether (Andreasch, M. 6, 832).—21. Di-chloro-acctic acid forms thichydautoin. a-Brono-propionic acid forms methyl-thichydautoin (206° uncor.) (Dixon, C. J. 63, 815) .- 22. Aldehyde heated in a sealed tube with thic-urea forms CSN,L,(CHMe), which is al. sol. ether and cold alcohol, and is which is 81. 801. Siner and containing and adecomposed by hot water (heynolds, C. N. 24, 87).—23. Succinic anhydrids at 140° forms C.H.N.SO, [211°].—24. Citraconic anhydrids at 130° forms C.H.N.SO, [223°] (Pike, B, 6, 1104).— 25. Acetyl-acetone and a small quantity of HClAq form CH₂(CMe:N.CS.NH₂)₂HCl [219°]. In presence of excess of HCl the product is CH₂ CMe:N CS [210°] (Evans, J. pr. [2] 48, 503).

Salts .- B'HNO. Crystalline. - B'HCL Formed from the stannous double chloride and

H.S. Crystalline.—B'HI. Tables.—B',NH,Cl. [154°]. Felted crystalline mass (Reynolds, C. J. 59, 385).—B',NH,I. [186°].—B',H,PtCl_s. Yellow prisms, v. sol. water and alcohol. Can be dried at 100°.—B',HPtCl_s. Got when saturated solutions of thio-urea and PtCl, are mixed. Darkred prisms, insol. water, alcohol and ether.—
B'_AuCl. Yellow monoclinic crystals, got by adding AuCl, to a saturated solution of thiourea.—B'TISO,.—B'_2CuSO,. White silky needles. Got by mixing conc. solutions of thio-urea and CuSO, -B', Cu₂(SO₄) 2aq. -B', CuCl. Colourless dimetric crystals, sol. water, but ppd. by HCl and KCl. Alkaline in reaction. Attacked by H.S with difficulty. Does not absorb CO (Rathke, B. 17, 801).-B',Cu,Cl, aq. Ppd. by adding CuCl.Aq to aqueous thio-urea (Rathke, B. 14, 1779; 17, 301). Minute needles, insolwater.—B'_CuCl. Flat needles. Formed by mixing the two preceding salts into which it is decomposed by water.—B'4HgO.—B'₂(HgO)₃ auq. Ppd. by adding neutral Hg(NO₂)₂ to a dilute solution of thio-urea (Emerson Reynolds, 4. 150, 235; Kurnakoff, B. 24, 3956). Crystalline. Loses thio-urea on washing with water.—B'₄HgCl₂: large crystals, v. sol. water.—B'₂HgCl₂: minute needles, nearly insol. water (Claus, B. 9, 227).—B'HgI₂ (Maly, B. 9, 173).—B'HgCyS. Needles, decomposed by heat into dicyandiamide, HCy, and HgS (Nencki, B. 6, 598).—B'_PbCl₂: HCy, and HgS (Nencki, B. 6, 598).—B'_zPbCl_2: needles (Claus, A. 179, 135).—B'Pb(CyS),—B'_SnCl_2.—B'_ZnCl_2: spherical groups of prisms (from water).—B'_ZdSO_.—B'_SiBr_ (Imerson Reynolds, C. J. 51, 202).—B'_ZAg.O 4aq. Crystalline.—B'AgNO_8 (K.).—B'_AgNO_8. [141°]. Silky crystals, sol. hot alcohol (Emerson Reynolds, C. J. 61, 249).—B'_ZAgCl. [171°]. Needles, m. sol. hot alcohol.—B'_ZAgBr. [121°].—B'_ZAgI.—B'_ZAgCl.—B'_ZAgCl. (176°].—B'_ZAgI.—Chloride (CSN_H_)_Cl_2. Formed by passing Cl into a conc. alcoholic solution of thiourea (Claus, A. 179, 139). Formed also by the action of CCl_xSO_Cl, and of ICl, ICl, or POCl_3.

action of CCl₃SO₃Cl, and of ICl, ICl₃, or POCl₃ on thio-urea (M'Gowan, C. J. 49, 191; J. pr. [2] 83, 188). Small needles, v. sol. water, m. sol. alcohol, insol. ether. Decomposed by alkalis, yielding cyanamide. Alcoholic KI removes chlorine, setting thio-urea free. Dilute HNO, forms crystals of (CSN₂H₄)₂(NO₃), which is sl. sol. water, insol. alcohol and ether.

Bromide (CSN₂H₄)₂Br₂. Formed by adding Br to an alcoholic or cold aqueous solution of thio-urea; in aqueous solution excess of Br produces urea (Claus, A. 179, 138; M'Gowan, C. J. 51, 378; J. pr. [2] 36, 216). Crystals. Its aqueous solution deposits S when heated.

Sodium-amalgam reproduces thio-urea.

Iodids (CSN₂H₄),I₂. Formed from thio-urea, I, and alcohol (M'Gowan, J. pr. [2] 33, 192). Priems.

Prisms.

Methylo-iodide (CSN₂H₄)MeI. [117°]. Formed slowly by combination of thio-urea with MeI in the cold (Bernthsen a. Klinger, B. 11; 498). Prisms, v. sol. water and alcohol. gives the chloride, which forms the platino-chloride (B'MeCl),PtCl, aq. Ethylo-chloride B'EtCl. Crystals.

Ethylo-bromide (CSN.H.)EtBr. Hexa-gonal plates (Claus a. Siegfried, A. 179, 145). Decomposes at 100°.

Ethylo-iodides (CSN.H.)Etl. Crystal-

line. Gives with moist Ag2O a base. Boiling aqueous alkalis liberate mercaptan.—B',Et,PtCl. (dried at 100°). Tables.—B'zEtI. Needles (from alcohol) (Claus, B. 8, 41).

Bensylo-chloride (CSN,H,)C,H,Cl. [168°].

Formed from benzyl chloride and thio-urea. Yields unstable benzyl-thio-urea CSN₂H₃C,H₄[72°], which decomposes at 100° into dicyandiamide and benzyl mercaptan (Bernthsen a. Klinger, B. 12, 574).—(CSN₂H₄C,H₄Cl)₂PtCl₄. Compound with oxalic ether

(CSN₂H₄)₂Et C₂O₄. [150°]. Monoclinic crystals (Nencki, B. 7, 780). Decomposed by hot water.

Compounds with amines (CSN₂H₄), NMeH₂Br. [138°]. Formed methylamine hydrobromide and thio-urea in alcohol (Reynolds, C. J. 59, 392). Felted crystals.—(CSN,H,),NEt,H,Br. [134°]. Formed by boiling thio-urea together with diethylamine hydro-bromide and absolute alcohol.— (CSN₂H₄)₃NEt₃HBr.—(CSN₂H₄)₂NEt₄I [135°].

Prisms.—(CSN_H_J_sNEt_Br [160°]. Rectangular prisms (Reynolds, C. J. 59, 388).

Acetyl derivative CSN_H_Ac. Mol. w. 118. [165°]. Formed by heating thio-ures with Ac_O (Nencki, B. 6, 598). Formed also from thio-acetic acid and cyanamide (Prätorius, J. pr. [2] 21, 147). Prisms (from hot water), v. sol. alcohol, m. sol. ether.—B'H₂PtCl_a. Crystalline.

Propionyl derivative (Freytag, J. pr.

[2] 20, 381).

Benzoyl derivative CSN2H3Bz. [170°]. Formed by warming thio-urea (2 mols.) with BzCl (1 mol.) (Pike, B. 6, 755). Got also from benzoyl sulphocyanide and NH₂Aq (Miguel, BL. [2] 25, 252). Needles (from alcohol); sl. sol. cold water. Tastes bitter. cold water. Tastes bitter.
o-Oxy-benzoyl derivative

NII, CS.NH.CO.C. H.OH. [182°]. S. (boiling alcohol) 7. Formed from salicyl thiocarbimide and aqueous NH_s (Miguel, A. Ch. [5] 11, 304).

THIO- URIC ACID v. THIO-URAMIDO-BARBI-TURIC ACID

THIO-VALERIC ALDEHYDE C, II, S. (115°). Formed, together with C5H6S, [95], by heating isovaleric aldehyde (23 pts.) with S (9 pts.) in scaled tubes at 250° for eight hours (Barbaglia, G. 11, 95; B. 17, 2654). Oil with penetrating odour like onions, sol. alcohol and ether. Does

not combine with NaHSO.

Isomeride C₂H₁₀S. [69°]. V.D. (H=1)
50.76. Formed by passing H.S into a dilute aqueous solution of isovaleric aldehyde. Fibrous

crystals (from ether), insol. water.

THIOXENE v. DI-METRYL-THIOPHENE. THIOXYLENOL v. XYLYL MERCAPTAN.

THIOXYL METHYL KETONE v. DI-METHYL-TRIENYL METRYL KETONE.

THORIUM Th. (Thorinum.) At. w. 232. Mol. w. unknown. The m.p. of Th has not been Mol. w. unknown. The m.p. of Th has not been determined; it is certainly very high (Nilson, B. 15, 2541). S.G. 11·1 at 17° (N., Lc., p. 2543). S.H. '02787 (N., B. 16, 161). Crystallises in regular octahedral and hexagonal forms, isomorphous with Si (Brögger, Z. K. 7, 442; cf. Nilson, B. 15, 2546; 16, 162 note). S.V.S. 20·9. Historical.—In 1818 Berzelius announced

the discovery of the oxide of a new element in a rare Norwegian mineral; to the metal of this oxide he gave the name thorium (from THORIUM.

the Scandinavian god Thor). A few years later Berzelius found that the substance he had supposed to be a new earth was really yttrium phosphate. In 1828, however, Berzelius isolated a new earth from another Norwegian mineral: he named the new earth thoria, and the mineral from which it had been prepared he called thorite (P. 16, 385). In 1851 Bergemann discovered a new metal and called it donarium: but this metal was shown to be identical with the thorium of Berzelius by Damour (C. R. 34, 685), Berlin (P. 87, 608), and Bergemann himself (P. 85, 558). In 1862 Bahr supposed he had found a new metal, which he called wasium, but soon afterwards he recognised that the metal was identical with thorium (P. 119, 572; 132, 227). The metal thorium was isolated by Berzelius in 1828 (P. 16, 385); it was also obtained by Chydenius in 1861 (Bl. [2] 1, 130); and in a state

of greater purity by Nilson in 1882 (B. 15, 2537).

Occurrence.—Compounds of Th have been found only in very small quantities in a few localities. Thorite from Lövön in Norway contains c. 59 p.c. ThO, according to Berzelius; an orange-coloured variety of this mineral, orangite, was found by Bergemann to contain 74 p.c. ThO₂; Nilson (B. 15, 2519) found from 50 to 59 p.c. ThO₂ in different specimens of thorite. Small quantities of ThO, have been found in specimens of pyrochlore, monazite, samarskite, euxenite, gadolinite, and orthite. Several minerals containing Th have been discovered by Hidden a. Mackintosh in North Carolina and Colorado; one of these is a silicophosphate of Th, another a silicate of Th and Y, another a silicate of Th and U, and another is a uranate of

Th, Pb, and Y (Am. S. [3] 36, 461; 38, 474).

Formation. — 1. By reducing ThCl, or 2ThCl, KCl, by heating with K (Berzelius, P. 16, - 2. By reducing fused ThCl, 2ThCl. KCl, by means of Na (Chydenius, Bl. [2]

1,130; 6,433; Nilson, B. 15, 2537).

Preparation.—Powdered thorite is evaporated with HClAq to dryness; the residue is heated to render silica insoluble, and treated with water; the solution is filtered and ppd. Ly H₂S; the filtrate from PbS is ppd. by NH₃Aq, and the pp. of crude ThO₂.xH₄O is thoroughly washed and dissolved in HClAq; $Th(C_2O_4)_2$ is ppd. from this solution by $H_2C_2O_4Aq$, and the pp., after being thoroughly washed with boiling water, is decomposed by heating; the crude ThO2 thus obtained is converted into Th(SO₄)₂ by treatment in a Pt basin with conc. H₂SO₄ after being thoroughly moistened with water. The impure Th(SO₄), thus obtained is freed from acid and water by heating, and is dissolved in as little ice-cold water as possible (c. 5 parts are required), and the solution is heated to c. 20°, when Th(SO₄₎₂9H₂O ppts. The Th(SO₄₎₂9H₂O is dehydrated by heating; the Th(SO₄₎₂ is dissolved in the minimum quantity of ice-cold water and the solution is heated to c. 20°; the crystals of Th(SO₄)₂.9H₄O that separate are dehydrated, dissolved in ice-cold water, and the hydrated sulphate is ppd. by heating to 20°. This treatment is repeated a few times, when pure Th(SO₄)₂.9H₂O is obtained. This method of purifying crude sulphate of Th, which is given by Nilson (B. 15, 2521), depends on the great differences between the solubilities in water of

Th(SO₄), and Th(SO₄), 9H₄O; the former, when pure, is soluble in 20.6 parts water at 0°, the latter requires 88 parts water at 0°, and much more at 20°, for solution. The sulphates of the metals present in the crude Th(SO₄), prepared as described are much more soluble in water at 20° than Th(SO₄)_x9H₂O. For other methods of preparing and of Th from thorits v. Berzelius (l.c.), Chydenius (l.c.), Delafontaine (Ar. Sc. [2]

18, 343), and Cleve (Bl. [2] 21, 115).

To prepare Th from pure Th(SO₁), Nilson (B. 15, 2538) dissolved the salt in water, ppd. by KOHAq and boiled, washed the ThO_{...}xH₂O thoroughly, dissolved in HClAq and repud. by KOHAq (to remove all traces of H.SO.); he thoroughly washed the pp. by decantation, dissolved it in HClAq, added KCl, in the ratio 2ThCl.:KCl, evaporated to dryness in a Pt basin. and dried the residue by warming over a flame, stirring constantly, and then powdering and heating again. The dry double salt of ThCl. and KCl was heated to redness in a stream of dry HCl (prepared from conc. H.SO, and sub-limed NH,Cl), HCl was removed by a stream of H. and some of the salt was transferred to a cylinder of wrought iron (fitted with a lid which screwed on), in which a layer of dry NaCl had been placed; pieces of sodium were arranged over the Th-K salt in the cylinder, on these was placed another layer of the Th-K salt, and the cylinder was thus nearly filled with alternate layers of Na and the double salt; the contents of the cylinder were pressed together by a piston which fitted into the cylinder, sufficient dry NaCl was added to fill the cylinder, the lid was screwed on, and the apparatus was heated to full redness for about fifteen minutes; after cooling, the contents of the apparatus were treated with cold water. whereby chlorides were dissolved and the excess of sodium was converted into NaOII and dissolved (the action is apt to be explosive); the thorium was washed with water, then with alcohol, and finally with ether, and dried at 100°.

The yield of thorium by this method is almost equal to that calculated from the equation. For a detailed description of the iron cylinder used for reduction v. Nilson a. Pettersson, W. 4, 554

(on the preparation of Be).

Properties.—Prepared as described, Th forms a greyish-white, glistening powder; the powder consists of small, thin, six-sided, crystalline leaflets; the larger crystals are as white and lustrous as silver, the smaller are grey and less lustrous. The crystals are somewhat brittle. S.G. at 17° 11.1 to 11.23; the latter number referring to the well-crystallised metal (Nilson, B. 15, 2543; 16, 160). S.H. (0° to 100°) ·02787, hence at. heat = 6.4 (N., B. 16, 161). Crystallises in combina. = 6.4 (N., B. 16, 161). tions of regular octahedra and hexahedra; isomorphous with Si (N., l.c., and note, p. 162). S.V.S. 20.9. The emission-spectrum of Th has been mapped by Thalen (Détermin. des Longueurs d'Onde des Raies Métalliques [Unsala, 1868]); the most marked lines are three in the indigo; 4393, 4382, and 4281. Soret (Ar. Sc. [2] 63, 59; [8] 4, 94) found that ThCl,Aq outs off almost the whole of the ultra-violet part of the spectrum.

Th is unchanged in air up to 1000-1200; when heated to a higher temperature it burns to ThO, with production of much white light. Th is readily oxidised by heating in O; on this account some of the metal is oxidised in the process of preparation if the lid of the cylinder does not fit tightly. Nilson's experiments (B. 15, 2541) show that Th does not melt at the full heat of a wind-furnace. Th does not react with water; it combines directly with Cl, Br, I and S. The metal is slowly acted on by H,SO, or HNO, rapidly by HClAq or aqua regia; alkali solutions do not seem to react.

The at. w. of Th has been determined: (1) by analysing Th(SO₄), and hydrates of this salt (Berzelius, P. 16, 898 [1829]; Chydenius, P. 119, 43 [1861]; Delafontaine, Ar. Sc. 18, 343 [1863]; Hermann, J. pr. 93, 114 [1864]; Cleve, Bl. [2] 21, 116 [1874]; Nilson, B. 15, 2527 [1882]; Krüss a. Nilson, B. 20, 1665 [1887]); (2) by analyses of the double Th-K sulphate (Berzelius, l.c.); (3) by analyses of the acetate, oxalate, and formate of Th (Chydenius, l.c.); (4) by determining S.H. of Th (Nilson, B. 16, 153 [1883]); (5) by finding V.D. of ThCl, (Krüss, a. Nilson, B. 20, 1665 [1887]). The mol. w. of Th is not known.

Th is distinctly metallic in its chemical relations; the only oxide that has been isolated with certainty, ThO,, is basic, forming salts ThX_2 ($X-SO_4$, $2NO_3$, &c.). There are indications of the existence of a higher oxide (? Th_2O_3). Thorium forms the last member of the even-series family of Group IV. in the periodic classification of the elements. The members of this family are C, Ti, Zr, Ce, -, Th. The four elements Ti, Zr, Ce, and Th closely resemble one another in their chemical properties; they are also similar to the odd-series family of Group IV., namely, Si, Ge, Sn, —, Pb. For a general account of Group IV. (and more especially of C and Si) v. CARBON GROUP OF ELEMENTS (vol. i. p. 682); for a description of the even-series family (Ti, Zr, Ce, Th) v. TITANIUM GROUP OF ELEMENTS (this yol. p. 749); and for the odd-series family (Ge, Sn. Pb; Si being described in vol. i. p. 652) v. TIN GROUP OF ELEMENTS (this vol. p. 735).

The atom of thorium is tetravalent in the

gaseous molecule ThCl..

Reactions and Combinations (Nilson, B. 15, 2541).—1. Heated in air, oxidation begins at c. 120°, and at much below red heat the metal burns brilliantly to ThO2. -2. Heated in a stream of oxygen, the metal burns to ThO2, with the production of dazzling white light.—3. The burns to ThX, when heated in chlorine, in bromine vapour, or in vapour of iodine.—4. When heated with sulphur part of the S. volatilises, and when the temperature is above the b.p. of S combination occurs with production of much light, ThS, being formed.—5. According to Troost (C. R. 116, 1227). The combines with carbon, when ThO₂ is mixed with C and heated in CO₂ in the electric are (v. Carbide, tafra).—6. Water does not react with Th at any temperature, so far as experiments have seen tried. Nilson (l.c.) gives no details, but says 'Thorium is not changed by water under any conditions.'—7. Sulphuric acid reacts slowly with Th; when dilute, the acid evolves H; when cone. and hot, SO, is given off.—8. The action of nitric acid is slight; the dilute warm acid acts very gradually; conc. acid is almost without action.—9. Hydrochloric acid rapidly dissolves Th, forming ThOL, and giving off H; the action

is most complete with conc. acid.-10. Acua regia dissolves Th easily .- 11. Alkaline solu. tions seem not to react with Th.

Detection and Estimation .- Salts of Th are colourless when the acid is colourless. Alkalis, and also (NH₄)₂SAq, ppt. gelatinous, white ThO₂2H₂O₄ insoluble in excess of the precipitant: alkali carbonates form a white pp. soluble in excess; solution in (NH₄)2CO3Aq becomes turbid at 60°, but goes clear on cooling; saturation of a solution of a salt of Th with K,SO, forms Th(SO,)2.K2SO,2H2O, insoluble in K,SO,Aq, but soluble in water; K,FeCy,Aq ppts. white ThreCy,; oxalic acid and alkali oxalates ppt. white amorphous Th(C₂O₄)₂, insoluble in dilute acids, soluble in solutions of alkali oxa-

lates or NH₄,C₂H₄O₂, especially on warming.

Th is generally estimated by ppn. as
ThO₂,2H₄O or Th(C₂O₄)₂, and subsequent conver-

sion into ThO, by heating.

Thorium, bromide of. The gummy, white mass obtained by Berzelius (P. 16, 385), by evaporating a solution of ThO2.2H2O in HBrAq, was probably ThBr. The hydrated salt ThBr. 10aq seems to have been obtained, from ThO... 2aq, by Jannasch, Locke, a. Lesinsky (Zeit. f. anorg. Chemie, 5, 283).

Thorium, carbide of. By heating an intimate mixture of ThO, and C in the electric arc, in an atmosphere of CO₂, Troost (C. R. 116, 1227) obtained a hard, brittle solid, containing from 8.2 to 9.5 p.c. C, and therefore approximating to the formula ThC₂ (which requires 9.38 p.c. C). S.G. 10.15 at 15°; scratches glass slightly; decomposes cold water, giving off H and strongly smelling hydrocarbons; gradually decomposes in moist air; burns rapidly and brilliantly when heated to redness.

Thorium, chloride of, ThCl,. Mol. w. 378-5-V.D. 172.2 at 1050°-1270° (Krüss a. Nilson, B. 20, 1671). This compound is formed by heating a mixture of ThO, and C in a stream of dry Cl; the ThCl, sublimes in white needles. Kriiss a. Nilson (B. 20, 1675) prepared pure ThCl, by heating Th to incipient redness in a stream of dry, air-free HCl; then raising the temperature to full redness, in order to sublime a little FeCl, formed from the iron in the thorium used; and finally subliming the ThCl, at an incipient white heat. (For details of the apparatus used v. Nilson a. Pettersson, J. pr. [2] 33, 1 [cn preparation of BeCl2]).

ThCl, crystallises in lustrous, white needles; moderately hygroscopic, but remains some hours in the air before deliquescing (K. a. N., Lc.). Does not volatilise at c. 420° (Ohydenius, P. 119, 43). The V.D. found by K. a. N. at temperatures from 1050° to 1270° shows that the formula ThCl, is molecular. K. a. N. got the value 142 for V.D. at 1400°, showing that dissociation had begun. Troest (C. R. 101, 860) obtained values for V.D. of ThCl, at c. 950° considerably lower than those of K. a. N. It is likely that his specimen was not pure, or that the apparatus used contained traces of O sufficient to cause decomposition to ThO, and Cl (K. a. N., *l.c.*, p.

Hydrated thorium chloride ThCl. 8H,0 was obtained by Cleve in thin, white prisms, by con-centrating a solution of ThO. 2H.O in HClAq. allowing to crystallise, and drying over H.SO.

(Bl. [2] 21, 116).

Double salts.—ThCl, combines with potassium chloride to form 2ThCl., KCl.18H.O: obtained by mixing very cone. solutions of the tained by mixing very cone. solutions of the constituents. Forms small, white crystals; v. sol. water, also sol. alcohol; dehydrated by heating in HCl (Cleve, Bl. [2] 21, 116). By heating a dry mixture of ThCl, and NH,Cl in HCl, Chydenius (Bl. [2] 1, 130; 6, 433) obtained a compound with ammonium chloride, which, when crystallised from water in vacuo, had the composition ThCl,.8NH,Cl.8H,O; loses 6H,O at 100°. Cleve (l.c.) prepared a compound with platinic chloride ThCl, PtCl, 12H, O; and Nilson (l.c.) a compound with platinous chloride 2ThCl, 3PtCl, 24H, O.

Thorium, ferrocyanide of, ThFeCy,4H₂O. A white powder; prepared by adding K,FeCy,4Aq to solution of a salt of Th (Cleve, Bl. [2] 21,

116)

Thorium, fluoride of, ThF, 4H,O. Obtained by adding HFAq to ThCl, Aq; the gelatinous pp. becomes powdery after a time (Chydenius, Bl. [2] 1, 130; 6, 433). Loses H₂O at 100°, and 2H₂O at 140°-200°; heated to redness gives ThO₂ and HF. Berzelius (P. 16, 385) obtained a heavy white powder by heating ThO, 2H,O a neavy write powder by neating 110,234,0 with HFAq. Combines with potassium fluoride; Chydenius (l.c.) obtained two salts, (1) ThF, KF by mixing ThCl, Aq with KHF, Aq, (2) ThF, 2KF, 4H, O by boiling ThO, 2H, O with conc. KHF, Aq and HFAq. The isolation of a third salt, 7ThF, 8KF, 6H, O, is doubtful.

Thorium, hydride of. By heating ThO, with excess of Mg powder, in a stream of H, Winkler (B. 24, 885) obtained a grey powder, which gave off H with dilute HClAq, and burnt when heated in O. Analyses of this powder gave 72.86 p.c. Th, 50 p.c. H, 17.57 p.c. Mg, and 9.07 p.c. O. Supposing the ThO, Mg, and H interacted in accordance with the equation ThO, + 2Mg + 2H =ThH2+2MgO, then, from the quantities of ThO, and Mg used, the product would give on and sis 73.77 p.c. Th, 63 p.c. H, 15.45 p.c. Mg, and 10.15 p.c. O. From these data Winkler concluded that a hydride, ThH₂, was formed in the reaction.

Thorium, hydroxides of, v. Oxides and Hy-

DRATED OXIDES (infra).

Thorium, iodide of. The white gummy mass, crystallising after a time, obtained by Chydenius (Bl. [2] 1, 130; 6, 433) by evaporating a solu-

(BL [2] I, 101; 0, 453) by evaporating a solution of ThO₂.2H₂O in HIAq, was probably ThI₄. The substance goes brown in the light.

Thorium, nitride of, By heating ThO₄ or ThCl, in NH₃, also by heating ThCl, and NH₄Cl in HCl, Chydenius (*l.c.*) obtained a small quantities. tity of what he supposed to be either a nitrida. of Th or a compound of the metal with N and

Thorium, oxides and hydrated oxides of. Besides the oxide ThO₂ a peroxide, probably

Th.O., is said to exist.

THORIUM DIOXIDE ThO. (Thoria.) Mol. w. THORIUM DIOXIDE ThO... (Thoria.) Mol. w. not known. Obtained by ppg. a salt of Th by alkali, (NH.), SAq. or KCNAq, drying, and strongly heating; also by decomposing Th(C₀), by heat. A fine, white powder. S.G. 10.22 at 17° (Nilson, B. 15, 2536). S.V.S. 25.87. S.H. (0° to 100°) 0548 (N. a. Pettersson, B. 13, 1459). By heating ThO, with borax in a porcelain oven, Nordenskjold obtained the oxide in microscopic crystals isomorphous with SnO, and ZrO₂ (P. 150, 219). ThO, has not been fused; it is not reduced by heating with C, but when mixed with C and heated in Cl the chloride ThCl is obtained. ThO, does not react with molten alkalis. It is scarcely acted on by acids; warm cone. H₂SO₁, however, converts it into Th(SO₂).

HYDRATES OF THORIUM DIOXIDE. The dihydrate ThO, 2H,O (4 ThO, H,, thorium hydroxide) arate 110.,211.,0 (= 110.,11, thorium hydroxide) is obtained by ppg. a solution of a salt of Th by an alkali, (NH₁)₂SA₃, or KCNAq, washing, and drying at 100°. It forms a hard, white solid. ThO₂2H₄O combines with CO₂ in the air; it dissolves in acids, forming salts ThX₂, where X = SO₁, 2NO₃, &c. Another hydrate, 4ThO₂H₄O (= Th₂O₁OH)₂, thorium metahydroxide) is obtained according to Close (H₁(2), 116) by tained, according to Cleve (Bl. [2] 21, 116), by theating ThO₂ (obtained by decomposition of Th(C,O)₂) with excess of HNO₂Aq or HClAq at 100° till the acid is driven off, adding water, and then ppg. the opalescent solution so obtained by NH, Aq, washing, and drying at 100°. This hydrate is said to be insoluble in dilute acids.

THORIUM PEROXIDE Th2O,. An oxide with this composition is said to be produced by adding H₂O₂Aq and NH₃Aq to a solution of a salt of Th (Cleve, Bl. [2] 43, 53; Lecoq de Boisbau-

dran, C. R. 100, 605).

Thorium, oxysulphide of. By strongly heating ThO₂, obtained from ThO₂, 2H₂O, in CS₂ vapour, Chydenius (Bl. [2] 1, 130; 6, 433) obtained a solid substance to which he gave the composition of the c formula 2ThO. ThS₂ = Th₂O₁S₂. According to Krüss a. Volk (Zeit. f. anorg. Chemie, 5, 75; 6, 49), the compound obtained by heating ThO₂ in CS₂. is ThOS, and the same compound is formed by

heating 2ThCl, KCl in H.3.

Thorium, phosphide of. By heating Th in vapour of P, Berzelius (P. 16, 385) obtained a dark grey, metal-like, lustrous solid, which was changed to Th phosphate by heating in air.

Thorium, platinocyanide of,

Th(PtCy.), 16H,O. Yellow green, orthorhombic prisms (Cleve, Bl. [2] 21, 116).

Thorium, salts of. All the normal compounds which have been isolated by replacing H of acids by Th belong to the class ThX, where X=2NO, 2IO, SO, SO, 3PO, &c.; basic salts also exist. The chief salts of oxyacids are borate, carbonate, chlorate, chromate, iodate and periodate, molybdate, nitrate, oxalate, phophates, selenate and selenites, silicates, sulphate and sulphite, and tartrate.

Thorium, silicofluoride of. By treating ThO₂2H₂O with H₂SiF₄Aq, Cleve (Bl. [2] 21, 116) obtained a semi-transparent, crystalline solid, probably Th(SiF,); insol. in excess of H₂SiF_s; over H_sSO, gave off, HF and SiF_s. Thorium, sulphide of, ThS_s. Obtained by heating Th with S; excess of S sublimes, and

when the temperature passes the b.p. of Sthe elements combine with evolution of heat and light (Nilson, B. 15, 2542; cf. Berzelius, P. 16, light (Nilson, B. 16, 202; 17, Berzenus, r. 10, 385). Also formed by heating ThO₂, obtained from Th(C₂O₂), to white heat in vapour of CS₂ (Chydenius, Bl. [2] 1, 180; 5, 483); but, according to Krüss a. Volk (l.c.), the compound thus formed is ThOS. A black powder. Burns when heated in air, giving off SO₂ and leaving ThO, Not acted on by HClAq or HNO, Aq; aqua regia dissolves the compound, forming Th(SO). Molten KOH forms K,S and ThO; heating in Cl produces ThCl.

Thorium, sulphocyanide of. The salt [? Th(SCy)] is obtained, as a viscid mass, by eva-The salt porating a solution of ThO2.2H2O in HSCNAq. A solution of the compound gives a pp. with HgCy, said to be Th(OH), SCy, HgCy, HgCy, HgO; and the filtrate is said to give crystals of Th(OH)(SCy), 3HgCy, 12H, O (Cleve, Bl. [2] 21, 116) 116). M. M. P. M.

THUJIGENIN C₁₄H₁₂O₇₅or C₂₂H₂₄O₁₄. Occurs in small quantity in Frondes Thujæ, the green parts of Thuja occidentalis (Rochleder a. Kawalier, Sits. W. 29, 10). Minute needles, v. sl. sol. water, sol. alcohol. NH, colours its alcoholic solution green. AcCl forms resinous C14H11AcO1.

THUJIN C₂₀H₂₂O₁₂. Occurs in the green branches of *Thuja occidentalis* (Rochleder a. Kawalier, Sits. W. 29, 10). Minute lemon-yellow four-sided tables, sol, alcohol. Tastes bitter. Its alcoholic solution is coloured vellow by alkalis, is turned reddish-brown by air, gives a yellow pp. with lead acetate, and gives a darkgreen colour with FeCl. Reduces ammoniacal AgNO. Boiling dilute H.SO, turns it first green, then yellow, and splits it up into sugar and thujetin. Boiling baryta-water hydrolyses it in like manner.

Thujetin $C_{28}H_{28}O_{16}$. Yellow solid, nearly insol. water, sol. alcohol and ether. Not altered by dilute HCl or H,SO,. Its alcoholic solution is turned a splendid bluish-green colour by NH, Aq. Gives, in alcoholic solution, a red pp. with lead acetate, and a black colour with FeCl, Boiling baryta-water converts it into thujetic acid $\hat{C}_{2a}H_{2a}\hat{O}_{1a}$, which crystallises in minute lemon-yellow needles, sol. alcohol and ppd. by water.

(B)-THUJOL is TANACETONE.

THUJONE C, H, O. (212°). S.G. 22 .9265. Occurs, together with the terpene C₁₀H₁₆ and lævorotatory fenchone, in the essential oil of thuja obtained by distilling the ends of the branches and the leaves of Thuja occidentalis with water (Schweizer, A. 51, 398; Jahns, Ar. Ph. 221, 748; Wallach, A. 272, 109). Yields an oxim.

Reactions. -1. When heated with ammonium formate it yields a formyl derivative which on C₁₀H₁₁, NH₂ (199°), which forms the salts B'₂H₂PtCl₂ and B'HCl. Thujone amine hydrochloride decomposes on distillation into NH,Cl and thujene $\hat{C}_{10}H_{10}$ (c. 173°), S.G. $\stackrel{20}{\sim}$ 84.—2. KMnO, forms two 'thujaketonic acids.'—3. Br forms C. H. Br.O [122°] (Wallach, A. 275,

179).

(a) Thujaketonie acid C₁₀H₁₆O₂ i.e.
CH₂CO.O₂H₁₇CO₂H. [76°]. S. c. 2·5 at 100°.
Transparent plates. Yields an oxim [c. 186°]. (B) Thujaketonic acid C₂H₁₇(CO.CH₂).CO₂H. [79°]. S. 1·43 at 100°. Small matted needles. On distillation it yields methyl heptyl ketone (186°) S.G. 2° 854, which gives \(\psi\$-cumene dihydride C₂H₁₄ on heating with ZnCl₂ at 100° (Wallach, A. 275, 166). Forms an oxim [106°] which crystalliaes in needles. AgA'; \(\psi\$, et al. acid. which crystallises in needles. -AgA': v. sl. sol. ould water.

THULIUM. This name was given by Cleve in 1879 to the metal of a new earth which he announced to be present in specimens of gado-linite (C. R. 89, 478). The name thulium was derived from Thule, the old name for Scandinavia. The presence of the new earth was more or less confirmed by the work of Nilson (B. 13, 1433), and of Soret (C. R. 89, 251). In 1880 Cleve said he had isolated thulia, and described it as a white earth, giving an emission spectrum characterised by two bright lines 5896 and 5306. and forming solutions of salts which showed two absorption bands 6840 and 4645. To this earth Cleve assigned the formula Tm.O., and he determined the maximum value of the atomic weight of the supposed element to be Tm = 170.7. In 1888 Krüss a. Nilson declared that thulium consists of two distinct elements (B. 21, 1681).

The absolute homogeneity of thulia has been

by no means established (v. METALS, RARE, vol.

iii. p. 245). M. M. P. M. THYME OIL. The essential oil from garden thyme, Thymus vulgaris, contains laworotatory thymene $C_{10}H_{16}$ (160°-165°), thymol $C_{10}H_{14}O$ and a little cymene (Lallemand, A. 102, 119; A. Ch. [3] 49, 155). The oil from wild thyme, Thymus scrpyllum, contains cymene, tryine, Inymus serppeum, contains cymenc, thymol, carvacrol, and a phenol coloured violet by FeCl, (Jahns, Ar. Ph. [3] 16, 277; Febre, C. R. 92, 1290; Buri, Ar. Ph. [3] 12, 485).

THYMO-ACRYLIC ACID v. OXY-GYMYL-

ACRYLIC ACID

THYMOHYDROQUINONE v. HYDROTHYMO.

THYMOL C₁₀H₁₁O i.e. C₅H₂MePr.OH [5:2:1]. Mol. w. 150. V.D. 75·3 (calc. 75) (Eykman, B. 22, 2757). [49·5°] (Reissert, B. 23, 2242). (232°). S.G. § '9941. O.E. (0°-10°) '00085. S. 3. S.C. $\frac{1}{10}$ '3941. C.E. (U-LU') '100000. S. c. S.V. 188-9 (Pinette, A. 243, 46); 189-3 (Ramsay). $R_{\infty} = 76\cdot56$ (Nasini a. Bernheimer, G. 15, 93). H.F.p. (liquid) 69,250; (solid) - 8768. Occurs in essential oil of thyme (Doveri, A. 64, 274. 1.2) 374; Lallemand, A. Ch. [3] 49, 148; A. 102, 119), of horsemint, Monarda punctata (Arppe, A. 58, 42), of *Ptychotis ajowan* (Stenhouse a. Haines, A. 98, 307; H. Müller, B. 2, 130) of Monarda Didyma, of Ammi Copticum (Buri, Ar. Ph. [3] 12, 485), and in the oil from wild thysic (Jahns, B. 15, 819).

Formation. - By boiling diazo-n-cymene with water (Widman, B. 15, 170; 19, 245).

Preparation.—By extracting oil of thyme with NaOHAq, ppg. by HCl, and recrystallising from HOAc.

Properties.-Plates (from alcohol), v. sol. alcohol, ether, and HOAc, v. sl. sol. water. Has a slight odour of thyme and a peppery taste. When solid it is slightly heavier than water, when liquid it is lighter. Not ppd. by adding water to its alcoholic solution. Not dissolved by NH₃Aq, but absorbs NH₃, becoming liquid, but re-solidifying after the NH₃ has escaped. Sol. KOHAq. FeCl, does not colour its aqueous solution. Bromine-water only gives a milkiness. An aqueous solution (1 vol.) warmed first with HOAc (\frac{1}{2} vol.) and then with H.SO, (1 vol.) is coloured reddish-violet, the solution showing two absorption bands at E and D (Wolff, Fr. 22, 96). KOHAq followed by I in KI gives on warming a fugitive red tint (Itallie, Fr. 29, 205). Estimation: Messinger, B. 23, 2754.

Reactions.—1. Decomposed by distilling with P₂O₂ into propylene and m₅cresol.—2. P₂S₃ yields symene (Fittica, B. 6, 938; A. 172, 805). 8. Oxidised by chromic acid to thymoquinone.-4. PCl, yields chloro-cymens. 5. Potash-fusion yields several oxy-acids (Barth, B. 11, 567, 1571).—6. Iodins and potash yield a red amorphous pp. [110°] converted by heat or by amorphous pp. [110] converted by neat of by boiling water into a yellow body [165°] (Messinger a. Vortmann, B. 22, 2316).—7. Boiling POCl, (1 mol.) acting on thymol (1 mol.) forms liquid C₁₀H_{1,0}O, POCl₂ (280°-285°) which is conwhich yields BaA" 4aq and is decomposed by heat into thymol and HPO₃ (Discalzo, G. 15, neas into tryinos and HPO₃ [Discalzo, C. 15, 279).—8. Boiling POCl, acting on thymol (2 mols.) forms (C₁₀H₁₃O₂POCl (330°-340° at 320 mm.), a liquid which is converted by water into $(C_{10}H_{13}O)_2PO.OH$, which is insol. water and yields NaA' [74°] (Kreysler, B. 18, 1705) and BaA'₄5aq. S. 197 at 21°.—9. PCl₅ (1 mol.) acting on thymol (4 mols.) forms $(C_{10}H_{13}O)_3PO$ [59°] crystallising from alcohol in prisms (E. a. L.).—10. SiCl, forms Si(OC, H12), [48°] (450°) L.).—10. Sici, forms Si(OC₁₀H₁₃), [40] (430) crystallising from CHCl₃ in prisms (Hertkorn, B. 18, 1693).—11. Cl.CO.NH₂ reacts forming C₆H₃MePr.O.CO.NH.CO.NH. [190°] (Gattermann, A. 244, 44).—12. C₈H₄(NM_c)(NH₂) [1:4] C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MeP. C. H. MePr. C. H. MePr. C. H. MePr. C. H. MePr. (2. H. MePr. C. H. forms indothymol C₆H₄(NMe₂).N<\(\frac{C_6}{O}\)H₂MePr

[69-5°] crystallising in needles, insol. water and alkalis, forming a blue solution in alcohol, a violet in ether, and a green in HOAc. HClAq decomposes indothymol into thymoquinone, dimethyl-aniline, and NH₄ (Bayrac, BL, [3] 7, 97).

13. Chloral forms C₁₀H₁,OC,HCl₂O [130°-134°) (Mazzara, G. 13, 272).—14. Chloral, conc. H₂SO, and HOAo yield CCl₂CH(C₁₀H₁₂OH)₂ (Jüger, B. 7, 1197).—15. Dilute H₂SO, gradually added to a mixture of benzoic aldehyde (1 mol.) and to a mixture of benzoic aldenyde (1 mol.) and thymol (2 mols.) forms $C_*H_*CII(C_{10}H_{11}.DII)_2$ [146°] which is sol. alkalis and yields a diacetyl derivative [126°] (Russanoff, B. 22, 1943).—16. COCl., passed into an aqueous solution of $C_{10}H_{13}ONa$ forms di-thymyl carbonate ($C_{10}H_{13}ONa$ forms di-thymyl carbonate value [482] (above 1860) and violate covered to the state of the second secon needles [48°] (above 360°) and yields o-oxybenzoic acid when heated with NaOPh at 180° ment with ClCH_CO₂H and NaOHAq produces C₁H_{1,0}CH₂CO₂H [148°] which yields BaA'₂ 2aq PbA'₂, AgA', oily EtA' (290°), and an amide [97°] (Saarbach, J. pr. [2] 21, 159; Spica, G. 10, 342). (Saarbach, J. pr. [2] 21, 159; Spica, G. 10, 342).
19. a-Chloropropionio acid and KOHAq yield
Ch.H., COLHM. CO.H. [48] (Scichilone, G. 12,
50).—20. Thymol (10 g.) mixed with H.SO.
(70 g.) containing nitrous acid gives thymolchroin C., H., N.O., a dark-violet amorphous body
which dissolves in alcohol, ether, CHCl., and
benzene, forming red solutions with pale green
fluorescence. Alkalis turn its alcoholic solutions
blue. Sublimes at 140° civing off violet vanours blue. Sublimes at 140°, giving off violet vapours.

Yields brown amorphous $C_{40}H_{40}Ac_1N_2O_4$ (Brunner a. Chuit, B. 21, 252; cf. Liebermann, B. 7, 1100).—21. By heating with ammonium-zine chloride it is converted into thymylamine $C_{10}H_{12}NH_2$ and di-thymylamine $(O_{10}H_{12})^2NH_2$.

22. Cyanuric chloride converts sodium thymol into (C₁₀H₁X₃C₃N₃O₃ [151°] a yellow crystalline powder, insol. water, sl. sol. alcohol (Otto, B. 20, 2239). \$\frac{4}{23}\$ Aqueous KOH and K₂S₂O₃ form C₁₀H₁₃O₃SO₂OK, which crystallises from alcohol is closed as cills. in slender silky threads (Heymann a. Königs, B. 19, 3307). It is oxidised by alkaline KMnO.

B. 19, 3307). It is exidised by alkaline KMnO₄ to experimine acid C₂H₄Pr(OH).CO.H [4:3:1].

Salts. — C₁₀H₃ONa. Crystalline. Its aqueous solution is ppd. by HgCl₂ and AgNO₃.—
C₁₀H₃O.Hg.HgNO₂.—C₁₀H₃O.Hg.HgOAc (Merck, G. P. 48539; Pharm. Zeit. 1889, 625).—
(O₁₀H₁₃O).Hg₂O (Lallemand).—(C₁₁H₁₃O),Al. Decomposed by heat into propylene and (C₄H₄Mc.O)₃Al., the m-cresylate then splitting up into alumina, m-cresol, di-m-tolyl oxide, and a body C₁₅H₁₄O [200°] S. (alcohol) 17 at 20°; 1 at 78°; S. (benzene) 93 at 21°; S.G. 805; V.D. 208.8, crystallising in pearly plates (Gladstone a. Tribe, C. J. 39, 9; 41, 11).

Acetyl derivative C₁₆H₁₃OAc. (245°).

S.G. º 1.009.

S.G. 2 1.009.

Benzoyl derivative C₁₀H₁₃OBz. [82°].

II.F. 90,480 (Stohmann, J. pr. [2] 36, 9).

Methyl ether C₁₀H₁₃OMo. (216° cor.).

S.G. 9 9531. C.E. (0°-10°) 00083. S.V. 214·3 (Pinette, A. 243, 47). H.F.p. 61,429 [C.O. 94,000; H₂₁O = 69,000] (Stohmann, J. pr. [2] 35, 26). Formed from thymol, KOII, and MeI (Engelhardt a. Latschinoff, Z. [2] 5, 43).

Ethylether C₁₀H₁₃OEt. (227) (Pinette; cf. Jungleisch, Bl. [2] 4, 17). S.G. 9 934. C.E. (0°-10°) 00089. S.V. 240. H.F.p. 68,858 (Stohmann). Yields the ethyl derivative of oxyterephthalic acid on oxidation (Paterno a.

terephthalic acid on oxidation (Paterno a. Canzoneri, G. 9, 460). Decomposes at 3603-400° into thymol and ethylene (Bamberger, B. 19, 1820).

Propyl other C₁₀II₁₈OPr. (243°). S.G. § 9276. C.E. (0°-10°) 00088. S.V. 265·5. Butyl ether C₁₀H₁₃OC₄H₁, (258°). S.G. § 9230. C.E. (0°-10°) 00085. S.V. 289·2. Isoamyl ether C₁₀H₁₉OC₄II₁, (238°-243°)

Nitroso thymol v. Oxim of THYMOQUINONB. Dithymol v. DI-OXY-DICYMYL.

References .- Amido-, BROMO-AMIDO-, BROMO-NITRO-, TRI-CHLORO-, IODO-, IODO-AMIDO-, and NITRO-THYMOL.

DI.THYMOL.ETHANE v. DI-OXY-DI-CYMYL-RTHANE.

THYMOL DICARBOXYLIC ALDEHYDE C₁₂H₁₁O₂ i.s. C₄HMePr(OH)(OHO)₂ [80°]. Formed as a by-product in the pfeparation of thymotic acid by the action of chloroform and NaOH on thymol (Kobek, B. 16, 2104). Needles. Gives a red colour with FeCl.

THYMOL (a)-SULPHONIC ACID

C.H.MePr(OH).SO,H. [92°] (Stebbins, Am. 3,

111). Formed from thymol by the action of

H₂SO, or Cl.SO₂OH at 50° (Engelhardt a. Latschinoff, Z. 1869, 44; 1871, 261). Pearly plates (containing aq), v. e. sol. water. FeCl. colours neutral solutions dark-wolet. Yields

colours neutral solutions dark-wiolet. Yields thymoquinone on oxidation.

Salts.—KA'2½aq. Efflorescent tables, v. e. sol. water.—NaA'2½aq. [167°].—NH,A'2aq. [172°].—CaA'22aq. [157°].—BaA'24aq. Prisms, decomposing at 100°.—PbA'24aq.

Bensoyl derivative C₁₀H₁₂(OB2).SO₂H.

—KA'2aq.—CaA'24aq.—BaA'25aq.—PbA'25aq.

Ethyl derivative C₁₀H₁₂(OEt)SO₂H.

Formed from the K salt, KOH, and EI.—KA'.

Thin plates.—BaA'25aq.—Pates. sl. sol. hot Aq.

Thin plates.—BaA'₂ Saq. Prates, sl. sol. hot Aq.
Isoamyl derivative O₁₉H₁₂(OC₁H₁₁).SO₂H.
—KA'. Needles, v. sol. water. -BaA'₂ Saq.

Thymol (β) sulphonic acid C₁₀H₁₂(OH) SO₃H.

Formed in small quantity by the action of H₂SO₄ on thymol.—KA'aq. Plates, sl. sol. cold water. Coloured violet-blue by FcCl..

Thymol (γ)-sulphonic soid C₁₀H₁₂(OH).SO₄H. Formed by heating thymol with fuming H₂SO₄ at 100° (E. a. L.).—KA'aq. Granular, v. sol. water.—BaA'₂Saq. Tufts of needles, more soluble than the color of the than the (a)-isomeride. Not decomposed at 120°

Bensoyl derivative C₁₀H₁₂(OBz).SO₂H.— KA'3aq. Flat needles, sl. sol. cold water. Ethyl derivative C₁₀H₁₂(OEt).SO₃H.— KA'. Flat needles.—BaA', 3aq. Six-sided tables.

Thymol-sulphonic acid

Ethyl derivative C_aH₂MePr(OEt)SO₂H [1:4:3:6]. Formed by boiling diazo-cymenesulphonics cid with absolute alcohol.—Ban', 3aq: white plates, sol. hot water, sl. sol. cold (Widman,

B. 19, 247).
Thymol sulphonic soid. Methyl derivative C₁₆H₁₂(OMe).SO₃H. Formed, together with an isomeride, by sulphonation of the methyl ether of thymol (E. a. L.; Paterno a. Pisati, B. 8, 440).-KA': large tables.-BaA', 3aq. Nodules, y. sol. hot water. S. 3.94 at 26°.

Thymol disulphonic acid C₁₀H₁₁(OH)(SO₂H)₂.

Formed by sulphonating thymol.—K₂A''1½ac.

Efflorescent needles (from alcohol), v. e. sol.

References. - AMIDO-, BROMO-, and IODO-

THYMOL BULPHONIC ACID.

THYMOQUINONE C10H12O2 i.e. C2H2MePro2 [2:5:4:1]. Mol. w. 164. [45.5°]. (232°). Formed by oxidation of thymol (Lallemand, J. Pormed by oxidation of thymol (Lallemand, J. 1854, 592), of the methyl ether of thymol (Paterno, B. 8, 440), of cymenol (Carstanjen, J. pr. [2] 3, 53; 15, 410), of di-oxy-di-cymylethane (Steiner, B. 11, 289), of carvaorol psulphonic acid (Claus, J. pr. [2] 39, 356), and of amido-thymol (Andersen, J. pr. [2] 23, 172; Armstrong, B. 10, 297; Liebermann a. Ilinski; R. 18, 3144) Velley carvate and the control of the property of the control of B. 18, 3194). Yellow crystals, with pungent odour, v. sl. sol. water, v. sol. alcohol and ether. Reduced by SO, to Evdrothymoquinone. K., SO, at 60° forms crystalline C₁₀H_{1,2}O,SK. Phenyl cyanate forms C₁₀H_{1,2}O:NO.CO.NHPh [132°], crystallising in large yellow needles (Goldsschmidt a. Strauss, B. 22, 3106).

Oxim C_sH₂MePrO(NOH) or C_sH₂MePr(OH)(NO). Nitroso-thymol. [162°] Formed by the action of nitrous acid on thymol (R. Schiff, B. 8, 1500; Widmann, B. 15, 170; Liebermann, B. 18, 3194). Formed also by the action of hydroxylamine hydrochloride on

thymoquinone (Goldschmidt a. Schmid, B. 17. 2061). Slender monoclinic needles, above = 1-987:1:1-8941; β = 94° 57' (Panebianco, G. 10, 78); sl. sol. hot water. Its alkaline solution 10, 78); \$1. 801. NOT WARET. IN BIRKHINE SOLUTION is red. Oxidised by alkaline K₂FeCy₆ to nitrothymol. Reduced by tin and HCl to amidothymol (Liebermann, B. 10, 77). Does not react with SO₂ (Schmidt, J. pr. [2] 44, 521). Fuming HCl forms di-chloro-thymoquinone and chloro-the state of the state of amido-thymol (Sutkowski, B. 19, 2315). KOH and BzCl form C₁₀H₁₂O(NOBz) [110°]. Hydroxylamine (3 mols.) in strongly alkaline solution forms, in 48 hours, a white substance which, if ppd. by HOAc, immediately dissolved in dilute NaOH, treated with an equal weight of a phenol, and exposed to the air, gives a deep-blue colour or pp. turned red by acids (Kehrmann a. Messinger, B. 23, 2818, 3557).

Di-oxim C₁₀H₁₁N₂O₂ i.e. C₁₀H₁₂(NOH),. Formed by boiling an alcoholic solution of nitroso-thymol (1 mol.) with hydroxylamine hydrochloride (2 mols.) and partially neutralising with alkali from time to time. Yellowishwhite granules, decomposing at 235° without melting. Insol. water and NH,Aq, sol. KOHAq.

Chlorimide C.H.MePr by adding a solution of bleaching powder to a cold acidified solution of the hydrochloride of p-amido-thymol (Andresen, J. pr. [2] 23, 169). Pungent oil, volatilising even at 15°. Decomposes at 160°-170°. Volatile with steam. Decomposed by conc. HClAq into chloro-amidothymol and mono- and di-chloro-thymoquinone. Conc. HBrAq behaves in a precisely similar way. Alcohol at 140° converts the chlorimide into thymoquinone. Conc. aqueous SO, reduces it in a few days to hydro-thymoquinone. Reduced by tin and HCl to p-amido-thymol, considerable quantities of hydrothymoquinone being formed at the same time.

Polymeride [201°]. Formed by the action of daylight on thymoquinone (Armstrong, B. 10, 297; Liebermann, B. 10, 2177; 18, 3193). Silky yellow needles (from alcohol), insol. ether. Ohanges to thymoquinone on distillation. Not actacked by SO, at 180°, but reduced by HI and P, or in alcoholic solution, by Zn and HClAq to hydrothymoquinone.

Phenyl hydrazide [249°]. Insol. benzene. Oxim (C₁₀H₁₃NO₂). [263°]. Crystalline, insol. water. Reduced by tin and HCl to amidohydrothymoquinone.

Dioxim (C₁₀H₁₁N₂O₂)_z. [c. 290°]. Powder. May be reduced to di-amido-cymene.

References .- DI - AMIDO-, BROMO-, CHLORO-,

IODO-, and OXY- THYMOQUINONE.

o-THYMOTIC ACID C₁₁H₁,O₂ i.e.

C₄H₄Me(C₄H₂)(OH).CO₂H[6:3:2:1]. Mof. w. 194.

[123°]. Formed by the action of CO₂ upon heated sodium thymol (Kolbe a. Lautemann, A. 115, 205; Kobek, B. 16, 2101). Silky crystals, 115, 205; Kobek, B. 16, 2101). Silky crystals, v. sol. alcohol, other, and benzene, almost insol. cold water. Volatile with steam. Gives a deep-blue colour with FeCl. Yields thymol when distilled with baryta. PCl. acting on the Na sait forms thymotide O₁₁H₁₁O₂ [187°], which is reconverted into thymotic acid by potash fusion (Naquet, Bl. 4, 92).

p-Thymotic acid O₁₁H₁₁O₂ i.s.
O₂H₂Me(C₂H₁)(OH).CO₂H[6:8:4:1].

Formed by heating thymol with aqueous NaOH and CCl₄ (Kobek). White plates, v. sol. alcohol, ether, and benzene, insol. cold water. Not coloured by FeCl₄.

Methyl derivative C.H.Me(C.H.)(OMe).CO.H.

needles (from dilute alcohol).—AgA': pp.

p-THYMOTIC ALCOMOL C, H, O, i.e. C,H,Me(C,H,)(OH).CH,OH. [120°-130°]. Formed O₂H₁Me(C₂H₁)(OH).CH₂OH: [120'-130']. Formed by reducing thymotic aldehyde with sodium-amalgam (Kobek, B. 16, 2098). Amorphous powder, v. sol. alcohol and ether, insol. water.

• p-THYMOTIC ALDEHYDE C₁H₁H₂O₂ i.e.
C₂H₂Me(C₂H₁)(OH)CHO[6:3:4:1]. [133°].

Formed, together with C₂HMe(C₁H₁)(OH)(CHO)₂ (16:3:4:5:1] [80°]. We have in a thread with chlore.

[6:3:4:5:1] [80°], by heating thymol with chloroform and NaOHAq (Kobek, B. 16, 2096). Silky needles, v. sol. alcohol, sl. sol. hot water. On heating with aniline it yields the compound C_sH_zMe(C_sH_z)(OH).CH:NPh [142°] crystallising in yellow needles.

Methyl derivative

C.H.,Me(C.H.)(OMe).CHO. (278°). Formed by methylation of the aldehyde. Oil, yielding an anilide C,H2Me(C,H,)(OMe).CH:NPh [80°] crystallising in transparent tables.

THYMYLAMINE C₁₀H₁₃NH₂. (230°). Formed, together with di-thymylamine, by heating thymol with ammoniacal ZnBr, or ZnCl, and NH, Br or NH, Cl at 350° 360°, the yield being 25 p.c. (Lloyd, B. 20, 1260). Colourless oil.— B'_H, PtCl,: yellow needles. Acetyl derivative Cl, H1, NAc. [112°].

Isomeride v. CARVACRYLAMINE. Di-thymyl-amine (C₁₀H₁₅)₂NH. (340°-345°). Formed as above, the yield being 25 p.c. Oil. Its solution in P₂SO₄ is coloured blue by nitrites or nitrates.—B'₂H₂PtCl₅.

Acetyl derivative (C,0H,3)2NAc. [78°]. THYMYL CYANURIC ACID v. CYANIC ACID. THYMYL CYANURIC ACID v. CYANIC ACID.
THYMYL MERCAPTAN C₁₀H₁₁SH. Thiothymol. (231°). S.G. 989. Formed by heating thymol with P₂S₂, (Fittica, A. 172, 325; Bechler, J. pr. [2] 8, 167). Liquid with pungent odour. Oxidised by HNO₂ to sulpho-toluc acid.
— Hg(SC₁₀H₁₃)₂. Greenish rhombohedra [78°].
— PbA'; golden needles (from alcohol).

THYMYL PHOSPHATE (C_{1.}H_{1,1}), PO₁. [99°]. Formed by heating thymol with POCl₁, the yield being 75 p.c. of the theoretical amount (Kreysler, B. 18, 1705). Colourless needles.

(c. 450°). Formed by heating thymol with SiCl, the yield being 70 p.c. of the theoretical amount (Hertkorn, B. 18, 1692).

TIGLIC ACID C.H.O. i.e. CH., CH.CMe.CO., H. Methyl-crotonic acid. Mol. w. 100. [65°]. (199° i.V.) (Kopp, A. 195, 84). Occurs as a glycerylether in croton oil (Geuther a. Frohlich, Z. 1870, 549; Schmidt a. Berendes, A. 191, 94; B. 10, 835; Ar. Ph. [8] 13, 213), and as isoamyl ether in Roman oil of chamomile (Kobig, A. 195, 101).

Formation.—1. By the action of heat or of conc. H.SO, on angelic acid (Demarcay, B. 9, 1933).—2. By reducing the dibromide of angelic acid with sodium-amalgam (Schmidt, A. 208, 253) .- 3. From CEtMe(OH).CO,Et (derived from oxalic ether, Etl, Mel, and Zn) by treatment with PCl, and saponification of the product

(Frankland a. Duppa, A. 186, 9).-4. By distilling CH, CH(OH).CHMe.CO, H (Rohrbeck, A. 188, 235), or by heating it with HIAq (Rücker, A. 201, 61).-5. By reducing methyl-acetoacetic ether with sodium-amalgam and heating the resulting CH, CH(OH), CHMe.CO, H at 200° (Wislicenus, A, 250, 243).—6. By heating veratrine with alcoholid potash (Wright a. Luff, C. J. 33. 347) .- 7. By heating veratrine with conc. HClAq (Ahrens, B. 23, 2704).

Properties. -Triclinic plates, Properties. -Triclinic plates, v. sol. hot water, alcohol, and other. Smells like benzoic acid. Volatile with steam. Not attacked by sodium-amalgam. Forms with isovaleric acid the double salts CaA'(C,H,O,) 4 aq and

AgA'C,H,O2.

Reactions.—1. Yields acetic aldehyde and acid on oxidation with KMnO, (Beilstein a. Wiegand, B. 17, 2261; Kondakoff, J. R. 20, 523).—2. Potash-fusion gives propionic and acetic acids.—3. Funning III forms an iodovaleric acid [877] (Schmidt, B. 12, 252).—4. HI mixture of CH, CH(OH), CCIMe, CO, H [112°] and CH3.CHCl.CMe(OH).CO2H [75°] (Melikoff, Bl. [2] 47, 166).

Salts.—KA'.—CaA', 3aq. S. (cf. CaA',) 6.4 at 17°.—BaA', 4aq. S. (of BaA',) 18.5 at 16°.— AgA'.

Ethyl ether EtA'. (155°). S.G. 2.942. Isalmyl ether C.H.A'. (205°).

Reference.—Chloro-tiglic acid. "
TIGLIC ALDEHYDE C,H,O. Guaiol. (118°).
V. 2-92. Formed by distillation of gum guniacum (Deville, C. R. 17, 1143; 19, 134; Völckel, A. 89, 346; Herzig, M. 8, 118). Formed also by heating acetic aldehyde (1 mol.) with propionic aldehyde (1 mol.) and aqueous (28 p.c.) NaOAc for 30 hours at 100° (Lieben a. Zeisel M. 7, 53). Pungent oil, miscible with alcohol and ether. Oxidised by air to tiglic acid. Alkaline sodium nitroprusside gives a violet-red colour destroyed by HOAc (Von Bitto, A. 267, 376). Br forms di bromo-valerio aldehyde. Iron and dilute (50 p.c.) acetic acid reduce it to valeric aldehyde (91°), an inactive amyl alcohol CHMeEt.CH₂OH (129°) and tiglic alcohol C₃H₁₀O (c. 130°). Reacts with phenyl-hydrazine, and combines with NaHSO. CrO, forms acetic acid (Gilm, A. 106, 379). Aqueous SO, at 0° forms oxy-pentane disulphonic acid (Haymann, M. 9,

TIGLYL ALCOHOL v. PENTENYL ALCOHOL.

TIN Sn. At. w. 118.8 (v. infra). Mol. w. not known with certainty (v. infra). Melts at 231.68° (Callendar a. Griffiths, C. N. 63, 1); for other data, giving m.p. from 220° to 235°, v. Carthard Melling and Review Points Table (2, 12). nelley's Melling and Boiling-point Tables (2, 12).
Boils between the m.p.s of Ni and Fe, t.e. between 1450° and 1600° (Carnelley a. Williams,
C. J. 35, 566). S.G. c. 73 (determinations vary from c. 7 0 to c. 7.5 (c. Clarke's Table of Specific Gravities [2nd ed.] b). The so-called allotropic variety of tin seems to have S.G. from 5.8 to 6.1 (v. Schertel, J. pr. [2] 19, 822). S.H. (0°-100°) 0559; so-called allotropic tin has S.H. 0545 (0°-100°) (Bunsen, P. 141, 1); S.H. liquid tin (250°-850°) = '0687 (Person, A. Ch. [8] 24, 129). C.E. (linear, 0°-100°) '00002296 (Matthiessen, Pr. 15, 220; v. also Kopp, A. 81, 1; Fizeau, C. R. 68, 1125). T.O. 15·2 (Ag=100) (Wiedemann, P. M. [4] 19, 243). E.C. (Hg at 0?=1) at 16°=8*828 (Kirchoff a. Hausemann, W. 18, 406); at 0°=8*726, at 100°=6*091 (Lorenz, W. 18, 422). Heat of fusion (for 1 kilo.,tin) = 14\text{N52} (Person, 4 Ch. [8] 24 120). For expectations of the A. Ch. [3] 24, 129). For spectrum of tin v. Thalén (A. Ch. [4] 18, 237); Sale. (U. J. [2] 9, 1147); also Hartley a. Adeney (T. 1884 [i.] 118).

Historical.—Tin was known long before the

Christian era. Pliny distinguished plumbum album or candidum from plumbum nigrum; in the fourth century A.D. the former of these substances began to be called stannum, from which

word the symbol Sn is derived.

Occurrence.—Tin has been found in Siberia and in South Australia. Tinstone or cassiterite, consisting essentially of SnO₂, is found in considerable quantities, both in veins and in alluvial deposits, in many parts of the world. Tin pyrites, containing SnS₂ with Cu_sS, FeS, and ZnS, is found in small quantities in various tin veins. Small quantities of SnO, occur in various lithia-micas (Sandberger, J. M. 1878, 291, 657). According to Lockyer (Pr. 27, 279), there are indications of the occurrence of tin in the sun.

Formation .- 1. By ppn. from solution of SnCl, in HClAq by tin; or by tin and iron simultaneously, with a little Fe₂O₃ to neutralise excess of acid (Schultze, B. 23,974).—2. By electrolysis of SnCl, in dilute HClAq. -3. By reduction of

SnO, by heating with C.

Preparation.—Tinstone is cleansed by agitation with water; it is then sorted, stamped or rolled to a certain fineness, and washed. The washed ore is calcined in reverberatory calciners to remove sulphur from the sulphides of Fe that are present in most tin ores; the calcined ore is exposed to the air for some days to insure the oxidation of any sulphides that remain in the ore to sulphates, and it is then washed in water, whereby sulphates of Fe, Cu, &c., dissolve and the tin oxide sinks to the bottom of the vessels. The tin oxide is then separated into lighter and heavier parts by agitation with water; the heavier parts are mixed with charcoal or anthracite, some lime or fluorspar is added as a flux, and the mixture is smelted in a reverberatory furnace. The product of the smelting is purified by melting, when the tin runs off, leaving the less fusible foreign metals behind; this purified tin is again melted, the mosten mass is stirred with billets of green wood for some hours, and is then allowed to partially solidify by cooling, when the metal separates into different strata, which are ladled into moulds: the upper stratum is the purest and the undermost is the least pure. Sometimes the smelting is conducted in a blast furnace. For details v. Tin in Dictionary of Applied Chemistry, vol. iii. p. 834.

Commercial tin generally contains small quantities of As, Ou, Fe, and Pb, and occasionally traces of Sb, Bi, Mn, Mo, W, and Zn. To prepare pure tin, the purest commercial metal is granulated and disapland in commercial. fated and dissolved in conc. HClAq; a little water is very slowly poured into the liquid so as to form two layers, and a plate of tin is placed in the liquid so that part of it is in the upper (less cone.) and part in the under (more cone.) layer. A slight electric current is thus produced,

and crystals of pure tin are deposited on the plate (Hiller, A. 85, 253).

Pure tin was prepared by Bongartz a. Classen (B. 21, 2903) by heating the purest commercial tin (Banca tin) in dry Cl and so forming SnCl., distilling fractionally, and collecting that which passed over at 120°, adding to the SnCl, about four times its volume of water, and then crys. tallised Na,S until the pp. of SnS, that formed was dissolved, then adding NaOHAq about equal to half the quantity of Na S used, allowing to stand for some days, drawing off the clear, almost perfectly colourless liquid into a Pt basin, and passing an electric current through this alkaline liquid, washing the ppd. tin with water, then with absolute alcohol, and drying at 100°. The current was arranged so that it produced c. 2 to 3 c.c. detonating gas per minute from water: c. 2 to 3 g. tin were obtained in 24 hours.

Properties .- Pure tin is a silver-white metal; the commercial metal generally has a slightly yellowish tinge. It is unchanged in pure air; but it tarnishes in the air of large towns from formation of a film of sulphide. Tin is one of the least tenacious metals; a wire 1.6 mm. diameter breaks with a weight of c. 14 kilos. Tin may be hammered into plates c. 0254 mm. thick; the malleability varies much with temperature, at 200° the metal is so brittle that it crumbles when hammereli. Tin readily crystallises; by fusing, allowing to cool partially, and pouring out the still fluid metal, fair-sized crystals are obtained. Crystals are formed by depositing tin by electrolysis. Stolba (J. 1873. 282) covers the outside of a Pt basin, all except a small portion, with wax, places the unwaxed surface of the basin on a plate of amalgamated zinc in a larger porcelain basin, fills the Pt basin with a dilute and not very acid solution of SnCl2 and the porcelain basin with water containing c. $\frac{1}{20}$ part of HClAq; crystals of tin deposit on the bottom of the Pt basin. The forms of the crystals of tin are probably rhombic and quadratic (von Foullon, J. M. 1885 (11) Ref. 266). According to Frankenheim (P. 40, 456), the crystals belong to the regular system; Miller (B. J. 24, 133) obtained quadratic prisms by separating tin by electrolysis. If a piece of tin is brushed over with warm, dilute aqua regia, or with a mixture of warm dilute H₂SO₄Aq and HNO₄Aq, the surface becomes covered with a fretwork of orystals, from the facets of which light is unequally reflected, and the surface appears like watered silk. When a bar of tin is bent a crackling sound may be heard due to the crystals in the inner parts of the bar breaking against one another. When warmed, tin has a characteristic smell.

By exposure for some time to a very low by exposure for some time to a very low temperature (c. -98°) tin crumbles to a grey powder (v. Fritzsche, B. 2, 112, 540); S.G. c. 5·8 to 6·1 (v. Schertel, J. pr. [2] 19, 322). Tin which had been kept for 300 to 400 years was found by Schertel (i.c.) to have become reddishgrey, and so brittle that it was crushed by pressure between the finger-nails; by immersion in boiling water the metal became more coherent and lighter in colour, and the S.G. increased to 7.3 (cf. Oudemanns, P. M. [5] 4, 470).

Tin remains lustrous in pure air at the

ordinary temperature, and also in water; a

greyish-white film of SnO, forms on the surface of tin kept molten in the air; when heated to whiteness in air the metal burns brightly to SnO,. Tin dissolves in HOlAq, forming SnCl, solution; dilute H.SO, Aq has only a slight action, cone. hot H.SO, produces SnSO, and SO,; dilute HNO,Aq dissolves tin, with formation of Sn(NO,)Aq and NH,NO,Aq, cone. HNO, transforms the metal into SnO,. Tin dissolves in hot cone. NaOHAq, forming Na,SnO, solution and giving off H.

When haloid compounds of tin are volatilized in a stream of H and the gas is ignited, the fame shows two cones; the inner cone is blue with SnCl₂, green with SnBr₂, and yellow with SnL₃, and gives a continuous spectrum; the outer cone is carmine-red, and gives a spectrum with two characteristic lines (Salet, C. J. [2] 9,

1147).

Tin is metallic physically, and in most of its chemical relations. The oxide SnO₂ interacts towards several acids as a basic oxide, forming salts SnZ₂ (X = SO₄, &c.); but with conc. KOHAQ or NaOHAQ this oxide reacts as an acidic oxide, forming salts M₂SnO₂. Tin is the third member of the odd-series family of Group IV. in the periodic classification of the elements; it is closely allied to Go and Pb, and less closely to Si; it shows very marked analogies with Ti, Zr, Ce, and Th, which (with C) form the even-series family of Group IV. For details of the chemical relations of tin v. Tin group of elements, this yol. p. 735.

vol. p. 735.

The atom of tin is divalent in the gaseous molecule SnCl, and tetravalent in the gaseous

molecule SnCl.

Supposed allotropic form of tin. The grey brittle powder formed by the action of great cold on tin, and also found in some very old specimens of the metal, is sometimes regarded as an allotropic variety of tin (v. supra). All the specimens of tin, however, which have been observed to undergo this change have contained small quantities of impurities; until the change has been effected with pure tin, and has been proved to occur without any change of mass, the existence of an allotropic variety of tin cannot be said to be established. According to von Foullon (J. M. 1885 [1] Ref. 266) there are three varieties of tin: (1) rhombic, S.G. 6:52 to 6:56; (2) quadratic, S.G. 7:196; (3) grey wittle tin, S.G. 5-781 to 5:809.

Atomic weight of tin. The at. w. has been determined (1) by oxidising Sn to SnO, by HNO, (Gay-Lussac, A. Ch. [2] 80, 163 [1812]; Berzelius, P. 8, 184 [1812]; Mulder, A. 72, 212 [1849]; Vlaanderen, B. J. 1858. 183 [1858]; Dumas, A. Ch. (3] 55, 134 [1859]; van der Plaats, C. R. 100, 52 [1885]; Bongartz a. Classen, B. 21, 2900 [1888]); (2) by ppg. Cl from SnCl, by AgNO,Aq (Dumas, A. Ch. (3) 55, 156 [1859]); (3) by electrolysing SnCl, 2NH, Cl and SnOl, 2KCl (B. a. C., l.c.); (5) by reducing SnO, in H. (v. d. P., l.c. [1885]); (6) by determining S.H. of Sn (Bunsen, P. 141, 1 [1870]); (7) by determining V.D. of, and analysing, SnCl, and SnCl, The older determinations gave values from 115.9 to 117.8. The results of the determinations of B. a. C. are summarised by them (L.c., p. 2909) as follows:—

Number of experi- ments	Method	At weight	Diff. be- tween min. and max. found
11	oxidation of Sn to SnO.	118-7606	•459
16	electrolysis of SnCl, 2NH,Cl	118-8093	-228
10	electrolysis of SnCl2KCl	118-7975	·163
10	electrolysis of SnBr	118-7309	•144

B. a. C. regard the second and third methods as the most trustworthy; in the oxidation of Sn to SnO, the Pt vossel was also slightly acted on, and there was the possibility of a very small loss in dissolving SnBr, in the last method. The mean of the results obtained by the electrolysis of the two double chlorides is 118.8 (O=15-96).

Molecular weight of tin. As the V.D. of tin has not been determined the molecular weight is not known. Ramsay determined the depression of the vapour pressure of Hg caused by dissolving tin therein; assuming that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved bodies, and that the mol. w. of liquid Hg is 200, the results obtained by R. gave the mol. w. of tin as 117.4 in one experiment and 149.5° in another.

Reactions and Combinations.-1. When tin is heated in air or oxygen, a film is formed on the surface, containing both SnO and SnO.; when heated to whiteness tin burns brightly, forming SnO₂ (v. Emich, M. 14, 345).—2. Heated in chlorine, bromine, or iodine, the compounds SnX, and SnX, are formed, according to whether there is excess of tin or halogen. - 3. Tin combines with sulphur, and with selenion, to form SnS and SnSe, when heated with these elements. - 4. Tin probably combines with phosphorus when heated in vapour of that element.—5. Tin forms alloys with many metals (v. Tin, allovs or, p. 720).—6. Water is decomposed by tin at a full red heat with formation of SnO and H.—7. Sulphydric acid has a slight action on tin, in moist air, forming a film of SnS .- 8. Hydrochloric acid dissolves the metal, forming solution of SnCl, and giving off H; the reaction proceeds more rapidly with warm cone. HClAq. 9. Pure cone. nitric acid, S.G. c. 1 55, has no action on tin. When the acid is diluted the products of the reaction vary with the concentration and the temperature; according to Walker (C. J. 63, 845), both Sn(NO₂), and Sn(NO₂), are formed, the quantity of Sn(NO₂), increasing as concentration increases at a fixed temperature; with very dilute acid an increase of temperature causes only a slight increase in the quantity of the stannic salt, but the effect of temperature is very marked with more conc. acid; the pro-portion of stannous to stannic salt formed is only slightly affected by changing the relative masses of tin and acid; when a fairly cone. solution of tin in HNO, Aq is heated, hydrated stannic nitrates, varying in composition, are deposited (v. also Montemartini, G. 22, 384, 397, 426; abstract in C. J. 62, 1402; p. also Hay, C. N. 23, 298; Scott, C. N. 23, 822). Pure

HNO, diluted sufficiently to start the reaction produces chiefly SnO, xH,O (v. Hydrated stannic p. 725). When tin dissolves in HNO,Aq, NH,NO, is formed; the gases evolved are NO, N₂O, and N (v. Ackworth a. Armstrong, C. J. 82, 84),—10. A mixture of nitric and sulphurio oz, oz, —10. A macture of narro and supparto acids, or nitric and hydrochloric acids, produces NH₂OH along with NH₂ (Divers, C. J. 43, 443; D. a. Shimidzu, C. J. 47, 597; cf. Hydroxyl-AMINE, vol. ii. p. 734). With certain proportions of UNO Acids 150. tions of HNO, Aq and H, SO, Aq, Bassett (C. N. 53, 172) obtained Sn(NO₂), in solution, and almost pure N₂O.—11. Dilute sulphuric acid reacts slowly when warmed with tin, forming SnSO, if the tin is kept in excess, and chiefly Sn(SO₄)₂ if the acid is in excess, and giving off Corc. sulphuric acid reacts to form SnSO... or Sn(SO₄), according to the proportion of tin to acid, and evolves H₂S or SO₂, or both, accord-ing to the concentration of the acid and the temperature; with pure hot H₂SO₄, SO₂ is given off, and S separates (v. Calvert a. Johnson, C. J. [2] 4, 435; also Pattison Muir a. Robbs, C. N. 45, 69).—12. Aqua regia dissolves tin, forming SnCl.,-13. Tin reacts with mercuric chloride and bromide. When heated with these compounds. forming SnCl₂ or SnBr₂, and Hg.—14. With sulphurous chloride, SnCl₂ is formed, with production of much heat (Wöhler, A. 73, 374).— 15. Tin dissolves in warm conc. caustic potash, or soda, solution, forming M,SnO, and giving off H .- 16. Fusion with nitre forms K, SnQ.

Detection and Estimation.—H.S ppts. dark brown SnS from slightly acidified solutions of stannous salts; the pp. is soluble in warm yellow ammonium sulphide, forming (NH,), SnS, Aq, from which acids ppt. yellow SnS. AuCl.Aq produces a purple pp., a compound of Sn, Au, and O (v. Purple of Cassius, under Tin oxides and HYDRATED OXIDES, p. 727). H.S ppts. yellow SnS, from acidified solutions of stannic salts; the ppt. dissolves in warm yellow ammonium sulphide, and acids re-ppt. SnS, from this solution. Tin is generally estimated as SnO,.

Tin, alloys of. Tin forms alloys with many

metals. For a general account of the properties of different classes of tin alloys, v. DICTIONARY of Applied Chemistry, vol. iii. p. 837. For alloys of tin with antimony, v. Karmarsch (D. P. J. 123, 267); Kestner (Kast. Archiv, 19, 424); Johnson (Chem. Gazette, 1855. 180); Chaudet (A. Ch. [2] 3, 376); with bismuth and lead, and with bismuth, cadmium and lead, v. vol. i. p. 511; with cadmium, v. vol. i. p. 655; with cadmium and gold, v. Heycock a. Neville (C. J. 59, 936); with copper, v. vol. ii. p. 251 (also Dictionary of Applied Chemistry, vol. iii. p. 888); with copper and lead, v. vol. fii. p. 125 (also French, S. C. I. 8, 36); with iridium, plattnum, and rhodium, v. Deville a. Debray (C. R. 81, 889); with iron, v. vol. iii. p. 53 (also Headden, Am. S. [3] 44, 464); with gold, v. Laurie (P. M.[5] 35, 94); with lead, v. vol. iii. p. 125; with (P. M. [9] 55, 34]; with lead, v. vol. in p. 125; (also Wright a. Thompson, Pr. 45, 461; 48, 25); with mercury, v. infra; with platinum, v. vol. iv. p. 288; with silver, v. W. a. T. (Pr. 48, 25); with sodium, v. Bailey (C. N. 65, 18). Tin alloys with sive in all proportions; the alloys are harder than tin, but softer than mino; they are less

malleable than tin. Many varieties of bronze are alloys of tin with sinc and copper (v. Rudberg, P. 18, 240). Amalgams of tin are readily formed by immersing tin in Hg; the action is more rapid if the Hg is warmed (v. Böttger, J. pr. 1, 305; Joule, Chem. Gasette, 1850. 339, also C. J.

Tin, bromides of. Tin combines with Br to form two compounds, SnBr, and SnBr. The V.D. of the latter has been determined, and the formula SnBr, is molecular; from the analogy of the chlorides it is probable that the formula SnBr, is molecular also. Watts a Bell (C. J. 33, 442) obtained both SnBr, and SnBr, by heating SnO, in Br vapour mixed with CO.

STANNOUS BROMIDE SnBr., (Dibromide of tin.) Obtained by Balard (A. Ch. [2] 32, 337); more fully examined by Rayman a. Preis (A. 223, 323). Prepared by heating tin in HBr gas, allowing the oily liquid so obtained to cool, dissolving the crystals that form in dilute HBrAq, and purifying the solid that separates by distilling it in a stream of N. A crystalline, slightly yellow, transparent solid; melts at 215.5° to a transparent liquid, which solidifies at 215°. S.G. 5.117 at 17°. Carnelley a. Williams (C. J. 35, 563) say that SnBr, boils between 617° and 634°. Partly decomposed by water, with separation of an oxybromide of tin (R. a. P., l.c.). By crystallising a colution of tin in warm conc. HBrAq, R. a. P. (l.c.) obtained the hydrate SnBr_xxH₂O (x=1 or 2), in colourless needles. By cooling a mixture of NH₄Cl and solution of tin in warm conc. HBrAq, the compound SnBr₂.2NH₄Cl.H₂O was obtrined in large rhombic,

porcelain-like crystals (R. a. P., I.c.).

STANNIC BROMIDE SnBr., (Tetrabromide of tin.) Mol. w. 437.8. Melts at 30° (Carnelley a. O'Shea, C. J. 33, 55), at 33° (Rayman a. Preis, A. 223, 323). Boils at c. 201° (C. a. O'S., Lc.), at 203.3° (R. a. P., Lc.). S.G. 3.349 (R. a. P., Lc.). V.D. at 228°-260° = 227-230 (C. a. O'S., l.c.). V.D. at 228°-200° = 221-200 (c. l.c.). Prepared by passing vapour of Br over melted tin in a tube shaped thus

the tin being at b and the Br at a. The tin burns in the Br vapour; the product is distilled backwards and forwards from b to c until the distillate is quite colourless. On cooling the liquid solidifies to colourless. On cooling the liquid solidifies to colourless crystals of SnBr, (C. a. O'S., l.c.). R. a. P. (l.c.) prepared SnBr, by heating tin with Br, and crystallising from SnCl, or SnBr, Cl. SnBr, forms white crystals, which are slowly decomposed in the air; according to R. a. P. (l.c.) the crystals deliquesce to a clear liquid, which when placed over H.SO, deposits crystals of the hydract SnBr, 4H,O. SnBr, is soluble in cold water; after some hours SnO₂.xH₂O is deposited; boiling hastens this change; addition of HNO, Aq to hot SnBr, Aq ppts, all the tin as SnO_xxH,O, with evolution of a little Br (C. a. O'S., l.c.). R. a. P. (l.c.) found that SnBr, absorbs NH,; on heating some NH, was given off, and a yellow sublimate of SnBr, 2NH, was obtained. According to Nickles (C. R. 51, 869), SnBr, combines with ether to form SnBr. Et.O.

Stannibromhydric acid H.SnBr. xH.O. (Bromostannic acid.) This compound was obtained by Seubert (B. 20. 194) by adding 74.1 parts HBrAq (50 p.c. HBr)

to 100 parts SnBr. (i.e. in the ratio 2HBr:SnBr.). A vellow liquid was formed which solidified after a time to a mass of yellow, needle-shaped crystals; the small quantity of mother-liquor was removed by melting and allowing to solidify partially. It is doubtful whether the acid crystallises with 7 or 9H₂O. The acid forms amberyellow needles, probably triclinic; it is very deliquescent; fumes in air, giving off HBr. By adding Na₂CO₂ to H₂SnBr₆Aq, and allowing to evaporate, Seubert (L.c.) obtained sodium stanni-bromide, Na₂SnBr_e.6H₂O, in yellow needles. Several other stannibromides are described by Rayman a. Preis (A. 223, 323); their composition is MSnBr_xxH₂O, where M = (NH₂)_x B₄Ca, Fe, Mg, Mn, Ni, Na_x, Sr, and x is 6, 8, or 10.

Tin, bromochlorides of. Rayman a. Preis

(A. 223, 823) obtained a compound to which they gave the formula SnBr,Cl by heating tin in Br that contained some Cl, and repeatedly distilling. The compound is a liquid boiling between 181° and 190°. It dissolves SnBr, which crystallises out unchanged. By adding Br to excess of SnCl, Ladenburg (A. Supplbd. 8, 60) obtained indications of the formation of bromochlorides, probably SnBr, Cl and SnBrCl,

Tin, chlorides of. Tin and Cl combine to form two compounds, SnCl2 and SnCl4. Both

formulæ are molecular.

STANNOUS CHLORIDE SINCL. (Dichloride of tin. Tin-salt.) Mol. w. 189-54; perhaps 379-08 tin. Tin.sait.) Mol. w. 189:54; perhaps 379:08 (= Sn.Cl.) in the liquid state (v. infra). Melts at 249:3° (Carnelley a. Williams, C. J. 35, 63).
Boils between 617° and 628° (C. a. W., l.c.); at 606° (Biltz a. Meyer, V. P. C. 2, 184). V. D. v. infra. H.F. (Sn.Cl'] = 80,790; [Sn.Cl', Aq] = 81,140; [Sn.Cl', 2H²O] = 86,520 (Th. 3, 327). Preparation.—1. By heating a mixture of carel posts in filters and HeCl. 1 Me sublines.

equal parts tin filings and HgCl, Hg sublimes and leaves SnCl.—2. By heating tin in HCl gas.—3. By dissolving tin in warm, fairly conc. HClAq, evaporating to the crystallising point, drying the crystals of SnCl, 2H,O that separate, heating them in a capacious crucible so long as gases are given off, pouring the liquid into a small crucible, pounding when cold, and distilling from a retort; the first portions of the distillate are said to be pure SnCl₂ (Capitaine, J. 1th. 25, 552).

Properties.—A semi-transparent, white solid; melts at c. 250° and boils at incipient redness (v. supra). Heated to bright redness, out of air, some SnCl, is given off, then SnCl. Heated in air gives SnCl, and SnO2. SnCl, dissolves in a little water; the solution is decomposed by much dilution, with separation of a hydrated oxychloride SnCl. SnO.2H.O. According to Michael a. Kraft (A. Ch. [3] 41, 471), 1,000 c.c. saturated SnCl_Aq contains, at 15°, 1,333 g. SnCl_ and 494g, water, and the S.G. is 1*27. Gerlach (D. P. J. 186, 131) gives the following data for solution of the hydrate SnCl_2H_O:—

P.c.	S.G.	P.c.	8.G.
BnCi,.2H,O	of solution	SnCl_2H_O	of solution
5	1.0331	45	· 1·3850
10	1.0684	50	1.4451
. 15	1.1050	n 55	1.5106
20	1.1442	60	1.5823
25	1.1855	65	1.6598
4 80	1.2300	70	1.7452
. 85	1-2779	75	1.8399
40	1.3298	. 1	
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An aqueous solution of SnCl, generally becomes turbid from ppn. of Sn,OCl₂; digestion with tin and a little HClAq dissolves the pp.; addition of tartaric acid, or NH,Cl, stops the solution from becoming turbid the from the solution from becoming turbid the first basis. from becoming turbid, the former by dissolving the oxychlorise, the latter by forming a double salt SnCl. 2NH Cl, which is very soluble in water. Mallet (G. J. 35, 524) obtained a semi-trans-

parent, jelly-like solid from an aqueous solution of SnCl, which had stood in a loosely closed bottle for a year of two; the solid dried to a substance like gum arabic; it reddened litmus; the composition of the substance was SnO, HCl. Mallet writes the formula as SnO.OH.Cl, and suggests the name chlor-stannic acid.

Molecular weight of stannous chloride. V.D. of the gas obtained by heating SnCl, has been determined repeatedly. The following table presents the results :--

Calculated for SnCl. 94.7	Calculated for Sn _z Cl _z		Temp., and Observers	
96·5 90·1	103·7 104·5 101·5 123·7 123·7 122·9 119·5 111·4 102·7	?temp. 185-9 189-2	Rieth, B. 3, 668 [1870], at 619° V. a. C. Moyer, 1980° B. 12, 1195 [1879], 800° Meyer a. Züb-1980° Meyer a. Züb-1980° Meyer a. Züb-1980° Meyer a. Züb-1980° Meyer, Z. 760° P.C.2, 184 [1888], 1113° Meyer a. Z. 790° Meyer a. Z.	

From their determinations, Biltz a. Meyer concluded that molecules of the composition SngCl4 do not exist in the gaseous state, and that the mol. w. of the gas comes to a constant value. corresponding with the formula SnCl, only at a temperature very much above the b.p. of the liquid (SnCl, boils at 606°). In some of the earlier determinations at c. 800° partial decomposition occurred, with production of Cl. The results, taken as a whole, seem to be explained by assuming that the molecules of the liquid, near to the b.p., have the composition Sn₂Cl₄, that some of these are dissociated to 2SnCl₂ at c. 30° above the b.p., and that this process of dissociatica continues slowly, and is not completed at even 500° above the b.p.

Reactions.—1. Heated strongly in air, SnCl. is given off, and SnO2 remains. Heated to its b.p. in a retort, SnCl2 and SnCl4 distil, and the oxychloride Sn2OCl2 remains (Capitaine, J. Ph. 25, 552).-2. When sulphur is added to molten Solution the products are SnCl, and SnS; with selenion the products are SnCl, and SnSe (Schneider, P. 127, 624).—3. Many salts are reduced by SnCl2Aq, either to lower salts or to metals. Au, Hg, and Ag are ppd. from solutions of their salts; ferric and manganic safts are reduced to ferrous and manganous salts; CuCl.Aq to Cu2Cl2-4. The higher oxides of Bi, Cr. Ph. Mo, W, &c., are reduced to the lower oxides of these metals .- 5. Arsenious oxide is reduced to As by a considerable excess of SnCl_Aq. -6. Ac. cording to Böttger (Polytech. Noticol. 35, 96), a mixture of 2 pts. SnCl, rubbed with 1 pt. potassium chlorate gets hot, and produces an oxychloride of tin, KClO₄, oxide of chlorine, and H_O. For reactions with water v. supra, Properties; also infra, Combinations, No. 1.

-1. With water to form the hy-Combinations.—1. With water to form the hydrate SnCl₂.2H₂O. This compound is prepared by dissolving tin in warm cone. HClAq and evaporating to the crystallising point, in contact with tin to prevent formation of SnCl₂. SnCl₂.2H₂O, commonly known by the name of tin-salt, forms large white, monoclinic crystals (Marignac, J. 1856, 394); melts at c. 37.7°; S.G. 2.71 at 15.5° (solid), 2.588 at 37.7° (liquid) (Penny, C. J. 4, 239). H.F. [Sn,Cl;2H°0] = 86,520 (Th. 3, 327). When gradually heated to 100°, most of the water is removed; when rapidly heated, H.O and HCl are given off and Sn₂OCl₂ remains, which gives off SnCl₂ when more strongly heated. SnCl₂·2H₂O decomposes slowly on exposure to the air, forming Sn₀OCl₂ and SnCl₃.—2. With ammonia, forming SnCl₂NH₃.—3. According to Engel (C. R. 106, 1398), a compound of SnCl₂ with hydrogen chloride is formed by passing HCl gas over SnCl_2H_O at 0°; the liquid thus formed solidifies at 27°, forming crystals of SnCl_HCl_3H_O, which melt at 40°.—4. With chlorides of the alkali and alkaline earth metals, to form MCl, ShCl, XH.20, where M = (NH), 2, K₂, Ba, or Sr (v. Marignac, C. R. 55, 650; Rammelsberg, Krystall. Chemie, 211; Richardson, Am. 14, 89). Poggiale (C. R. 20, 1180) described a salt SnCl, 4NH, Cl.3H, O. Richardson (l.c.) obtained to the control of t táined SnCl₃.KCl.H₂O as well as SnCl₃.2KCl.2H₂O. These double salts are perhaps best regarded as stannochlorides, derived from the acid HSnCl. (v. Combinations, No. 3) and the hypothetical acid H2SnCl.

STANIO CHLORIDE SnCl., (Tetrachloride of tin.) Mol. w. 260-28. Boils at 113-9° at 760 mm. (Thorpe, C. J. 37, 372); at 114-1° at 760 mm. (Young, C. J. 59, 912). Solidifies at -33° (Besson, C. R. 109, 940). S.G. 6° 2·27875; 1·97813 at b.p. (Thorpe, l.c.). V.D. 133·1 at 124° (Dumas, A. Ch. [2] 33, 385). S.H. 1402 (10°-16°) (Regnault, A. Ch. [3] 9, 332). Heat of vaporisation = 30,530 (gram-units for 1 kilo.) (Andrews, C. J. 1, 27). H.F. [Sn,Cl·] = 127,250; [Sn,Cl·,Aq] = 157,170; [SnCl·,Cl·] = 46,460; [SnCl·,Aq,Cl·] = 76,030 (Th. 3, 327). C.E. (cubical, 0°-100°) 00130244 (Thorpe, l.c.). S.V. 131·07 (Thorpe, l.c.); for S.V. from 0° to 280° v. Young, C. J. 59, 933, 935). For vapour pressures from = 10° to 319° v. Young (l.c., p. 927). Critical temperature = 818-7°; critical pressure = 28080 mm. (Y., l.c., p. 928).

Formation.—1. By heating tin in excess, of Cl.—2. By heating 1 pt. tin filings intimately mixed with 4 or 5 pts. HgCl.1—3. By heating a mixture of Sn(SO₄), and NaCl.—4. By passing vapour of CCl. over heated SnO₂ (Watts a. Bell, C. J. 33, 442).—5. By adding fuming sulphurio acid to tin, and then passing in HCl gas and distilling (Heumann a. Köchlin, B. 15, 416).

Preparation.—Dry Cl is led over tin filings heated in a retort connected with a dry flask, which is kept cold; the distillate is distilled from tin filings, and then repeatedly redistilled in a current of dry CO. A solution of SnCl, is obtained by passing Cl into SnCl, Aq until no pp. is produced with HgCl, Aq, or by dis-

solving tin in dilute HClAq containing a little HNO.

Properties.—A thin, mobile, colourless, fuming, very corrosive liquid. Solidifies at -33° to small white crystals (Besson, C. R. 109, 940). SnCl, dissolves crystalline S, also P, I, Br, CS, &c. (Girardin, C. R. 51, 1057). SnCl, does not conduct electricity, even at its b.p.; addition of absolute alcohol forms crystals, probably (SnCl, 5EtOH), which conduct when dissolved; ether behaves similarly to alcohol (Coldridge, P. M. [5] 29, 383, 480). SnCl, withdraws moisture from the air, probably forming SnCl, 3H,O (v. infra, Hydrates of stannic chloride). SnCl, dissolves in water, with production of heat [SnCl, 4g] = 29,920 (Th. 3, 327), and considerable contraction of volume (v. also Reactions, No. 1). Gerlach (D. P. J. 178, 49) gives the following table:—

Pentge. SnCl.	S.G. SnCl ₄ Aq	Vol. of 100 pts. by wt. of solu- tion; vol. of 100 pts. water=100	Vol. of mixture of SnOl, and water; vol of sum of consti- tuents=100
0	1.000	100:00	100.00
10	1.082	92.42	97.82
20	1.174	85.18	95.76
30	1.279	78.19	93.72
40	1.404	71.12	91.42
50	1.556	64.26	88.78
60	1.743	57:37	85.81
70	1.973	50.68	82.63
100	2.234	44.76	100.00
	1	,	,

Hydrates of stannic chloride.—Various hydrates have been isolated: (1) SnCl.,3H.O. by exposing SnCl., to air (Casselmann, A. 83, 272); also by adding 18 pts. water to 260 pts. SnCl., when \$\frac{2}{2}\$ of the SnCl., remains unchanged, and \$\frac{1}{2}\$ forms the hydrate, which sinks in the excess of SnCl., (Gerlach, D. P. J. 178, 49); also by dissolving 260 pts. SnCl., in 54 pts. water, and letting the solution cool to 60° (C., l.c.); (2) SnCl.,2H.O. by keeping the trihydrate in vacuo (Scheurer-Kestner, C. R. 50, 50); also by drying the pentahydrate over H.SO. (Lewy, A. Ch. [3] 16, 303); (3) SnCl.,5H.O. by dissolving SnCl., conpletely in water and evaporating (G., l.c.; L., l.C.); (4) SnCl.,8H.O. by strongly cooling dilute SnCl.,4d (G., l.c.); (6) SnCl.,9H.O., obtained by Nöllner (Z. [2] 1, 445) by treating SnCl.,4d with aqua regia, and exposing the solution to a winter temperature. Gerlach (l.c.) gives a table (v. next page), showing the S.G. and percentage composition of solutions of the pentahydrate.

tion of solutions of the pentahydrate. Reactions.—1. With vater: SnOl, dissolves in water (v. supra) with production of much heat. Vignon (C. R. 108, 1049; 109, 372) found that H.SnO., ppd. from freshly prepared SnCl.Aq, from SnCl.Aq after keeping, and from SnCl.Aq after heating, showed markedly different heats of neutralisation by potash. He concluded that SnCl.Aq contains HClAq and H.SnO.Aq, and that the F.SnO, in solution gradually polymerises. Dilute SnCl.Aq gradually decomposes, giving HClAq and SnO.xH.O. Casselmann, A. 83, 272). Heating in a scaled tube with a little water is gaid to give SnO.x—2. With conc. neitric acid SnCl.4 forms SnO.xH.Q.—2. With conc. neitric acid SnCl.4 forms SnO.xH.Q.—3. Dry hydrogen sulphide forms white crystals of SnCl.5H.S., which gives off H.S and HCl when heated, and

Pontge. SnCl., 8H,0	S.G. of solu- tion at 15°	Pentge. SnCl ₄ .5H ₄ O	S.G. of solu- tion at 15°
0	1.000	48	1.347
i	1.006	49	1.357
2	1.012	50	1.3661
3	1.018	51	1.376
4	1.024	. 52	1.386
5	1.0298	53	1.396
6	1.036	54	1.406
7	1.042	55	1.4154
8	1.048	56	1.426
9	1.053	57	1.437
10	1.0593	58	1.447
11	1.066	59	1.458
12	1.072	60	1.4684
13	1.078	61	1.480
14	1.084	62	1.491
15	1.0905	63	1.503
16	1.097	64	1.514
17	1.104	65	1.5255 1.538
18	1.110	66	1.550
19	1·117 1·1236	67 68	1.563
20 21	1.130	69	1.575
21 22	1.130	70	1.5873
22 23	1.144	71	1.601
25 24	1.151	72	1.614
25	1.1581	73	1.627
26	1.165	74	1.641
27	1.173	75	1.6543
28	1.180	76	1.669
29	1.187	77	1.683
. 30	1.1947	78	1.698
31	1.202	79	1.712
32	1.210	80	1.7271
33	1.218	81	1.743
34	1.226	82	1.759
35	1.2338	83	1.775
36	1.242	84	1.791
37	1.250	85	1.8067
38	1.259	86	1.824
39	1.267	87	1.842
40	1.2755	88	1.859
41	1.284	89	1.876
42	1.293	90	1.8939
43	1.302	91	1·913 1·932
44	1.310	92	1.952
45	1.3193	93	1.969
46	1·329 1·338	95	1.9881
47	1.990	30	

leaves SnS₂ (Coldridge, P. M. [5] 29, 383, 480).--4. SnCl, dissolves stannous oxide, forming SnCl,

2. Short, dissolves statements of the control of Short, and a solution of ShO, HO in excess of ShOl, (Scheurer-Kestner, C. R. 50, 50).

Combinations.—1. With hydrogen chloride.

By passing dry HCl over ShOl, 5H,O, then saturation of the control o rating the liquid so formed with dry HCl at 28°, and cooling to 0°, Engel (C. R. 103, 213) obtained white crystalline leaflets of the compound SnCl. 2HCl.6H2O, melting at c. 20°, and giving off HCl when more strongly heated. The same compound was prepared by Seubert (B. 20, 793) by adding to SnCl, such a quantity of conc. HClAq that the ratio of water in the acid was to the SnCl, as 6H2O:SnCl, (100 pts. SnCl, require 62·15 pts. of 33 p.c. HClAq), and after a little passing in c. 8 pts. dry HCl; the whole then solidified to a crystalline mass, melting at 19.2°. This

compound is best called stannichlorhydric acid; it has also been called chlorostannic acid (Mallet gave the name chlor-stannic acid to SnO.OH.Cl, v. Stannous chloride, Properties, p. 721), and hydrochlorostannic acid. Chassevant (A. Ch. [6] 39, 5) has described a compound SnCl, HCl.3H.O.—2. With several metallic chlorides. The double salts of SnCl, and alkali and alkaline earth chlorides have the composition MSnCl₀.xH₂O, where M = (NH₄)₂, K₂, Na₂, Ba, Ca, Mg, or Sr; these selts are best named stannichlorides (for details, v. Bolley, A. 39, 101; Lewy, J. pr. 37, 479; Rammelsberg, Krystall. chemis; J. pr. 37, 479; Rammetsverg, Arystatt. Greens; Wittstein, R. P. 64, 74, Topsov, W. A. B. 69 [2] 261; Morel, G. G. 1891 [1] 492; Chassevant, A. Ch. [6] 30, 5). Cleve (Bt. [2] 31, 195) obtained double salts of the form rSnCl, 2MCl, 2H₂O, where M = Ce, Di, La, or Y, x = 2 and 5, and s had large values (from 18 to 45) . -- 3. With certain nonmetallic chlorides; the compound SnCl, 2SCl, is said to be obtained by the interaction of Cl and SnS (H. Rose, P. 44, 320; Casselmann, P. 42, 517); the compound SnCl, PCl, was obtained by Casselmann (l.c.) by heating a mixture of SnCl, 2SCl, and PCl, in a stream of HCl.— 4. With certain nonmetallic oxychlorides: (1) SnCl, POCl, formed by the reaction of POCl, and SnCl., POCl., formed by the reaction of POCl., and SnCl. (Casselmann, A. 91, 248; 98, 213); (2) SnCl., 2SeOCl., by combining the constituent compounds (Weber, B. B. 1865, 2154); (3) SnCl., 2NOCl., by passing the dry vapour from aqua regia over SnCl. (Hampe, A. 126, 43), also by, subliming SnCl., N.O., formed by the action of N.O. and NO. on SnCl. (Weber a. Hampe, P. 118, 471).—5. With hydrogen sulphide to form SnCl., 5H.S.; decomposed by heating to SnS₂, H.S., and HCl (Coldridge, P. M. [5] 29, 383).—6. With hydrogen canada. to form crystals that 6. With hydrogen cyanide, to form crystals that are decomposed in moist air (Rlein, A. 74, 85).
7. With ammonia, to form SnCl, 2NH, according to H. Rose (P. 24, 163), to form SnCl₄4NH₂ according to Grouvelle a. Persoz (A. Ch. [2] 44, 322) .- 8. With phosphorus trihydride, to form 3SnCl, 2PH, (H. Rose, P. 24, 159); heated to 100° in CO, there are formed HCl and Sn.P.Cl., according to Mahn (J. Z. 5, 160).—9. With certain nonnetallic oxides: (1) with SO₃ to form a solid [? composition] (H. Rose, P. 44, 320); (2) with NO a compound is formed, according to Kuhlmann (A. 39, 319), but no action occurs according to Hampe (A. 126, 43); (3) with N2Os to form STALLING (2.1.20), 20], (c) with 1303 to 10 ml SIG, 10.0, produced by passing NO₂ and N₂O over SnCl, (Hampe, l.c.).—10. With ethylic alcohol, to form SnCl, 5£tOH (Coldridge, P. M. [5] 29, 383, 480).—11. With amylic alcohol, to form SnCl, 2C,H₁₁(OH) (Bauer a. Klein, Z. [2] 4, 370) 19. With other to form SnCl, 24th C[Coldridge 12. With ether, to form SnCl, 2Et,O (Coldridge, l.c.) .- 13. With various nitriles, forming crystallisable compounds (Lewy, C. R. 21, 371).

Tin, chlorobromides of, v. TIN BROMOCHLOR-IDES, p. 721.

Tin, chloro-iodide of; v. TIN IODOCHLORIDE. y. 724.

Tin, chlorosulphide of; v. Tin THIOCHLORIDE, p. 733).

Tin, ferricyanides of; v. vol. ii. p. 840.

Tin, ferrocyanides of; v. vol. ii. p. 337.

Tin, fluorides of. Only one fluoride, SnF., has been isolated; double salts of stannic fluoride (SnF.) are known.

STANDOUS FLUORIDE SnF. (Diffuoride of tin.) Formed, in small opaque, lustrous, prisms, by dissolving SnO.xH.O in HFAq, and evaporating; heated in air it forms the oxythoroide SnOF₅(= SnF₄,SnO₂) (Marignac, Ann. M. [5],15, 221; Fremy, A. Ch. [3] 47, 37). By dissolving treshly ppd. SnO.zH₂O in solutions of alkali fluorides acidified by HFAq, Wagner (B. 19, 896) obtained stannofluorides of the form xSnF, 2MF, yH₂O, where x = 1 and 3, y = 1 and 2, and M was NH₄, K, and Na.

STANNIC FLUORIDE. This compound has not been isolated; a solution of SnO₂.xH₂O in HFAq coagulates when heated, but does not yield any definite compound; when evaporated in air HF is given off, and an oxyfluoride, SnOF, is depo-

sited (Marignac, l.c.).

Stannifluorides. A series of these salts, MSnF_e.xH₂O, where M = one atom of a divalent metal or two atoms of a monovalent metal, has been obtained by Marignac (Ann. M. [5] 15, The salts are isomorphous with the corresponding silicofluorides and titanifluorides; they are generally obtained by saturating the stannates with HFAq and evaporating, some are formed by double decomposition from the Pb or Ag salt. The following salts have been obtained: $MSnF_{\bullet}.xH_{\nu}O$; $M = NH_{\bullet}$, Ba, Cdx = 6, Cax = 2, Cu x = 4, Pb x = 3, Li x = 2, Mg x = 6, Mn x = 6, Ni x = 6, Ka x = 1, Ag x = 4, Na, Sr x = 2, Zn x = 6.

Tin, haloid compounds of. Tin and the halogens combine to form two series of compounds, SnX₂ and SnX₄ (SnF₄ has not been isolated). The V.D.s of SnCl₂, SnCl₄, and SnBr₄ have been determined; it is probable that the simplest formula in every case is molecular. One or two compounds of the forms SnXX' and SnXX, are known, where X and X' are different halogens. A few oxyhaloid compounds are known, and probably also one or two thiohaloid compounds. The compounds. SnBr, and SnCl, combine with HBr and HCl respectively, forming acids H₂SnBr_e and H₂SnCl_e, from which series of salts, stannibromides and stannichlorides, are derived; stannifluorides are also known. An acid HSnCl, has also been isolated, and a few stannochlorides-MISnCl, and M'snCl,-are known, as also some stanno-

Tin, hydrosulphide of. The compound SnS₂H₂, which has probably been isolated, may be called hydrosulphide of tin (v. Tin, Juno-

ACIDS AND SALTS OF, p. 733).

Tin, hydroxides of, v. Tin oxides and hy-DRATED OXIDES, p. 725; also TIN OXYACIDS AND

SALTS, p. 727.

Tin, hydroxyl chloride of, SnO.OH.Cl, v. Chlor-stannic acid, under STANNOUS CHLORIDE.

Properties, p. 721.
Tin, iodides of. Two compounds are formed by combining tin and I; they correspond in composition with the two bromides and the two chlorides. The V.D.s of the iodides have not been determined, but the simplest formulæ afe probably molecular.

STANNOUS IODIDE SnI₂. (Di-iodide of tin.) Formula probably molecular.

Preparation.—1. Tin and I are heated to-gether in the ratio Sn:2I (1 pt. tin to 2:14 pts. I); the brown crystalline solid so formed (a mixture of SnI, and SnI,) is mixed with tin

filings and heated, when orange-red-SnI, sub. limes, and SnI, remains as a red crystalline solid mixed with particles of tin which are easily separated (Henry, T. 1845. 363).—2. Conc. KIAq is added to warm conc. SnCl.Aq; the yellow crystalline pp. is dried and melted, out of contact with air, and a red crystalline mass of SnI, is formed on cooling (Boullay, A. Ch. [2] 34, 372).-3. Tin foil is heated for some hours with fairly conc. HIAq in a sealed tube at 1200-150° (Wöhler a. Dünhaupt, A. 86, 374); SnI, separates, on cooling, in shining yellow-red prisms

Properties and Reactions.—A red, crystalline solid. Melts at 316° (Carnellan a William) Melts at 316° (Carnelley a. Williams, C. J. 35, 564). Slightly soluble in cold, more soluble in hot, water, without decomposition (Boullay, l.c.). According to Personne (C. R. 54, 216), SnL is decomposed by a large quantity of water, forming HIAq and several oxyiodides (q. v.). SnI₂ is soluble in SnCl₂Aq. When heated out of contact with air, SnI₂ melts without decomposition, but when heated in the air it is decomposed to an oxylodide, which remains

in the vessel, and SnI, which sublimes.

Combinations.—1. With stannous chloride to form SnI, SnCl, (v. Iodochloride, infra).—2. With stannous ozide to form several oxyiodides (q. v.).— 3. With annonia, probably forming SnI₂2NH₄ (Rammelsberg, P. 48, 169).—4. With alkali iodides and with iodides of the alkaline earth metals to form stanno-iodides: these salts have the composition M.SnI4.xH2O and MSnI, xH,O, corresponding with the stanno-chlorides (v. Stannous chloride, Combinations, p. 722); $M = NH_4$, K, Na, also $\frac{1}{3}Ba$ and $\frac{1}{2}Sr$. The stanno-iodides are formed by mixing solutions of the constitutent salts, or by adding SnCl.Aq to excess of the alkaline fodide in solution; the salts must be crystallised from alcohol, as they are decomposed by water, forming stannous oxyiodides (v. Boullay, l.c.; Personne, l.c.).

STANNIC IODIDE SnI, (Tetra-iodide of tin.) Formula probably molecular. This compound is probably formed by heating tin with 4.2 pts. I, and subliming from the product (Henry, T. 1845. 363). Schneider (P. 127, 624) recommends to add 6 pts. CS₂ to 1 pt. tin filings, and then to add gradually, cooling frequently, 4 pts. I.

and to allow the yellow liquid to evaporate.

Sul crystallises in orange-red octahedra;
melts at 146°, sublimes at 180°, and boils at 295°
(Personne, C. R. 54, 216). S.G. 4.696 at 11° (Bödeker, Die Beziehungen zwischen Dichten Locater, Diction of Secretary of the Secretary Liquiden Stoffen [Leipzig, 1860]). Solubility in CS₂ at 15°=145 (Schneider, Lc.); it is also soluble in CHCl₄, EtOH, Et₂O, and C₆H₆. Decomposed by water to SnO₂xH₆O and HIAq. Combines with ammonia to form SnI₄xNH₂, where x = 3, 4, and Chemical Stoffens and Chemical Stoffens SnI₄xNH₂, where x = 3, 4, and Chemical Stoffens SnI₄xNH₂. 6 (Personne, *l.c.*), also = 8 (Rammelsberg, *P.* 48, 169). SnI₄ is said not to combine with alkali

iodides.

Tin, iodochloride of, SnICl (= SnI, SnCl). According to Henry (T. 1845, 363) the addition of I to conc. SnCl,Aq causes ppn. of SnI, and on evaporating the mother-liquor (which contains SnCl₃, SnCl₄, and Snl₂) straw-yellow orgatals are deposited that have the composition Snl₂SnCl₃. The crystals are decomposed by water, with separation of Snl₂. Tin, iodosulphide of, v. TIN THIO-IODIDE, p.

Tin, oxides and hydrated oxides of. . oxides have been isolated, SnO and SnO2; various compounds of these oxides with H.O seem to exist, but their composition readily undergoes change with variation of temperature. Both oxides interact with acids to form corresponding salts, SnX_2 and SnX_4 , where $X = NO_3$, \$SO4, \$PO4, &c. Some of the hydrates of SnO. also react as weak acids, especially SnO...H.O (=H₂SnO₃), from which is derived a series of stannates $MSnO_3$, $M = Na_2$, Ca, Pb, &c.; and $xSnO_2$. xH_2O (= xH_2SnO_3), x probably = 5, from which a series of metastannates, xMSnO_s is derived. Stannic and metastannic acids and salts derived from them are described under the heading Tin oxyacids and salts and derivatives тневеог (р. 727). The oxides SnO and SnO, are described in this section of the article Tin, and a brief account is also given of the experiments on the hydrates of these oxides other than stannic and metastannic acids.

When tin is strongly heated in air or oxygen a film forms on the surface consisting of SnO and SnO2; at a full red heat, or incipient white heat, tin burns to SnO... According to Vignon (C. R. 107, 734), tin ppd. by zinc from neutral SnCl,Aq or SnCl,Aq oxidises easily in air; after being exposed to the air for some days it contains from 20 to 33 p.c. SnO. Emich (M. 14, 345) found that the surface of tin that was kept molten in the air became covered with crystal-

line nodules of SnO₂.

STANNOUS OXIDE SnO. (Protoxide of tin.) Mol. w. not known.

Formation.—1. By heating finely-divided tin in the air; the metal becomes covered with a film of SnO (Vignon, C. R. 108, 96). Also by exposing tin ppd. by zinc from SnCl2Aq or SnCl4Aq to the air at ordinary temperatures (V., C. R. 107, 734).—2. By dehydrating SnO.xH₂O, ppd. from SnCl2Aq by alkali carbonates, either by heating in a stream of CO2, or by boiling with water containing a little KOH .- 3. By dissolving SnO.xH₂O in cold KOHAq, and allowing the solution to stand in the air (Ditte, A. Ch. [5] 27, 145).—4. By heating SnC₂O₄ in a tube of hard glass without free access of air (Liebig, A 495, 116) .- 5. By ppg. a stannous salt by KCNAq, and boiling the pp. for some days with KCNAq (Varenne, C. R. 89, 360).

Preparation. - SnCl_Aq is ppd. by Na_CO_Aq, the white pp. of SnO.H.O is thoroughly washed with cold water, and is then boiled with water containing a little KOHAq or NaOHAq (less than sufficient to dissolve the pp.), when the SnO.xH₂O is gradually dehydrated, and small black, lustrous crystals of SnO are obtained (Fremy, A. Ch. [3] 12, 460).-2. Tin is dissolved in warm HClAq, the solution is evaporated, in contact with tin, until it solidifies to SnCl2 on cooling; 7 parts, or rather more, Na₂CO₂.10H₂O are then added for each part of SnCl, in the . basin, and the liquid thus formed is heated with constant stirring until # becomes black, and is then allowed to cool; the brownish-black powder, SnO, thus obtained is thoroughly washed with cold water, and dried at 100° (Sandall, J. pr. 14, 254).—3. A solution of SnCl, is ppd. by a slight excess of KOHAq in the cold, the pp. is thoroughly washed and dissolved in cold KOHAa (c. 1 part KOH in 10 parts HO); the solution, which should be saturated with SnO.xH.O, is allowed to stand in the air, when SnO is gradually ppd. as small, blue-black, shining crystals (Ditte, A. Ch/[5] 27, 145).

Properties and Reactions.—Prepared by any of the methods described above, SnO forms small, black, lustrous, regular crystals (for crystalline form v. Nordenskjöld, P. 114, 612). S.G. 6:1 (N., l.c.); 6 6 at 0° (Botzelius; Ditte, A. Ch. [5] 27,

According to Fremy (A. Ch. [3] 12, 460), another modification of SnO is obtained by heating the black crystals (prepared by the first process given above) to 258°; the crystals are said to swell up and change into soft, olive-green laminæ, without any change in weight.

By evaporating very dilute NH ClAq, holding SnO.xH₂O in suspension, until NH₄Cl began to crystallise, Fremy (A. Ch. [3] 12, 460) obtained a cinnabar-red powder, which he took to be a third form of SnO. Retli (A. 60, 214) obtained red, crystalline SnO by digesting SnO.xH2O, at 56°, with a solution of SnO.xH2O in acetic acid; the solution containing a little free acetic acid, and having S.G. 1.06.

For the S.G. and appearance of SnO prepared

in various ways v. also Ditte (l.c.).

SnO is unchanged in air at ordinary temperatures. According to Ditte (A. Ch. [5] 27, 145), SnO that separates from an alkaline solution is unchanged at 300°-310°; when heated to redness it is partly decomposed to Sn, and SnO2 which combines with unchanged SnO to give 2SnO.SnO₂. SnO is readily converted into SnO₂ by heating with oxidising agents; the change is effected by heating to 500° in NO (Sabatier a. Senderens, C. R. 114, 1429). SnO dissolves in acids to form stannous salts, SnX2, X = NO3, ½SO4, ½PO4, &c.; it is not acted on by NHAq; boiled with fairly conc. KOHAq or NaOHAq it. gives a solution of an alkali stannate (M2SnO2) and tin; heated in Cl forms SnCl, and SnO2; mixed with S and strongly heated, SnS2 and SO2 are produced; SnO is reduced to tin by heating to redness in H or with C.

HYDRATED STANNOUS OXIDE. The white pp. formed by adding an alkali carbonate to solution of a stannous salt, washing with air-free cold water, and drying at a temperature not above 80°, is said to have the composition 2SnO.H.O = Sn.O(OH)... According to Ditte (A. Ch. [5] 27, 145) the pp. formed by adding KOHAq or NaOHAq to SnCl.Aq, washing thoroughly, and drying in vacuo at 14° is $S_{11}O.2H_2Q(=S_{11}O_2H_2H_2O)$. Stannous hydroxide is a yellowish white amorphous powder. It is dehydrated, to SnO, by heating in CO₂; also by the action of boiling water containing a little KOH, or a trace of HCl, or acetic acid—HNO.Aq and H.SO.Aq form stannous salts; also by boiling with NH.ClAq (Ditte, l.c.). The hydroxide is gradually oxidised by exposure to air to SnO₂.xH₂O. Boiled with conc. KOHAq it gives K2SnO3Aq and tin. Many metallic salts are reduced, to lower salts or to the metals, by the action of SnO.xH2O (for details of the interaction with CuO in presence of alkali v. Lenssen. J. pr. 89, 90).

STANNIC OXIDE SnO2. (Dioxide of tin.) Mol.

w. unknown: probably at least Sn, 0, 0, (v. Carnelley a. Walker, C. J. 53, 92). Occurrence.—Tinstone is more or less pure

Occurrence.—Tinstone is more or less pure SnO₂; the percentage of the oxide varies from c. 85 to c. 99, the other constituents are generally SiO₂, and oxides of Al, Fe, and Mn. Tinstone crystallises in quadratic forms. Crystalline SnO₂ has been found in the fused slag from a turnace used for casting gun-metal (Abel, C. J. 10, 119).

Fornation.—1. By expo.ing molten tin to the action of the air (Emich, M. 14, 345).—2. By heating to c. 600° SnO_xxH₂O formed by the interaction of tin and HNO_xAq, or of alkalis and stannic salts, or of alkali stannates and dilute acids.—3. By strongly heating SnO or SnO_xxH₂O.—4. By passing a mixture of vapour of SnO_xA, and steam through a rod-hot tube.—5. By heating SnC_xO_x, in small quantities, in contact with the air (Vogel, C. C. 1855. 413).—

6. By passing a little CO, into a dilute solution

of an alkali stannate (Ditte, A. Ch. [6] 30, 282). Preparation.—A. Crystallin—stannic oxide.—I. Molten tin is kept in contact with the air until the surface becomes covered with crystalline nodules of SnO₂ (Emich, M. 14, 345). 2. A stream of CO₂ is passed through SnCl, and then through a red-hot porcelain tube through which a current of steam is passed at the same time (Daubrée, C. R. 29, 227).—3. Amorphous SnO₂ is strongly heated in a rapid current of dry HCl (Deville, C. R. 53, 161).—4. SnC₂O₄ is strongly heated, in small quantities at a time, in an open

porcelain or silver dish (Vogel, C. C. 1855, 418).

B. Amorphous stannic oxide.—5. The hydrated stannic oxide obtained by ppg. a stannic salt by an alkali, decomposing an alkali stannate solution by dilute acid, or by treating tin with HNO₂Aq, is thoroughly washed and dried, and then heated to c. 630°, at which temperature dehydration is complete (Carnelley a. Walker, C. J. 53, 83).

Properties.—Crystalline stannic oxide is a hard, lustrous, white solid. It is dimorphous. Prepared by heating the amorphous oxide in HCl gas, SnO₂ crystallises in quadratic forms isomorphous with tinstone and anatase (TiO₂) (Daubrée, C. R. 29, 227); prepared by decomposing vapour of SnCl₄ by steam, it crystallises in trimetric prisms isomorphous with brookite (TiO₂). S.G. of crystalline SnO₂=6.7 to 6.85 (Playfair a. Joule, C. J. 1, 137; Mallet, J. 3, 705; Bergemann, J. 10, 661; Daubrée, C. R. 29, 227). The crystalls obtained by long continued heating molten tin in air had S.G. 7.0096 at 4° (Emick, M. 14, 345). Crystalline SnO₂ is hard enough to scratch glass. The amorphous oxide has S.G. 6.6 to 6.9 (P. a. J., Lc.; Herapath, P. M. 64, 321; Boullay, M. Ch. [2] 43, 266). It is a bard, yellowish-white powder. SnO₂ has not been fused. It is not acted on by acids (but v. Reactions, No. 6). Fusion with KOH or NaOH forms, SnO₂ which dissolves in water. The product of fusion with KHSO₄ dissolves in water, but addition of more water ppts. all the tin as SnO₋₋ MLO.

all the tin as SnO_xxH_zO.

Mailet (O. J. 85, 524) obtained a compound SnO_xHO₁, to which he gave the formula SnO.OH.Cl, and the name chlor-stannic acid, by keeping SnO₁ for a year or two in a loosely slosed bottle.

Reactions.—1. Fusion with sulphur produces SnS₂ and SO₂.—2. When strongly heated it chlorine SnCl₂ is formed.—3. SnO₂ is reduced to tin by heating to a high temperature in hydrogen, or with polassium, sodium, or carbon, or in carbonic oxide.—4. Fusion with caustic polash or caustic soda forms alkali stannate (M₂SnO₂), which dissolves in water.—5. Heating with phosphorus trichloridate 160° forms SnCl₂, SnO₁, and P₂O₂ (Michaelis, J. Z. 6, 239; 7, 110).—6. According to Ditte (C. R. 104, 172), SnO₂ dissolves very slowly in hot sulphuric acid (1 acid to 8 water), and on concentrating till not more than 3 or 4 vols. water are present to 1 vol. H₂SO₄ crystals of SnO₂.2H₂SO₄ separate.

Hydrated stannic oxide. Carnelley a. Walker (C. J. 53, 60, 68, 83) examined the dehydrating action of heat on SnO2.xH2O, obtained by decomposing Na SnO Aq by cold dilute HClAq and drying the pp. in the air for five months. The pp. lost less and less weight for each increase of c. 10° from 50° to c. 110°, at which temperature rather less water was present than corresponded with the formula SnO2.H2O, the loss of weight for each rise of 10° was then approximately constant up to c. 360°, at which temperature the composition was nearly that required by the formula 3SnO...H.O; at a little above 360° the solid changed colour from brown to pale yellow, and at the same time lost weight at a rate nearly three times as great as during the previous rise of 100°; after changing colour the solid had the composition 7SnO2.2H2O; the loss of weight, per 10° increase, then decreased very much for the next 30° or 40°, and after that dehydration continued irregularly until at 630°-635° the oxide SnO₂ remained. From these results, considered with results obtained by the same method for other hydrated oxides, C. a. W. concluded that probably a large number of hydrates of SnO, exists, but that none of these is stable through more than a very small range of temperature. The results of J. van Bemmelen (B. 13, 1466) on the dehydration by heat of stannic hydrates, obtained by oxidising tin by HNO, Aq, and by decomposing SnCl, Aq by CaCO,, and on the rehydration of the products obtained by heat, by placing them in air more or less saturated with mçisture, at different temperatures, show that the quantity of water of hydration varies with variations in température, in the molecular states of the solids, and in the moistness of the surrounding air. Not only does the quantity of water of hydration vary with variations in the molecular state of the hydrates, but the firmness or looseness wherewith the water is held also varies much as the molecular condition varies. According to J. van B. the loosely held water is given up in dry air; and when the product is placed in moist air water is taken up until a state of equilibrium is attained wherein as many molecules of water are taken up as are lost in the unit of time.

The following compositions have been given to different hydrates of SnO₂.

I. Hydrates obtaines by decomposing soluble stannates by dilute acids: (1) 3\$nO₂.7H₂O, by drying in a stream of dry air (Fremy, A. Ch. [3] 12, 462); (2) \$nO₂.2H₂O, by drying in the air at the ordinary temperature (Weber, P. 122, 358); (3) \$nO₂.H₂O, by drying in vacuo (Fremy,

l.c.); (4) 8SnO₂2H₂O, by drying at 140° (Fremy, l.c.); to these should probably be added (5) 7SnO₂2H₂O, by drying at c. 365° (Carnelley a.

7SnO_x2H_xO, by drying at 0.365° (Carnelley a. Walker, l.c.).

II. Hydrates obtained by oxidising tin by HNO_xAq: (6) 5SnO_x10H_xO, by drying at the ordinary temperature (Fremy, l.c.); (7) 5SnO_x6H_xO, by drying at the ordinary temperature (Thomson, Ann. Phil. 1817. 149), by drying over H_xSO_x (Weber, l.c.), by drying in vacuo, or at 100° (Fremy, l.c.); (8) 5SnO_x4H_xO, by drying at 130° (Fremy, l.c.); (9) 5SnO_x3H_xO, by drying at 150° (Fremy, l.c.); (10) 2SnO_xH_xO, by drying at 55° (Thomson, l.c.). by drying at 55° (Thomson, l.c.).

The hydrates obtained by decomposing stannates by dilute acids, or by ppg. stannic salts by CaCO, or BaCO, differ in properties from the hydrates obtained by oxidising tin by HNO, Aq; the former are generally distinguished as stannic hydrates, and the latter as metastannic hydrates. The stannic hydrates, dried in air, form hard, semi-transparent lumps, like gum arabic; soluble in the stronger acids, forming stannic salts SnX₄, where X=NO₃, ½SO₄, &c.; soluble in alkali solutions, forming stannates M¹₂SnO₃ (v. Stannates, under TIN ONYACIDS, AND SALTS AND DERIVATIVES THEREOF, infra). Metastannic hydrates are white solids (? crystalline) that do not dissolve in HNO₃Aq, or H.SO₄Aq (v. infra). These hydrates interact with HClAq, and the product is soluble in water but insoluble in conc. HClAq; according to Weber (P. 122, 358), the solution gives SnCl, 3SnO, 5H,O, when evaporated over H₂SO,; by prolonged boiling, with fresh additions of water, all the tin in the solution is ppd. as metastannic hydrate (Fremy, A. Ch. [3] 12, 463; 23, 393). Metastannic hydrates dissolve in KOHAq and NaOHAq, forming metastannates M₂H₂Sn₃O₁₅ (v. Metastannates, under Tin oxyacids, and SALTS AND DERIVATIVES THEREOF, p. 730).
According to Ditte (C. R. 104, 172), both stan-

nic and metastannic hydrates dissolve in warm H2SO,Aq (1 part acid and 8 parts water), and on concentrating till not more than 3 to 4 vols. water are present to 1 vol. H.SO, the solution deposits white crystals of SnO 2H SO: these crystals are very deliquescent; they are decomposed by water; if so much water is added that not more than 43 g. H₂SO₄ are present in 1,000 c.c. of the liquid, a pp. of SnO₂xH₂O is formed. By dissolving stannic or metastannic hydrate in

warm H₂SeO₂Aq, and concentrating, D. (l.c.) obtained crystals of SnO₂2H₂SeO₄.

For further details of reactions of stannic and metastannic hydrates v. TIN OXYACIDS, AND SALTS AND DERIVATIVES THEREOF (infra).

Oxides OF TIN OTHER THAN STANNOUS AND STANNIC OXIDES. Oxides which are most simply

regarded as xSnO.ySnO, seem to exist.

According to Fuchs (J. pr. 5, 318), a greyishwhite, slimy solid, having the composition SnO.SnO₂(=Sn₂O₃), is obtained by diffusing freshly ppd. Fe₂O₂xH₂O in SnCl₂Aq free from acid, and boiling

(2SnCl_Aq + Fe₂O₃ = SnO.SnO₂ + 2FeCl₂Aq).

This oxide is said to dissolve completely in

This oxide is said to dissolve completely in NH₂Aq, and also in HClAq.
By digesting SnO₂xH₂O, ppd. by alkali from SnO₄Aq, with SnCl₂Aq, Schiff (A. 120, 53) obtained an orange-yellow solid, to which he gave

the composition SnO.6SnO.5H.O; by digesting SnO₂xH₂O, formed by oxidising tin with HNO₂Aq, with SnOl₂Aq Schiff (*l.c.*) obtained a yellow powder, said by him to be SnO.68nO.9H.O. or when dried at 85° to be SnO.6SnO.4H.O (v.

also Tschermak, C. C. 1862, 305).
PURPLE OF CASSIUS. A purple-coloured solid is obtained by adding solution of a stannous salt to dilute AuCl, Aq; this solid has been examined by many chemists, who have generally assigned to it formulæ which represent it as a compound of SuO, sometimes of SnO.SnO, and AuO. According to the most recent investigations the composition varies according to the conditions of preparation, and all that can be said with certainty is that the purple solid is a compound of tin, gold, and oxygen (v. Buisson, J. Ph. 16, 629; Bohlen, Ar. Ph. 57, 277;
 Capaun, J. pr. 22, 153; Fuchs, J. pr. 5, 318; Wächter, A. 68, 116; Figuier, Ph. C. 1844, 724; Debray, C. R. 100, 1035; Müller, J. pr. [2] 30, 252; and, for a bibliography (to 1866), Fischer, D. P. J. 182, 39).

Tin oxyacids, and salts and derivatives thereof. Some of the hydrates of SnO2 interact with alkalis to produce salts wherein tin forms part of the acidic radicle; compounds are also known the acidic radicles whereof contain tin in combination with other negative elements besides oxygen, or tin in combination with both

metallic and nonmetallic elements.

The reactions of the hydrates of SnO2 ppd. from solutions of stannates by dilute cold acids, or ppd from stannic salts by alkalis, are distinctly different from the reactions of the hydrates of SnO2 obtained by oxidising tin by HNO3Aq, or by ppn. by dilute acids from solutions of another class of salts which have the same composition as stannates, except that they always contain H and O in the ratio 2H;O in addition to the constituents of stannates. is therefore usual to distinguish the acidic hydrates of SnO2 as stannic and metastannie acids; to the former is given the composition H_SnO₃(=SnO_H_O), and to the latter the composition $H_{10}Sn_{s}O_{1s} (=5SnO_{s}5H_{s}O)$. Neither of these formulæ is to be regarded as more than an attempt to connect the differences in the chemical behaviour of two compounds having identical percentage compositions (if the H₂O in one class is omitted) with differences in the complexities of their interacting atomic aggregates; the molecular weight of neither compound is known. It is, indeed, doubtful whether a compound with the composition xH2SnU, can exist apart from other hydrates of the composition ySnO_zH₂O; it is certain that the composi-tion of the hydrates of SnO₂ varies with very small variations of temperature, by whatever methods these hydrates are prepared (v. p. 726, HYDRATED STANNIC OXIDE)...

That the hydrates of SnO, obtained respectively by ppg. solution of stannates by dilute acids and by oxidising tin by HNO, Aq, differed in their reactions, was noticed by Berzelius in 1811 (v. Lehrbuch [5th ed.] 2, 596). Berzelius regarded these compounds as hydrates of two different modifications of stannic oxide; he called the oxide supposed to be a constituent of the hydrates obtained by ppg. solutions of stannates stannic oxide, and designated it as aSnO₂; the other oxide he called metastannic oxide, and designated it as bSnO₂. Gmelin called the hydrate from stannates ordinary stannic acid, and the other hydrate abnormal stannic acid.

STANNIO ACID H. SRO.

Preparation.—By adding cold dilute HCIAq to an aqueous solution of K.SnO. prepared by fusing SnO. with KOH, or by heating tin with KOH and KNO. (v. Potassum Stainler, p. 730), a gelatinous pp. is obtained which, when washed and dried in vacuo, has the composition SnO. H.O. H.SnO. (Fremy, A. Ch. [3] 12, 463). The same hydrate is formed, according to F. (i.c.), by adding CaCO. or BaCO. to excess of SnCI.Aq, washing, and drying in vacuo. (For details regarding the results obtained by different chemists who have examined the compositions of the stannic hydrates, v. Hydrated Stannic acid (no analyses are given) by dissolving SnO. xH.O ppd. from a stannic salt (? by alkali from SnCI.Aq) in SnCI.Aq, and dialysing until all the Cl had passed into the dialysate. Colloidal forms of stannic acid are also obtained (1) by dialysing a solution of the ppd. acid (J. van Bemthelm, R. T. G. 7, 87; abstract in C. J. 54, 1160 [1888]; the results of experiments on the dehydration of the colloidal acid are given).

Properties and Reactions.—A gelatinous, amorphous solid, drying (in air or in vacuo) to hard, semi-transparent lumps, like gum arabic, Reddens litmus paper. Vignon (C. R. 108, 1049) found that the heat of neutralisation, by KOHAq, of stannic acid formed by ppg. SnCl, Aq by KOHAq, decreased when the ppd. acid was kept in contact with water for some days, and decreased more rapidly when the acid was heated with water in a sealed tube for some hours. J. van Bemmelen (J. pr. [2] 23, 324) found that when stannic acid is shaken with solutions of HCl, or H.SO,, or with solutions of certain salts, such as KCl or K.SO, a definite number of molecules of the acid or salt is taken up by the stannic acid so as to form a loose combination therewith; and that the number of molecules thus absorbed varies with the proportion between the quantities of stannic acid and the soid or salt in the solution used, and also with the concentration of the solution used. The loose compounds thus formed are called absorptioncompounds by J. van B. Dissolves in the stronger neids (HNO₃, H₂SO₄, HCl, &c.). According to Ditte (C. R. 104, 172), when a solution of stannic acid in warm H₂SO₄Aq (1 part acid to 8 parts water) is evaporated until not more than 3 to 4 water) is evaporated until not more than 5 to 4 vols. water are present to 1 vol. H₂SO₄, and allowed to cool, it yields white deliquescent crystals of SnO₂.2H₂SO₄; and a solution of stannic acid in warm H₂SeO₄Aq yields a similar crystalline compound SnO₂.2H₂SO₄. Dissolves in excess of caustic alkali solutions, forming stannates of caustic alkali solutions, forming stannates of caustic alkali solutions. (g. v. p. 780) M. SnO. According to J. van. B. (i.e.) colloidal stannic acid does not form any compound when shaken with dilute cold KOHAq, but only complex molecular aggregates, the composition of which varies considerably with temperature and concentration. Stannic acid, dried at the ordinary temperature by pressure, is

gradually changed to metastannic acid by heat; the change begins at c. 55° (J. van B., L.c.; v. also infra, Change of stannic to metastannic acid, and vice versa). For other reactions of stannic acid v. infra, Distinctions between stannic and metastannic acids.

METASTANNIC ACID H₁₀Sn₅O₁₈. Preparation.—Tin, in thin pieces or granu-lated, is heated with HNO₃Aq, S.G. c. 135, until the metal is converted into a greyish-white powder, which is washed with dilute HNO, Aq, and then with water, and dried. The solid is said to have the composition H₁₀Sn₂O₁₅ (= 5SnO₂.5H₂O) when dried in vacuo (Fremy A. Ch. [3] 12, 463), when dried over H₂SO₄ (Weber, P. 122, 358), or when dried at the ordinary temperature (Thomson, Ann. Phil. 1817, 149). For details of the results obtained by different chemists who have examined the compositions of the metastannic bydrates v. Hydrated Stannic oxide (p. 726); v. also J. van Bemmelen, R. T. C. 7, 87 (abstract in C. J. 54, 1160 [1888]). It should be noted that the empirical formula assigned to metastannic the empirical formula assigned to metastannic acid dried in vacuo (Fremy), or dried over H₂SO₂ (Weber), is the same as that assigned to stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); this formula is a constant of the stannic acid dried in vacuo (Fremy); the st mula is SnO₂.H₂O. The different reactions of the two compounds show that if both have the same empirical formula one must be an isomeride or a polymeride of the other. Metastannic acid is also obtained by decomposing an aqueous solution of the sodium salt (v. p. 730, Metastannates) by boiling. Graham (T. 1861. 213) obtained colloidal metastannic acid by addand obtained constitute Helaq to the acid obtained by the action of HNO₂Aq on tin, dissolving the solid so formed in water, and dialysing. Vignon (C. R. 108, 1049) found that the heat of neutralisation of metastannic acid by KOHAq decreased when the acid was dried at 110°, and decreased very considerably when the acid was heated with water, for some hours, at 250° in a sealed tube.

Properties and Reactions.—A white powder, Insol. in nitric acid. Contact with conc. HClAq for a short time produces a compound (according to J. van Bemmelen, R. T. C. 7, 87; abstract in C. J. 54, 1160 [1888], no definite compound is formed, but only complex molecular aggregates of metastannic acid and HCl) which dissolves in water, but is insol. in HClAq. According to Barfoed (J. pr. 101, 258), the compound with HCl is quite insol. in HClAq S. G. 1·1, and may be purified by washing with acid of that concentration. The solution of this substance in water gives off HCl and H_O, with a very little SnCl, when distilled; and metastannic acid separates out (Freny, A. Ch. [3] 12, 463; 23, 893; H. Rose, A. 68, 272). Evaporation of the aqueous solution over H_SO, is said to give an oxyohloride \$3\text{NO}_S, \text{SnCl}_S, \text{ShL}_O (Weber, P. 123, 358). Metastannic hydrate dissolves in conc. HClAq after prolonged boiling, forming SnCl, solution (Löwenthal, J. pr. 77, 321). Barfoed (L.C.) says that conc. HClAq gradually converts recently ppd. and moist metastannic acid into stannic acid, and that the quantity of metastannic acid thus changed increases with the quantity of conc. HClAq, the time of contact, and the temperature. J. van Remmelen (J. pr. [2] 23, 324) found that metastannic acid forms absorption compounds with HCl, H_SO, KCl, KSO, &c.

(cf. STANNIO ACID, Properties, p. 728). For other reactions of the solution in water of the product of the action of HClAq on metastannic acid v. infra, Distinctions between stannic and metastannic acids. According to Ditte (C. R. 104, 172), metastannic acid dissolves in warm H₂SO₄Aq (1 pt. acid to 8 pts. water), forming a solution which gives crystals of SnO₂2H₂SO₄ when evaporated until not more than 3 to 4 • vols. water are present for one vol. H2SO4; the crystals are decomposed by water, with ppn. of SnO,xH2O (? metastannic hydrate), when sullicient water is added to insure that not more than 43 g. H2SO, are present in 1,000 c.c. of the liquid. A similar compound was obtained with selenic acid, viz. SnO₂2H₂SeO₄ (D., l.c.). Allen (C. J. 25, 274) found that metastannic acid dissolved in boiling conc. H2SO4, forming Sn(SO4)2 solution; by pouring this solution into water some of the tin was ppd., after a time, as stannic acid, but on boiling the whole of the tin came down as metastannic acid. Metastannic acid is said to dissolve slowly in fairly dilute cold KOHAq or NaOHAq; addition of conc. KOHAq or NaOHAq is said to ppt. K or Na metastannate; when the solution in KOHAq or NaOHAq stands in the air metastannic acid gradually deposits. According to J. van Bemmelen (l.c.), colloidal meta-stannic acid does not form any definite compound with KOH when shaken with KOHAq of different concentrations. By fusing metastannie acid with KHSO₄ or NaIISO₄, Allen (C. J. 25, 274) obtained a product which dissolved partially in water; the aqueous solution gave a pp. of metastannic acid on boiling.

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Distinctions between stannic and metastannie acids (v. Frenny, A. Ch. [3] 12, 462; 23, 398; H. Rose, P. 75, 1; 105, 561; Löwenthal, J. pr. 77, 321; Bartoed, J. pr. 101, 368; J. van Bemmelen, R. T. C. 7, 87; abstract in C. J. 54, 1160 [1888]).—Stannie acid is soluble in dilute HNO, Aq, H, SO, Aq, or HClAq; metastannic acid is insol. in these acids. Cold conc. HClAq dissolves stannic acid, and the solution gives the reactions of SnCl.; cold cone. HClAq forms a compound (? molecular aggregates) with metastannic acid, which is insol. HClAq of S.G. 1·1, or greater S.G., but dissolves in cold water.

The following reactions apply to solutions of stannic acid in HClAq on the one hand, and to solutions in water of the substance formed by the action of HClAq on metastannic acid on the other hand. Stannic acid solution, if conc., does not become turbid on boiling; long continued boiling, with additions of water, ppts. all the acid. Metastannic acid solution, even when conc., goes turbid on boiling; long-continued boiling, accompanied by dilution, ppts. all the acid. Stannic acid solution, when distilled, gives off H.O. with a little HCl and SnCl.; and a little stannic acid separates. According to Barfoed (J. pr. 101, 368), when a solution of stannic acid in HClAq S.G. 1 1 is distilled, the whole of the tin passes over as SnCl. Metastannic acid solution, when distilled, gives off H₂O, with some HCl and a very little SnCl, and the meta-acid separates in the retort. Addition of tartaric acid to the stannic solution, followed by gradual addition of NH,Aq, excess of NH,Aq being avoided, produces no pp. Treatment of the metastannic solution with tartaric acid and NH,Aq (not in excess) ppts. the meta-acid. SnCl,Aq gives no pp. with the stannic solution; SnCl,Aq gives a yellowish pp. (? SnO.6SnO,9H,O) with the metastannic solution. Addition of dilute H,SO,Aq to the stannic solution produces no pp., unless the stannic solution is very much diluted. Dilute he stands solution is very much diluted. Dilute H₂SO₄Aq profluces a pp. even in very dilute metastannic solution; by washing this pp. with hot water, metastannic acid remains (cf. Ditte's experiments are described under both STANNIC ACID and METASTANNIC ACID, pp. 728, 729). The stannic solution is not ppd. by conc. HClAq. The metastannic solution, if nearly neutral, is ppd. by conc. HClAq. Addition of K,FeCy,Aq to the stannic solution, in the ratio K,FeCy,Sn present, ppts. all the tin as SnFeCy. To ppt. all the tin from the metastannic solution, the K, FeCy, Aq must be added in c. the ratio 19K, FeCy,:Sn present; the pp. is not SnFeCy, it is said by some observers to be metastannic acid; J. van B. (l.c.) calls it an absorption conpound of metastannic acid and K,FeCy. stannic solution gives no pe. with excess of fairly conc. NaOhAq. The metastannic solution is completely ppd., as sodium metastannate, by excess of fairly conc. NaOHAq.

vice versa. A solution of stannic acid in HClAq gradually changes to metastannic acid; the change is the more rapid and complete the more dilute the solution (H. Rose, l.c.; Barfoed, l.c.); by boiling for some time with repeated additions of water the whole of the stannic acid may be converted into metastannic acid. A very conc. solution of stannic acid in HClAq remains unchanged (cf. reaction of meta- acid with conc. HClAq, infra). According to Löwenthal (l.c.), the change from stannic to metastannic acid is stopped by addition of tartaric acid, even when the solution of stannic acid in HClAq is dilute; the amount of change to the meta- acid may be determined (according to L., l.c.) by finding the quantity of K,FeCy, Aq required to completely

Change of stannic to metastangic acid and

add excess of fairly conc. NaOHAq, which ppts. all the meta-acid (as a sodium salt) but none of the stannic acid.

Stannic acid is converted into the meta- acid by heat (H. Rose, Lc.). J. van Bemmelen (Lc.) found that stannic acid dried by pressure at the ordinary temperature is completely soluble in cone. HClAq, but that by heating to c. 55°, or by heating with water to below 100°, some metastannic acid is formed which is insoluble in conc. HClAq.

ppt. the tin in solution. Barfoed (l.c.) says the best way to measure the amount of change is to

A solution of stannic acid in excess of KOHAq gradually deposits metastannate of K on exposure to air, with formation of K₂CO₂Aq.

Metastannic acid is gradually changed to stannic acid, according to Barfoed (l.c.), by constanne sent, according to Dartoea (s.c.), by con-tact with cone. HClAq; the quantity of stannic acid produced increases with the quantity of HClAq used, the time of contact, and the temperature.

Stannic acid is said to be obtained from the meta- acid by fusing the latter with a large excess of KOH, dissolving in water, and ppg. by cold dilute HClAq (H. Rose, i.e.; Fremy, i.e.).

Onyacids of Tin other than Starnic and Metastannic. (1) H.Sn.O., Spring. (Bl. [5] 1.

180) obtained a colloidal solid, drying at 100° to a white mass with the composition H.Sn.O., by adding excess of BaO, xH,O to a solution of SnCl, in HClAq, and dialysing the turbid liquid until BaOl, ceased to pass into the dialysate. S, regarded the new compound as an acid of the hypothetical perstannic oxide SnO, analogous to CeO, TiO, and (?) ZnO, (2) PLSnO, and H.Sn.O. The empirical formula of both these hydrates of stannic oxide is SnO, H,O. According to Musculus (C. R. 65, 961), the hydrates differ somewhat in properties both from stannic and metastannic acids; they are said to be

formed by keeping stannia acid under water, and to form K salts, KH,Sn,O, and KH,Sn,O,. Stannates, M,SnO, and M,SnO,. The alkali stannates are obtained by dissolving stannic acid in MOHAq (M=NH₄₀ K, or Na), and evaporating over H₂SO₄; the stannates of the alkaline earth metals may be obtained by the interactions of solutions of the alkali stannates with MO2H2 or MCO3 (M = Ba, Ca, Sr).

Ammonium stangate. A salt, said to have the composition (NH₄)₂SnO₃.SnO₂.IH₂O, is obthe composition (NH₁)₂snO₂,SnO₂,Xn₂O, is outained, as a yellowish jelly, by evaporating a solution of stannic acid in NH₂Aq over H₂NO₄ (Moberg, J. vr. 28, 230). When K₂SnO₂Aq is added to NH₂ClAq, stannic acid is ppd. according to Ditte (C. R. 96, 701).

Barium stannate. The normal salt

Barium stannate. The normal salt BaSnO₂.6H₂O is said to be obtained by adding BaCl, Aq to K, SnO₃Aq; it is described as a heavy, white powder (Moberg, Lc.). By adding K, SnO₃Aq to excess of BaCl, Aq, Ditte (Lc.) obtained a basic salt R: SnO₃BaO.10H,O as lustrous leaflets.

Calcium stannate. Ditte (l.c.) obtained the normal salt CaSnO3.5H2O, in white crystals, by normal sate Usero, or 1,0,1,1,1, white capenage adding K₂SnO₂Aq to excess of CaCl_Aq, washing, and drying at 100°. By heating for some hours a mixture of stannic acid and CaCl₂Aq, with a little CaO, D. obtained CaSnO, in regular crys-

Potassium stannate K₂SnO₈.xH₂O. pared by dissolving stannic acid in KOHAq, or by fusing SnO2 or metastannic acid with excess of KOH for some time and dissolving in water, and evaporating over H2SO,; transparent, rhombic prisms; crystallising with 4H_O (Fremy, A. Ch. [3] 23, 393), with 3H₂O (Moberg, l.c.). Marignac (Ann. M. [3] 15, 277) obtained the salt, in rhombohedral crystals, by gradually heating 8 pts. metastannic acid with 8 pts. KOH till the mixture boiled, allowing to cool, dissolving in water, filtering, and evaporating. Ordway (Am. S. [2] 40, 173) prepared the pure salt by adding an equal volume of absolute alcohol to a solution of the commercial salt (v. infra), repeatedly treating the syrupy layer that separated with alcohol, drying the pasty mass so obtained by pressure, dissolving in water, evaporating in vacuo, and washing the crystals with alcohol. K stannate dissolves easily in water; O. (l.c.) gives S. at $10^{\circ} - 106 \cdot 6$, and at $20^{\circ} - 110 \cdot 5$; solution reacts alkaline. Insoluble in alcohol. By adding u dilute soin solution sufficient to neutralise ? of the alkali, a white freculent pp. of K meta-stannate is said to be produced (O. L.c.); excess of cold dilute seid ppts. stannic acid. K_SnO_wH_0 is dehydrated at a red heat.

mercial stannate of potash solution is prepared (1) by fusing tinstone with KaS, KOH or

KNO, and dissolving in water; (2) by boiling tinstone with KOHAq; (8) by fusing tin with KNO4, and K₂CO₂, or boiling the metal with KOHAq containing KNO₂ and KCl (ν . Haeffeld, D. P. J. 144, 66; Vaughan, B. 5, 396; and DIOTIONARY OF APPLIED CHEMISTRY, vol. iii. pp. 843-4).

Sodium stannate Na2SnO2.xH2O. Prepared similarly to the K satt. Crystallises in hexagonal plates with 3H₂O (M., l.c.; O., l.c.). Marignac (l.c.) obtained rhombohedral crystals. Jonas (C. C. 1865, 607) obtained rhombic crystals. tals of Na, SnO, 9H,O by recrystallising the commercial salt. Haeffely (D. P. J. 144, 66) obtained crystals of Na SnO 3.3H2O by heating an aqueous solution of S.G. 1.3; on allowing to cool again the crystals dissolved, the S.G. became 1.35, and after a time crystals of Na, SnO, 8H, O were deposited. Scheurer-Kestner (Bl. [2] 8, 839) obtained crystals of the composition Na, SnO, 10H, O by evaporating a dilute solution of the ordinary salt, free from excess of NaOH, at a low tem perature. Na2SnO3.3H2O is more soluble in cold than in hot water; O. (l.c.) gives S. at 0°=67.4, and at 20°=61.3. Insoluble in alcohol. According to H. (l.c.), an aqueous solution of the octohydrate gives a crystalline pp. of Na metastannate when heated, or when left at the ordinary temperature for some weeks. Commercial stannate of soda solution is prepared similarly to the solution of the potash salt (v.

Strontium stanuate. A basic salt 2SrSnO₃.SrO.10H₂O was obtained by Ditte (C. R. 96, 701), in lustrous octahedra, by adding

K.SnO,Aq to excess of SrCl.Aq.

METASTANNATES. Only alkali metastannates have been prepared. The empirical formula of these salts is M₂O.5SnO₂.4H₂O; as they are dethese salts is M₂U.55NO₂-\$H₂U; as oney are uccomposed by removing water, the formula is generally written as M₂H₂Sn₂O_{1s} (cf. Metastannic acid dissolves slowly in KOHAq or NaOHAq; on adding cone. MOHAq the salts are ppd. The salts are better obtained by adding cone. MOHAq to a solution in water of the substance obtained by the interaction of metastannic acid and conc. HClAq (Barfoed, J. pr. 101, 368). Dilute acid solutions ppt. metastannic acid from solutions of metastannates. Metastannates heated with excess stannates. Metastannatos neated with excess of MOH give stannates. For more details regarding M.H.,Sn.O., (M = K or Nn) v. Fremy (A. Ch. [3] 23, 393); Weber (P. 122, 358); Haeffely (D. P. J. 144, 66).

ARSENIO-STANNATES. A compound

Na₂O.2As₂O₃.6SnO₂.5H₂O was obtained by Haeffely (D. P. J. 140, 290) by adding excess of HNO, Aq to a boiling solution of Na, SnO, and Na, AsO,, and treating the gelatinous pp. with

excess of NaOHAq.
OXALO-STANNATES. 2KHC₂O₂SnO₂SH₂O was obtained, in lustrous leaflets, by Péchard (C. R. 116, 1513) by dissolving stannic acid in hot KHC₂O₂Aq and allowing to cool.

PLATINO-STANNATES. Compounds of SnO and SnO₂ with PtO₂, derived from the acids H₂Sn₂Pt₂O₄ and H₂Sn₂Pt₂O₄ (v. Platino-stan-

NATES, this vol. p. 285).
PLATINO-SELENO-STANNATES v. this vol. p. 285.

BILLIOU-SLANNATES. Bourgeois (Bl. [2] 47, 197) obtained the salt CaO.SiO₂.SnO₂ in monolinic, lustrous crystals, by fusing SiO₂ and snO₂ with excess of CaCl₂, and extracting with water.

In connection with stannic and metastannic soids and their derivatives, v. Chlor-stannic acid, under Stannous chloride (p. 721); Tin, oxides and hydrated oxides of (p. 725); and Tin, thio-acids and salts of (p. 735).

ONDES AND HIRATED VALUES OF (p. 1207), and TR, THIO-ACIDS AND SALTS OF (p. 735).

Tin, oxybromides of. By adding pieces of tin to the mother-liquor from BaSnBr. (v. Stannibromides, under Stannib romales, p. 720).

Rayman a. Preis (A. 223, 323) obtained colour-less, prismatic crystals to which they gave the formula Sn,OBr.,12H.O; and from the mother-liquor from this compound fine, colourless needles of Sn,O.,Br.,10H.O separated after a time.

Tin, oxychlorides of. According to Ditte (A. Ch. [5] 27, 145), when SnO.xH₂O, obtained by ppg. a stannous salt by NH₂Aq, is boiled with water containing a trace of SnCl₂, a gelatinous oxychloride is obtained having the compositior. Sn₂OCl₂:6H₂O (= SnO.SnCl₂:6H₂O); and when this compound is boiled with a little more dilute SnCl₂Aq another oxychloride, Sn₂O₃Cl₄:6H₂O (= 3SnO.2SnCl₂:6H₂O) is formed in small, white, pearly tablets.

The oxychloride SnOCl, is obtained, according to Scheurer-Kestner (A. Ch. [3] 47, 1), by evaporating SnCl,Aq at 50° to 60°; also by heating 100 pts. SnCl,2H,O, dissolved in 50 pts. water, with HNO,Aq containing 16 pts N.O.

An oxyohloride is also formed by treating metastannic acid with conc. HClAq, pouring off the excess of acid, dissolving in water, and evaporating over H.SO, and CaO; to this oxychloride, which is an amorphous, white solid, Weber (P. 122, 358) gave the formula Sn,Oc01,5H,O(=3SnO_.SnCl,5H,O). Tschermak (W. A. B. 44, 2) obtained a crystalline oxychloride Sn,Oc01,4 (=4SnO_.3SnCl,SnCl,2) by dissolving moist metastannic acid in hot conc. SnCl_Aq containing HCl.

Mallet (C. J. 35, 524) obtained a semi-transparent, jelly-like solid from SnCl_Aq which had been kept in a loosely-stoppered bottle for a year or two; to this solid he gave the farmula SnC MCL_SNCOMED

SnO..HCl (= SnO.OH.Cl).

Tin, oxyfluoride of When SnF, is heated in air it is said to form the oxyfluoride SnOF, (= SnO.SnF,) (Fremy, A. Ch. [3] 47, 37; Marignae, Ann. M. [5] 15, 221).

Tin, oxyiodides of. According to Personne (C. R. 54, 216), various oxyiodides are formed by decomposing SnI, by much water; P. analysed four compounds, to which he assigned the compositions Sn.O.I. (= 25nO.SnI.), Sn.OI. (= SnO.SnI.), Sn.OI., (= SnO.SnI.), and Sn.OI.

Tin, phosphides of. By heating finely divided tin in vapour of P, Schrötter (W. A. B. 1849, 301) obtained a silver-white, brittle solid to which he gave the formula SnP; S.G. 6:56; easily acted on by MClAq, but not by HNO,Aq. Other crystalline solids have been obtained by heating iin and P together, but their compositions are not determined with certainty (v. Pelletier, S. 55, 106; Berthier, A. Ch. [2] 33, 180; H. Rose, P. 24, 326; Lüpke, C. C. 1890

[ii.] 643). Natanson a. Vortmann (B. 9, 1459) obtained a phosphide of tin by heating glacial phosphoric acid with C and tin; HClAq gave of PH, and left SnP.
Tin, saits of. Tin forms two classes of

Tin, selenides of. Tin and Se form two compounds, SuSe and SuSe. The former can be prepared by the direct union of the elements; the latter does not seem to be obtained by this method. Both selenides dissolve in alkali solutions, and in solutions of alkali sulphides.

STANNOUS SELENIDA SnSc. (Tin mono-sclenide or protosclenide.) Mol. w. unknown. Obtained by melting together So and tin (Berzelius; Welsmann, A. 116, 122). With excess of Se the disulphide SnSe, was said to be formed (Little, A. 112, 213), but this was probably a mistake (Schneider, P. 127, 624). Also formed by adding powdered Se to molten SnCl., heating till SnCl, is volatilised, and allowing to cool, when SnSe crystallises; excess of SnCl, is removed by washing with dilute HClAq (Schneider, i.e.). Steel-grey, lustrous prisms; probably isomorphous with SnS; S.G. 5-21 at 152 (S., i.e.). Also obtained, as a black powder, by passing H.Se into SuCl.Aq, washing, and drying at 100° SnSe prepared by ppn. is soluble in alkali solution; the crystals prepared by heating Se with SuCl, are insoluble, even in boiling alkali solu-Both crystalline and amorphous SnSe are soluble in solutions of alkali sulphides or sclenides. SnSe is insoluble in HClAq; oxidised by HNO,Aq to SnO,xHO, HSeO, and HSeO, Heated with I forms SnI, and SnSe,; or, with an excess of I, SnI, and Se; reacts similarly with Br. SnSe is not reduced by heating in H. Heated in air it is gradually oxidised to SnO, and SeO, (S., l.c.). According to Ditte (C. R. 96 1790), SaSe can be sublimed in a stream of H at a red heat; D. says S.G. is 6.179 at 0°.

STANNIC SELENINE SINSe. (Tin disclenide.) Mol. w. unknown. Not formed by heating together tin and Se, as excess of Se over that required to form SinSe sublimes; Little's statement that SinSe, is formed by directly combining tin and Se by heat (4. 114, 213) is probably wrong (Schneider, P. 127, 624). Prepared by rubbing 5 pts. I and 8 to 10 pts. crystallised Sul₂ (the Sul₃ is used to enable the 1 to be thoroughly powdered), adding 4 pts. powdered vinSe, then sufficient CS, to form a pasty mass (stirring constantly), and then adding more CS, to dissolve Sul₃, and washing with CS, when SinSe, remains as a dark, red-brown, indistinctly crystalline powder, which becomes darker when dried at 100° (Schneider, l.c.). S.G. 4-85. According to Welsmann (4. 116, 122), SinSe, is obtained, as a dark reddish-brown powder, by passing H.Se into SinCi,Aq; heated in H. this powder gives off Se and leaves SinSe.

SnSe, is not acted on by water, or by dilute soids; it is slowly attacked by cone. boiling HClAq; aqua regia, or cone. HNO,Aq, oxidises it to SnO₂, H₂SeO₃ and H₂SeO₄; it dissolves in hot conor H₂SO₄, and when the olive-green solution is poured into water Se separates and Sn(SO₂), remains dissolved. SnSeA is easily soluble in caustic alkali solutions, including NHAO, forming blood-red liquids. Heated NH,Aq, forming blood-red liquids. Heated with I, in the ratio SnSe,:4I, SnI, and Se are formed; Br reacts similarly to I (Schneider, l.c.).

Tin, silicides of. No definite compound has been isolated. Substances which seem to be of the nature of alloys are for med by heating together tin and Si; treatment with HClAq dissolves tin from these bodies, and separates Si along with SiO₂ (v. Winkler, J. pr. 91, 193).

Tin, silicofluoride. According to Berzelius (Lehrbucn [5th ed.] 3, 767), the salt SnSiF. separates (? from solution of SnO.xH.O in H.SiF.Aq) in prismatic crystals, which are

readily crystallised from water.

Tin. sulphides of. . Two sulphides of tin are known, SnS and SnS,: the former is readily obtained by heating tin and S; the latter by heating tin with an excess of S and some sub-stance (e.g. NH₄Cl) which readily volatilises, and so removes heat, which would else drive off the S above that required to form SnS. Both sulphides are also formed by ppn. by H2S from corresponding salts in solution. Both sulphides dissolve in solutions of alkali polysulphides. torming thiostannates, M.SnS₃.

Stannous sulphide SnS. (Tin monosulphide

or protosulphide.) Mol. w. unknown.

Preparation.—1. Finely divided tin is heated

with c. equal parts of S; the product is powdered, and repeatedly heated with S in a closed vessel. Ditte (C. R. 96, 1790) recommends to sublime the SnS thus prepared, by heating to redness in a porcelain tube in a stream of H .-2. H₂S is passed into a solution of a stannous salt until the liquid smells strongly of H₂S; the brownish black pp. of amorphous SnS is washed and dried, and is then added, little by little, to molten SnCl, as long as it is dissolved thereby; after cooling, SnCl₂ is dissolved out by dilute HClAq, and any dark-brown powder that is present is washed away from the heavier, greyish, lustrous, crystalline particles of SnS (Schneider,

P. 95, 167).

Properties.—A dark, lead-grey, crystalline solid; S.G. 4'85° (Karsten, S. 65, 394), 5'27 (Boullay, A. Ch. [2] 43, 266). Ditte (l.c.) describes SnS, after sublimation in H, as crystallising in thin, lustrous squares with an angle of c. 90°; with a groy-blue, metal-like lustre; soft and friable; S.G. 5.0802 at 0°. Crystalline SnS melts at a red heat; it expands considerably on cooling (Ditte, l.c.). Prepared by ppn. SnS is a brownish-black, amorphous solid

Reactions.—1. SnS, prepared by heating together tin and S, may be sublimed in hydrogen at a red heat (Ditte, C. R. 96, 1790); but continued heating in H is said to reduce it to tin, H.S being given off .- 2. Heated in air SnS is gradually converted into SnO, and SO, -3. Reacts with chlorine, even at the ordinary tempera-ture, to form SnCl, and SnCl, 28Cl, = (SnS,Cl,) (H. Rose, P. 47,517).—4. Fusion with potassium syssids produces tin and KONS.—5. SnS dis-

solves gradually in boiling hydrochloric acid, forming SnCl, solution and giving off H,S (for details of interaction with HClAq of different concentration, and with HCl gas, v. Ditte, C. R. 97,42).—6. Gradually oxidised to SnO, by heating with nitric acid.—7. Dissolves in solutions of alkali polysulphides, forming alkali thiostannates M2SnS3.-8. SnS is generally said to be nearly insoluble in solutions of alkali monosulphides (M2S). According to Ditte (C. R. 94, 1419, 1470), SnS is not acted on by K.SAq at the ordinary temperature if the concentration of the solution does not exceed 20K,S:100H,O; but a more conc. solution of K2SAq, out of contact with air, gradually converts the SnS into a grey, spongy mass of tin; and still more conc. K,SAq dissolves this, forming K,SnS,Aq and giving off H: if air is admitted the reactions are more complex.

STANNIC SULPHIDE SnS . (Tin disulphide.) Mol. w. not known.

Preparation .- 1. By saturating SnCl Ag containing a little HClAq with H.S, warming, again saturating with H.S, warming gently for some hours, collecting the pp., washing with dilute H2SAq, drying, and heating to above 100° out of contact with air. Pure SnS2 can scarcely be prepared in this way; there seems to be always prepared in this way; there seems to be always some Sno_x2H₂O present in the pp. (Kühn, A. 84, 110; Barfoed, J. pr. 101, 368).—2. By passing the mixed vapous of SnCl, and H₂S through a red-hot porcelain tube, or by passing H₃S into SnCl, and heating the white crystals of SnCl₄.5H₂S so obtained (Coldridge, P. M. [5] 29, 383).—3. A mixture of finely-divided tin and S, or of SnS and S with some substance that or of SnS and S, with some substance that gradually volatilises and so removes heat, is slowly heated to redness in a glass retort, or a loosely covered flask, imbedded in sand; the volatile substance gradually passes off, then the excess of S is volatilised and the SnS, remains, partly on the sides and partly on the bottom of the vessel. If tin is heated with S only, the heat produced in the reaction is so great that the SnS, formed is resolved into SnS and S. Various mixtures have been employed by different chemists; the following give good results: (1) equal parts sifted tin-filings, S, and NH,Cl (Pelletier); (2) 4 parts tin-filings, 3 parts S, 2 parts NH₄Cl (Woulfe); (3) a pulverised amalgam of 12 parts tin and 6 parts Hg, with 7 parts S, and 6 parts NH,Cl (W.); (4) 5 parts SnS and 8 parts HgCl2 (W.).

Patts Ligul₂ (W.).

References.—Pelletier (Crell's Chem. Ann.
1797 [1] 46); Woulffe (ibid. 1, 149); Bullion (ibid.
1793 [1] 89); Proust (Gehlen's Journ. f. Chem.
und Phys. 1, 250).

According to Gmelin (Handbuch [5th ed.] 3,75) if NH Cl is heated with tin and S there is formed a compound of NH₁Cl and SnCl₂, which then interacts with the S, forming SnS₂ (?2Sn + 8NH₂Cl = $2(2NH_1Cl.SnCl_2) + 2H_2 + 4NH_3$;

2(2NH,Cl.SnCl.) + 2S = SnS₂ + 2NH,Cl.SnCl₄ + 2NH,Cl)

Properties .- Prepared by sublimation, SnS. is a soft golden-yellow, lustrous, crystalline solid; S.G. 4.6 (Karsten, S. 65, 294), 4.42 (Boullay, A. Ch. [2] 43, 266). Crystalline SnS₂ is known chemistry, vol. iii. p. 845).

Reactions and Combinations.—1. Heated in

a closed vessel gives SnS and S, and a sublimate

of SnS,—2. Heated in air SnO, and SO, are formed.—8. Chlorine liquefies SnS, on cooling formed.—S. Chlorine liquefies SnS₂, on cooling yellow crystals of SnCl₄.2SCl₄ are formed (H. Rose, P. 42, 517). — 4. The compound SnS₄I₄(=SnSI₂.SI₂) is said to be formed by heating SnS₂ with iodine in a stream of CO₂ (Sohneider, J. pr. 79, 419; v. also Tin, Thiotodom, infra). According to Schneider (l.c.) a boiling alcoholic solution of I does not act on SnS₂ arcoard by sublimation between the configuration. SnS, prepared by sublimation, but with amor phous SnS, prepared by ppn. it gives SnS, I, -5. Amorphous, but not crystalline, SnS, is slowly decomposed by boiling cone. hudrochloric acid, H2S being given off and SilCl, solution formed. -6. The amorphous sulphide is slowly oxidised by hot nitric acid; aqua regia oxidises both amorphous and crystalline SnS₂ to SnO₂ and H2SO4Aq. -7. Fusion with lead monoxide produces a mixture of sulphides and oxides of tin and lead; with excess of PbO, SO₂ is given off and lead remains.—8. SnS₂ was said by Dumas (S. 66, 409) to combine with stannic chloride, forming SnS₂,2SnCl₄; the compound being produced by the interaction of SnCl, and H.S. According to Coldridge (P. M. [5] 29, 383) this compound to Coldridge (P. M. [5] 29, 383) this compound does not exist, the product of the reaction being SnCl₄5H,S.—9. SnS₂ dissolves in alkali sulphide solutions, forming thiostannates (q. v., infra), M.SnS₃.—10. In alkali solutions SnS₃ dissolves, probably forming stannates and thiostannates (?3SnS₂+6KOHAq

= K_SnO₂Aq + 2K₂SnS₂Aq + 3H₂O).
Tin Sesquisurphide. Berzelius (*Lehrbuch* [5th ed.] 2, 600) gave the formula Sn₂S₃ to a greyish-yellow, lustrous solid obtained by heating a mixture of 3 parts SnS and 1 part S in a retort; the substance was almost certainly a

mixture of SnS and SnS...

Tin, sulphochlorides of: v. Tin This-CHLORIDES, infra. Tin, sulpho-iodide of; v. TIN THIO-IODIDE,

Tin, sulphocyanide of; v. vol. ii. p. 352.

Tin, telluride of, SnTe. A grey, lustrous, metal-like, crystalline solid; S.G. 6:478 at 0°: obtained by heating together tin and Te, and alowly subliming in a stream of H (Ditte, C. P. 96, 1790).

Tin, thio-acids and salts of. It is doubtful whether a thio-acid of tin has been isolated with certainty; a few salts derived from the acid

H_SnS, have been obtained.

THIOSTANNIC ACID. (Sulphostannic acid.) Kühn (A. 84, 110) obtained an olive-brown pp. by adding HClAq or H.C.H.O.Aq to a conc. solution of Na.SnS. Na.S.12H.O (v. infra); after washing, and drying at 100°, the pp. was a leadengrey, lustrous solid having the composition H.SnS.. Storch (M. 10, 255), repeating Kühn's experiments, always obtained brown pps., which did not contain more S than required by the ratio Sn:S=1:2'19. S. concluded that the pps. were mixtures of H_SnS_s and SnS_s. By adding dilute oxalio soid sojution to solution of Na_SnS_s (prepared by saturating Na_SnO_sAq with H_SS) in quantity just sufficient to combine with the Na present, S. (l.c.) obtained a deepyellow liquid which remained clear for hours; after removing the H.S by a current of air S. found that the liquid contained tin and S in the ratio Sn:3S; he concluded that H.SnS, was present in the liquid. The liquid was decolourised by NH,Aq, KOHAq, Na,CO,Aq, (NH,),CO,Aq, and NH,ClAq; strong soids gave brownish pps. containing rather more S than required by the formula SnS..

THIOSTANMATES (Kühn, I.c.; Höring, Hirsel's Zeit. für Ihiarm. 1851. No. 8). The alkali salts are obtainal by dissolving SnS, in alkali sulphide solutions, M.SAq; the alkaline earth salts are formed by double decomposition from the alkali

Potassium thiostannate K,SnS,.10H,O. Obtained by dissolving SnS, in K,SAq, and adding alcohol, when the salt separates as a dark

brown heavy oil; all H_oO is given off at 100°.

Sodium thiostanuates. The normal salt Na, SnS, 2H,O is obtained, in yellow, glassy, regular crystals, by adding tin, little by little, to molten Na.S., treating the fused mass with water, and evaporating at a low temperature. A solution of SnS and S in Na SAq deposits colourless, monoclinic crystals of the basic salt, which, when dried over H.SO, has the composition Na.SnS.,Na.S.12H.O. The stronger acids (HCl, H.SO, CliCl.,CO,H) ppt. SnS., at once from Na.SnS.,Aq; but weak acids yellow solutions from which red-brown pps, separate more or less slowly (Storch, M.10, 255). Kühn (l.c.) gives the reactions of the two Na thiostannates with solutions of several metallic . salts; many of the pps. were doubtless thiostannates of the metals employed.

PLATINO THIOSTANNATES. (Z. [2] 5, 629; 6, 270, 613) obtained scalts to which he gave the composition M.Pt.SnS. (= M.S.3PtS.SnS₂), where M=K or Na, by fusing SnS₂, Pt, M₂CO₃, and S, and lixiviating

with water.

Tin, thiochlorides of. A compound SnS₂Cl₁₈ (= SnCl₁, 2SCl₁) is said to be formed, along with SnCl., by the interaction of Cl and SnS or SnS. (H.Rose, P. 42,517). Dumas (S. 66, 409) described a compound Sn₂S₂Cl₄(= SnS₂SnCl₄) as obtained by passing H₂S into SnCl₄; but according to Coldridge (P. M. [5] 29, 383) this compound is not formed. C. (l.c.) says that the passage of H.S. into SnCl, produces white crystals of SnCl, 5H, which are decomposed by heat, giving off HCl

and H₂S, and leaving SnS₂.

Tin, thic-iodide of. By melting together crystalline SnS₂ and I, in the ratio SnS₂4I, allowing the liquid to cool, and either heating in a stream of CO2, or dissolving in CS2 and crystallising, Schneider (J. pr. 79, 419) obtained brown, lustrous crystals of SnS.1, (=SnSI,SI). This thio-iodide is disselved unchanged by CS. or CHCl2; alcohol separates S; water, or a soluor CHCl₂; alcoholseparates S; water, or a solu-tion of a caustic alkali, produces SnS₂, S, and HIAq (or MIAq); HClAq or HNO₂Aq decom-poses it, with separation of S. The compound SnS₁I, is also produced by the interaction of a solution of I in CS₂ and ppd., dried SnS₂. (S., l.c.).
TIN ORGANIC COMPOUNDS. м. м. Р. м.

1.313. V.D. 6.00 (calc. 6.15). Got 1 an alloy of tin and 1. 1 313. V.D. 6 00 (calc. 6 15). Got by heating an alloy of tin and sodium (14 p.c.) with Med (3 pt.) at 100°-120° (Ladenburg, A. Suppl. 8, 74; cf. Cahours, A. 111, 236; 114, 879). Oil, with attended to the control of with ethereal odour. Reduces alcoholic AgNO. Staunic tri-methylo-iodide SnMe₃L. (170°). S.G. ² 2·148. Formed by the action of I on SnMe. Oil. Yields crystalline SnMe,OH and the salts (SnMe₃)₂SO₄, SnMe₃O.CO.H, and SnMe₃OAc. Forms the compounds SnMe₃OEt (Ladenburg, B. 3, 358) and SnMe, I2NH, (Ca-

hours. A. 122, 56).

Stannie di-methylo-di-lodide SnM 3.L. [30°]. (228°). S.G. 22 2.872. Formed by heating tinfoil with MeI at 150° (C.). Monoclinic crystal standard of the standard Converted by ammon tals (from ether-alcohol). Converted by ammonia into amorphous SnMe₂O, which is insol. water, but dissolves in acids forming the following crystalline salts: SnMe₂Cl₂ [90°] (189°), forming trimetric crystals; a:b:c = 834:1: 941.— SnMe₂PtCl₆7aq, forming trimetric crystals; a:b:c = 888:1:977. — SnMe₂Br₂. (209°). —

2093. — ShMe,BO, forming monoclinic crystals (Hjort-dahl, C. X. 88, 584).

Stannic ethide SnEt., Mol. w. 234. (181°).
SG. 32 1-187. Formed from SnEt,L, and Etl (Buckton, A. 109, 218; 112, 223; Frankland, A. 111, 44). Formed also, together with tin and ZnEtCl, by adding fused SnCl₂ to cooled ZnEt₂ and then distilling (Frankland a. Lawrance, C. J. 35, 134). Propared by heating powdered tin with Etl and the zino-copper couple; and also by heating ZnEtl with powdered tin at 160° (Letts a. Collie, C. J. Proc. 2, 166)., Oil. Has no action at 180° on Al, Na, or Mg. Slowly absorbs sulphur dioxide, forming crystalline SO₂(OSnEt₃)₂, insol. ether and an oil SnEt₄.SO₂Et, sol. ether. Hot conc. HClAq forms ethane and SnEt Cl. Iodine forms SnEt I and IEt.

Stannous ethide SnEt. S.G. 15 1.558.
Formed by adding zine to a warm solution of SnEt. Cl. (Frankland). Oil. Decomposed at 150° into SnEt. and tin. Br forms SnEt. Br...

Distannic hexa-ethide Sn_Et,. (265°-270°).

6.G. ² 1.412. V.D. 14.8 (calc. 14.7). Got by distilling SnEt,I with sodium (Ladenburg, A. Suppl. 8, 66; B. 3, 647). Pungent oil. I forms SnEt, I. Conc. HClAq forms SnEt, Cl, ethane,

and hydrogen.

Stannic tri-ethylo-iodide SnEt, (231°) S.G. 22 1.833. Formed by the action of EtI on an alloy of tin and sodium (Ladenburg, A. Suppl. 8, 60; B. 3, 353, 647; cf. Löwig, A. 84, 308). Liquid. Combines with NH, (2 mols.). On distilling with KOHAq it yields SnEt,OH crystallising from ether in prisms [43°] (271°) converted by heat into oily (SnEt₂)₂0, which recombines with water forming the hydroxide. NaOEt converts the iodide into SnEt,OEt (191°) S.G. 2 1.263, which is at once changed by water into the hydroxide. The hydroxide water into the hydroxide. The hydroxide SnEt₀NH is sol, water, strongly alkaline, absorbs CO₂ from the air, and is converted by acids into the salts:—SnEt₂Cl. [c. 0°]. (209°). S.G. * 1.428.—(SnEt₂).PtCl.*—SnEt₂PtCl.*—SnEt₂PtCl.*—SnEt₂PtCl.*—SnEt₂Cy.—SnEt₂Cy.—SnEt₂Cy.—SnEt₂Cy.—SnEt₂Cy.—SnEt₂Cy.—SnEt₂Cy.—SnEt₂Cy.—Hexa-SnEt₂VQ.—SnEt₃NO₂—(SnEt₃),SO₂. Hexagonal prisms terminated by pyramids (Hjortdahl).—(SnLt₂)₃S.—SnEt₃SH.—(SnEt₃)₄CQ.
—SnEt₂OAc.—SnEt₂OBz.—(SnEt₃)₄CQ.
(SnEt₃)₄CQ.
(SnEt₃)₄C

to sunlight or by heating with EtI at 150° (Frank. land, A. 85, 829; Löwig, A. 84, 308; Cahours a. Riche, A. 84, 333). Needles (from alcohol), sl. sol. cold water. May be sublimed. Alcoholic NH, forms SnEt₂O, which is an amorphous powder, insol. water, converted by acids into the powder, insol. water, converted by acids into the following salts: SnEt_Cl_* [65°]. (220°), forming trimetric crystals; a.b.c= *85°:1: 945.—
SnEt_Cl.OH: plates.—SnEt_Br_* (238°). V.D.
'l1-6 (calc. 11·7).—SnEt_kNc_*)_2—SnEt_ICy.—
SnEt_(SCy)_2—SnEt_S.—SnEt_SO_*.—Crystals.
SnEt_ClOAc)_2.—SnEt_Co_*.—Formate SnEt₂(CHO₂)

Stannic ethylo-trimethide SnEtMe. (125%, 128°). Formed from SnMe, I and ZnEt, (Cahours, A. 122, 59). Oil; converted by I into EtI and

SnMe,I.

Stannic di-ethylo-di-methide (145°). S.G. 9 1.260. V.D. 6.84 (calc. 7.14). formed from ShEt L and ZnMe, (Frankland, A. 111, 50; Morgunoff, A. 144, 157). Oil.
Stannic methylo-tri-ethide SnMeEt. (163°).

V.D. 6.72 (calc. 6.65). Formed from SnEt I and ZnMe, in the cold (C.). Heavy oil.

Stannic tetrapropylide SnPr. (224°). S.G. 14 1.179. Formed from SnPr.I and ZnPr.

(Cahours, C. R. 76, 133). Pungent oil. Stannic tripropylo-iodide SnPr,I. S.G. 10 1 692. Formed from PrI and an alloy of Na and tin (Cahours a. Demarçay, C. R. 88, 725, 1112). Oil, converted by moist Ag.O into crystalline SnEt.OH.

Stannic di propylo-di-iodide SnPr2I2. (272°). Formed from tin and PrI. Oil. Converted by alkalis into amorphous SnPr₂O, insol. water, which yields SnPr₂Cl₂ [81°].

Stannic tri-isopropylo-iodide SnPr.I. (257°).

Got in like manner.

Stannic di-isopropylo-di-iodide SnPr.I.. (267°). Yields SnPr2Cl2 [57°

Stannic tri-isobutylo-iodide Sn(C,H₀),I. (285°). S.G. ¹⁵ 1.540. Formed from CH_PrI and a 9 p.c. alloy of Na in tin (Cahours a. Demarcay, C. R. 89, 68). Pungent oil, converted by KOH into $Sn(C_4H_{\nu})_3OH$ (313°).

by KOH into $Sn(C_4H_9)_3OH$ (313°). Stannic di-isobutylo-di-iodide $Sn(C_4H_9)_2I_{\bullet}$. (290°-295°). Formed by heating tinfoil with isobutyl iodide at 125°. Liquid, converted by alkalis into amorphous $Sn(C_4H_9)_2O$, and by HCl into $^4Sn(C_4H_9)_2O_2$ [261°). Stannic tetra-isoamylide $Sn(C_3H_1)_4$. Formed from isoamyl iodide and an alloy of Na (1 pt.) and tin (6 pts.) (Grimm, A. 92, 383). Liquid. Stannic tri-isoamylo-iodide $Sn(C_4H_1)_4I$.

(304°). Accompanies the preceding compound (C. a. D.). Converted by potash into oily Sn(C,H,,),OH (337°).

Stannic tetraphenylide SnPh. (over 420°). Formed by heating bromo-benzene with a tin-sodium alloy and acetic ether (Polis. B. 22, 2915). Colourless prisms, insol. ligroin, v. sl. sol. alcohol, v. sol. boiling benzene. Stannic tri-phenylo-chloride SnPh.Cl. [105].

11, 2285; A. 194, 145). Triclinic prisms; a:b:c=-588:1:1067; a=62° 47'; B=76° 48'; a:b:c='588:1:1067; $a=62^{\circ}$ 47'; $\beta=76^{\circ}$ 48'; $\gamma=94^{\circ}$ 8'. Sol. alcohol and ligroIn, missible with ether. Converted by means of water into SnPh₂(I.OH, an amorphous insoluble powder [187°]. Potash forms SnPh₂(O. Ether, alcohol, and sodium-amalgam form SnPh₂(OEt)₂ [124°]. Stannie di-phenylo-di-bromide SnPh₂Br. [c. 38°]. (230° at 42 mm.). Formed from SnPh₂ and Br (Polis), and from the oxide and HR (A.).

HBr (A.).

Stannic di-phenylo-chloro-bromide

SnPh.BrCl [39°]. Crystalline. Formed from SnPh₂Cl(OH) and HBr.

Stannic di-phenylo-chloro-iodide SnPh₂ClI.

[69°]. Yellow monoclinic crystals (from ether), decomposed by water.

TIN GROUP OF ELEMENTS. Group IV. in the periodic classification of the elements contains the following members :-

6 Even series 2 Тi Zr Ce С 11 Odd series 3 5 7 9 Si Ge Sn Ρh

Subdividing this group in accordance with the chemical similarities of the elements we get the following families :-

Carbon family: C and Si.

Titanium family: Ti, Zr, Ce, —, Th.

Tin family: Ge, Sn, -, Pb.
The carbon family is considered in the article CARBON GROUP OF ELEMENTS (vol. i. p. 682); and that article also gives a sketch of the chemical relations of all the members of the group. The elements of the titanium family are considered under the heading TITANIUM GROUP OF ELEMENTS (this vol., p. 749). The tin family is considered in the present article.

Ge occurs in small quantities, as sulphide, in a very few rare minerals. Tin and lead are found native in not very large quantities. chief ore of tin is tinstone, which contains SnO2; SnS, is also found in tin pyrites; and various micas contain more or less SnO₂. Galena, containing PbS, is the chief ore of lead; sulphate, carbonate, phosphate, &c., are also found in considerable quantities. Ge is obtained by heating siderable quantities. Ge is obtained by heating its ore with Na₂CO₂ and S, dissolving in water, decomposing Na₂S by H₂SO₄Aq, ppg. Ag (Ag.S is a constituent of the ore) by HClAq, then ppg. GeS₂ by H₂S, oxidising the GeO₂ to GeO₂ by HNO₂, and reducing the GeO₂ by heating in H or with C. Tin is obtained by calcining tinstone, washing, and reducing the SnO₂ by heating with C. To obtain lead, galena is roasted in which appearing of in the strength of the state of in such a quantity of air that it is partially oxidised, both PbO and PbSO, being formed; by then heating out of contact with much air the PbS, PbO, and PbSO, interact to form SO, and lead. Tin and lead have been known from very early times. Ge was isolated in 1885.

The table on page 736 presents some of the principal physical and chemical properties of the

tin elements.

General formulæ and characters of compounds. Oxides:—MO, MO; also Pb₂O, and Pb₂O; various hydrates of most of these oxides rp, v, various nyuraes of most of sless chards are known. Sulphides:—MS, MS, (?PbS,). Haloid compounds:—MX, and MX, Acids:—H,MX, where M=Ge or Sn, and X=either Br, Cl, F, or I; also H,PbI,; H,SnO,

and $H_xH_sSn_sO_{1s}$; $?H_2SnS_s$. Salts:—MX, and MX, where M = Sn or Pb and X = NO_s, $\frac{1}{2}SO_{ss}$ PO, &c. Salts containing M in the gPO, &c. Salts containing M in the acidic radicle: — R'₂MX_s, where M = Ge, Sn, (?Pb), and X is a halogen; R'₂MO_s, where M = Sn, or Pb; also R'₂PbO₃; also R'₂HS₀O₁& also R'₂SnS₃.

The oxides MO are basic; they react with acids to form solts MX₂, X = NO₃, §SO₄, §PO₄, &c. (no salts of GeO have yet been isolated). PhO also dissolves in matter KOM forming K PbO

also dissolves in molten KOH, forming K.PbO. The oxides MO, where M = 8n or Pb, are both basic and acidic; they react with some acids to form salts MX,; several of these salts have been isolated when M = Sn, very few when M = Pb: they also react with molten KOH or NaOH (SnO.,xH,O also with MOHAq) to form salts K2(orNa2)MOs; when M = Sn two classes of salts are known, stannates MaSnO, and metastannates, probably M. H. Sn. O13. GeO, dissolves in acids, also in molten KOH or K. CO, but the products of these reactions have not yet been products of these teactors have not yet examined. Pb₂O₂ reacts with dilute strong acids to form Pl₂O₃, and PbN₂ which dissolves; with glacial acetic acid Pb₂O₄ forms Pb(C₂H₁O₂)₂ and Pb(C₂H₂O₂)₄. Pb₂O₃ probably reacts with dilute strong acids to give PbO₂ and a sult of PbO. The hydrates of MO and MO, react similarly to the oxides. Some of the hydrates SnO, xH,O are acidic; one class of these is probably polymeric with the other. There are indications of the existence of an oxide MO, in the case of tin; this oxide seems to be acidic.

The sulphides of Ge have not been much investigated; GeS, dissolves in alkali sulphide solutions, and is probably acidic. GeS has been gasified and V.D. determined. The sulphides of tin are both basic and acidic; with hot conc. HClAq they give SnCl, and SnCl, respectively; both dissolve in alkali sulphide solutions to form thiostannates M.SnS₂. PbS is basic; with acidsit gives salts PbX₂, and H₂S; there are indications of the existence of a higher sulphide, perhaps PbS2, which will probably form thioplumbates

with the sulphides of strongly positive metals.

The haloid compounds MX₂ (none isolated yet when M = Ge) may be formed by the direct union of the elements, and by the other usual methods. SnCl₂ and PbCl₂ have been gasified, and the formulæ are molecular; molecules of the composition Sn₂Cl₄ probably exist, but are decomposed at c. the boiling-point of the compound. Several salts are known of the form M.SnX, where X = Br, Cl, F, or I; and an acid to exist. H.PbI, and salts M.PbI, have been isolated; and also several salts coming under the general formula $x \operatorname{PbX}_x y \operatorname{NH}_i \operatorname{Cl}_i$, where $X = \operatorname{Br}$ or Cl. The haloid compounds MX, have been gasified, and V.D.s determined, when M - Ge and X = Cl or I, and when M = Sn and X = Br or Cl. PbCl, has not been isolated with certainty, but Poul has not been isolated with certainty, our salts of the form M₂PbCl₂ are known, and also seems salts xPbCl₂yNH,Cl. The acids H.GeF., H.SnBr., and H.SnCl., have been cotained, and also salts derived from these acids; salts M.SnF. and M.PbCl, are also known. GeHCl, has been isolated. Many oxyhaloid compounds x.MO.yMX.

and xMO_xyMX₄ are known.

The oxyactis of tin, H₂SnO₂, and (probably)
H_xH_zSn₂O₁, are to be classed with the weak

	Germanium.	Tox.	LEAD.
Atomic weights.	72:3	118-8	206.4
	also been determiqued dir	each element have been ga ectly. There is some evidences of tin and lead, in solution	ence in favour of the con-
Melting- points.	900° , \$	2320	830°
(approx.).	· _	1,450°-1,600°	1,450°_1,600°
points. (approx.). Spec. gravs.	ნ∙5	7∙3	11-4
(approx.). Spec. heats. Atom. wts.	•0737 13·2	•0559 16·3	•0315 18·1
Spec. gravs. (approx.).			
Occurrence and preparation.	Double sulphide of Ge and Ag occurs as a rare mineral. GeO ₂ also found in some specimens of euxenite, with oxides of Nb, Ta, and Y.	Metal found in small quantities. SnO ₂ occurs in tolerable quantities widely distributed.	Small quantities of lead found. Chief ore con- tains PbS; widely dis- tributed in considerable quantities.
61	Prepared by reducing GeO ₂ by H or C.	Prepared by reducing SnO ₂ by C.	PbS, PbO, and PbSO,; also by reducing PbO by
Physical ' properties.	Greyish white, lustrous, very brittle. Crystallises in regular octahedra. Molts at c. 900°; slightly volatilised at 1,350° in N or H.	Silver-white, lustrous, malleable, but malleability varies with temperature; tenacity very small. Crystallises very easily in rhombio and quadratio forms. Melts easily (at 232°), and boils between 1,450° and 1,600°.	C, White, with tinge of blue; lustrous; very malleable and ductile; tenacity very small; very soft. Crystallises easily in regular octahedra. Melts easily (at 330°), but at higher temperature than tin, and boils be- tween 1,450° and 1,600°.
Chemical properties.	Unchanged in air at ordinary temperature; oxidised to GeO ₂ when heated in fine division. Combines readily with Br, Cl, and I when heated, forming GeX ₄ . Heated in HCl gas forms GeHCl ₂ . Dissolves in H ₂ SO ₄ Aq. No salts have yot been isolated by replacing H of oxyacids by Ge. GeO ₂ dissolves in fused KOH or K ₂ CO ₂ . H ₂ GeF ₂ Aq and salts of this acid are known.	Unchanged in pure air at ordinary temperature. Heated in air gives SnO and SnO ₂ . Heated in Br, Cl, or I forms SnX ₂ and SnX ₄ . Heated with S forms SnS and SnSe ₂ . Reacts with acids forming two series of salts, SnX ₂ and SnX ₄ , X = NO ₂ , \$\$\frac{1}{2}\$\text{PO}_1\$, \$\frac{1}{2}\$\text{Conc.}\$ HNO ₃ produces SnO ₂ xH ₂ O, SnO is basic; SnO ₂ xH ₂ O, SnO is basic; SnO ₂ xH ₂ O, SnO is basic; SnO ₂ xH ₂ O, SnO ₃ show and acidic, with strong acids forms salts SnX ₄ , and with caustic alkalis forms stannates M ₂ SnO ₂ , SnS ₂ forms thio-stannates M ₂ SnS ₃ with alkali sulphides. Stanni fluorides M ₂ SnF ₂ are known; the cids H ₂ SnCl ₂ and H ₂ SnE ₃ have been isolated. Mol. w. perhaps same as at w. in solution in Hg. Valency of atom varies from 2 in SnCl ₂ gas to 4 in SnCl ₄ gas.	Tarnishes in air, film of oxide (? Pb ₂ O) forming on surface. Melted in air forms PbO and Pb ₂ O ₂ . Combines with halogens to form PbX ₂ ; PbCl ₄ also probably isolated. Combines with S and Se, forming PbS and PbSe; PbS.xS also probably exists. Reacts with aoids forming salts PbX ₂ , X = NO ₃ , \$SO ₄ , \$PO ₃ , &c. PbO is basic; PbO ₄ feebly basic and feebly acidic; PbC(2,H ₂ O ₂), has been isolated, and probably PbCl ₄ ; with molten KOH, PbO ₄ forms K ₂ PbO ₅ . No thioplumbates isolated. No acid H ₂ PbF ₂ , or salts thereof, isolated; but 3KF.HF.PbF ₄ probably exists. Mol., w. perhaps same as at. w. in solution in Hg. Atom is divalent in gaseous molecule PbMo ₂ , as a second of the pbF ₂ .

acids; the one is probably a polymeride of the other. The salts of these acids show very distinct differences: the acids themselves interact with strong acids to form salts containing tin in the positive radicles. Of acids containing tin and halogens the following have (probably) been isolated: HSnCl_s, H_SnBr_s, and H_SnCl_s. H_GeF_s is known, and H_PbI_s is said to exist. It is doubtful whether thiostannic acid H_SnS_s, has been obtained pure, but salts of this acid have been isolated.

The salts of oryacids containing these metals in the negative radicles are MaSnO, and M.H.SnO₁, M.PbO₂ and M.PbO₃. These salts are generally easily decomposed. Oxyacids and salts of oxyacids of Ge have yet to be searched for.

Salts derived from oxyacids by replacing II by M are known when M=Sn or Ph; no Go salts of oxyacids have yet been isolated. The tin salts belong to two classes, SnX, and SnX, where X=NO₃, \(\frac{1}{2}SO_4\), \(\frac{1}{2}CO_4\), \(\frac{

The elements of the tin family are distinctly metallic in their physical properties, and in most of their chemical properties also; they exhibit, however, non-metallic characters in their highest salt-forming oxides, MO₂, which are acidic towards strong bases, while they also react as basic oxides towards several acids. The tin elements are less chemically metallic, on the whole, than the members of the even-series, or titanium family, of Group IV.; the two distinctly non-metallic elements of the group are the first member of the even series—carbon, and the first member

of the odd series -silicon.

In considering the chemical analogies of the tin elements, the position of the members of the family in their respective series should be looked to (v. table in vol. iii. p. 811). Ge comes in series 5; it is preceded by Ga, Zn, and Cu, and succeeded by As, Se, and Br: tin comes in series 7; it is preceded by In, Cd, and Ag, and succeeded by Sb, Te, and I: lead comes in series 11; it is preceded by II, Hg, and Au, and succeeded by Bi and two unknown elements. The highest salt-forming oxides of the elements preceding and succeeding the tin elements in the series are: series 5, CuO, ZnO, Ga,O,; GeO₂; As,O₃, SeO₃, —; series 5, Ag,O, CdO, III,O₃; ShO₂; Sb,O₃, TeO₃, ?I₃O, ——. The preceding oxides GeO₂ are, on the whole, more basic than the oxides preceding SnO₂ or PbO₂; and the oxides succeeding GeO₂ are on the whole more acidic than the oxides succeeding SnO₂ or PbO₃. Hence we should expect the three oxides, GeO₃ SnO₅ and PbO₂ to be about equally acidic and equally basic; SnO₂ perhaps, being the most acidic of the three. Looking at the position of the tin elements in the general periodic system, we may express the relationship of these Vol. IV.

odd-series elements to the first member of the odd-series elements to the first member of the odd series of their group (Si) by the following statements: (1) Pb:Si = Ti:Ai = Hg:Mg = Au:Na = Bi:P. — (2) Sn:Si = In:Al = Cd:Mg \(\frac{1}{2}\) Ag:Na = Sb:P. — (3) Ge:Si = Ga:Al = Zn:Mg = Cu:Na = As:P. O) the whole, Bi is more unlike P than Tl is palike Al, Hg is unlike Mg, or Au is unlike Al, Cd is unlike Mg, or Ag is unlike Na; and As is more unlike P than In is unlike Al, is more unlike P than In is unlike Al, Cd is unlike Mg, or Ag is unlike Na; and As is more unlike P than Ga is nulike Al and As is more unlike P than Ga is unlike Al, Zn is unlike Mg, or Cu is unlike Na. Hence the differences between Pb and Si, tin and Si, and Ge and Si, respectively, will be very decided. If the relations expressed in the preceding statements are worked out in detail, they show that the differences between Pb and Si will be more marked than those between tin and Si, and still more marked than those between Se and Si; but at the same time there will not be anv very great differences between these three pairs of differences. Lead, then, will on the whole be the most metallic, and the the least metallic, of the tin elements. But the three elements will resemble each other closely in so far as their general positive or negative character is concerned. Then, considering the resemblances and differences between consecutive pairs of elements in (1) series 3 and 5 (i.e. Si and Ge series), and (2) series 5 and 7 (i.e. Ge and tin series) and (3) series 7 and 11 (i.e. tin and lead series), it is evident that Ge and Si will be more alike than Ge and tin, and that Ge and tin will more closely resemble one another than tin and lead. Hence, on the whole, we may expect that Ge will form several compounds wherein the element acts distinctly as a non-metal; it is possible that GeH4 may be isolated (GeHCl, exists). Ge will form volatilisable organic compounds; GeO, will probably be found to be di- or trimorphous.

In connection with this article v. Carbon group of elements, vol. i. p. 682; and Titanium group of elements, this vol. p. 749.

M. M. P. M. TITANATES, and derivatives of, v. p. 747.

TITANIC ACIDS v. p. 746.

TITANIFLUORHYDRIC ACID II, TFIF v. TTITANIC FLUORIDE, Combinations, No. 1, p. 742.

TITANIFLUORIDES M., TFIF v. TITANIC FLUORIDES, Combinations, No. 2, p. 742.

"ITANIUM. At. w. 47.9. Mol. w. not known. Has not been fused. S.G. \$\frac{\pi}{2}\$ 3.5888 (K. Hofmann, B. 26, 1025); some older determinations ga'e S.G. c. 53 (c. Fritz, M. 1892. 772; Wilson, Pr. 32, 457 [1881]). S.H. 0° to 190° -1135, 0° to 211° -1288, 0° to 301° -1485, 0° to 440° 162 (Nilson a. Pettersson, Z. P. C. 1, 34); Fritz (M. 1892. 772) gives 13. S.V.S. 13.4.

Historical.—In 1791 Gragor found indications of a now element in a Cornish ironsand called menaccanite, from the village near which is was found (Crell's Ann. 1791 [1] 40, 103). The element was called menachin by Kirwan. In 1795 Klaproth found a compound of a new element in a mineral known as rother Schoerl zu Boinik in Hungarn, and called the element titanium (derived from Titan). In 1797 K. geognised that the chief constituent of the Hungarian mineral was the same as the characteristic constituent of menaccanite examined by

8 B

Gregor (K., Beiträge sur Kentniss der Mineralsurper). The element was isolated for the first

time by Berzelius in 1824 (P. 4, 3).

Occurrence.-Ti never occurs native. chief ore of Ti is more or less pure TiO2, which occurs in different crystalline forms as rulile and anatase (tetragonal) and brookin (rhombic). Various minerals contain TiO, con bined with SiO, and alkaline earths, e.g. titanite or sphene and ferrotitanite; compounds of titanates and nichates are found in some ware minerals, e.g. polycrase, euxenite, and pyrochlore. Varying quantities of TiO, occur in many titaniferous Varving iron ores. The ores of Ti are found in small quantities. Some of them, especially the titaniferous iron ores, are widely distributed (for analyses of Ti ores v. H. Rose, P. 3, 163; 14, 501; 15, 276; Mosander, P. 19, 211; Hermann, J. 25, 368; Berzelius, J. pr. 43, 50; Rammelsberg, P. 1858. 507; Scheerer, P. 64, 489; Groth, Tabellarische Uebersicht der Mineralien [2nd ed.] 35; O. v. d. Pfordten B. 22, 1485). Mazade (C. R. 34, 952) found traces of Ti compounds in the mineral spring of Negrac in France. For analyses and descriptions of anatase, brookite, Rath (ibid. 1878. 652). Cornu (C. R. 86, 101, 102). 983) obtained spectroscopic indications of the occurrence of Ti in the sun's atmosphere. bright-reddish crystals that are often found in blast furnaces wherein titaniferous iron ore has been smelted were supposed for many years to be Ti; but Wöhler (A. 73, 34) showed that they contain C and N besides Ti (v. TITANIUM CARBONI-TRIDE, p. 739).

Formation .- 1. By heating K, TiF, with K or Na, out of contact with air (v. Preparation) .-2. Ry heating TiCl, with Na in a closed iron crucible heated in a wind furnace (Nilson a. Pettersson, W. 4, 554; cf. Kern, C. N. 33, 57). According to Robinson a. Hutchings (Am. 6, 74), Ti is formed by heating TiCl, with Na to 130° in as sealed tube; but O. v. d. Pfordten (A. 237, 201) says that very little, if any, Ti is obtained, and that the main product is TiCl₂.—3. By fusing K₂TiF₂, with an equal weight of iron filings, and dissolving away the iron by HClAq (Wehrlin Climat C. 200, 200). a. Giraud, C. R. 85, 288).-4. By heating TiCl, to 180° with Ag obtained by reducing a salt of Ag; Ti₂Cl₆ is also formed (Friedel a. Guérin, A. Ch. [5] 7, 24).

Preparation.—Finely-powdered rutile is mixed with double its weight of K₂CO₃, and the mixture is fused in a Pt orucible placed inside an earthenware crucible. The fused mass is powdered and dissolved in the necessary quantity of HFAq in a Pt dish; water is added to dissolve which begins to separate, the liquid is boiled and filtered while boiling; the K_TiF, which separates from the filtrate in lustrous crystalline crusts, is pressed between filter-paper, washed repeatedly with cold water, again pressed. and recrystallised several times from boiling water (Wöhler, A. 74, 212). The dry K,TiF_e is and recrystalised several times from boiling water (Wöhler, A. 74, 212). The dry K,TiF_e is placed in a porcelain boat in a porcelain (or hard glass) tube connected with a supply of pure dry H; another boat, containing Na, is also placed in the tube; H is passed through the apparatus, and the Na is gradually vaporised and driven over the K,TiF_e, which is heated.

When the action is completed and the tube has cooled (the H stream being maintained), the solid is treated with water, which dissolves out KF, NaF, and Na (W. a. Deville, A. 103, 230). The Ti is finally washed with ether and dried over H.SO. (v. Kern, C. N. 33, 57). Merz (P. 73, 48) prepared Ti by heating a mixture of six pts. K₂TiF_s and three pts. NaCl with two pts. Na in a glass bulb placed in a sand-bath, while a stream of H was passed through the bulb, then adding zinc-powder and fusing, and dissolving

out the zinc by cold dilute HClAq.

Properties.—A dark-grey or black lustrous powder; has not been obtained crystallised. resembles iron reduced from Fe₂O₂ by H at a

low temperature.

According to Junot (J. 1853. 336), Ti was obtained by him as a silver-white lustrous deposit by electrolysing a solution prepared by dissolving titanate of K in boiling H₂SO₄Aq, evaporating to a syrup, and extracting with Na, SO, Aq. J.'s experiments do not seem to have been repeated. Lévy (C. R. 110, 1368) obtained hard, steel-white, cubicle crystals, which he took to be nearly pure Ti, by passing TiCl, vapour over Si, B, or several metals heated to bright redness. L. found only 80 p.c. Ti in the crystals. Ti burns brilliantly in a flame. When heated to redness in O, it is oxidised with production of an intensely Brilliant white light. also burns in Cl. It decomposes water at 100°. Warm HClAq dissolves Ti easily; it is also at once dissolved by HFAq. Heated by electric sparks, Ti gives an emission-spectrum very rich in lines (v. Thalen, A. Chr. [4] 18, 239; Troost a. Hautefeuille, C. R. 73, 620; Cornu, C. R. 86,

101, 983; Liveing a. Dewar, Pr. 32, 402).

The atomic weight of Ti has been determined The atomic weight of Ti has been determined (1) by analyses of TiCl₄ (H. Rose, P. 15, 145 [1829]; Pierre, A. Ch. [3] 20, 257 [1847]; Thorpe, C. J. 47, 108 [1885]); (2) by determining the weight of TiCl₂ (H. Rose, l.c.; Thorpe, l.c.); (3) by analyses of TiBr₄ (Thorpe, l.c.); (4) by determining the weight of TiO₂ got from a determinate weight of TiBr₄ (Thorpe, l.c.); (5) by measuring S.H. of Ti (Nilson a. Pettersson, Z. P. C. 1, 34); (6) by determining V.D. of TiCl₄ and TiI₄ (v. these confpounds). Rose's determinations gave values for the at. w. of Ti varying from 47-92 to 48-32; Pierre's values varied from 50-2 to 50-29. 48.32; Picrre's values varied from 50.2 to 50.29. The very accurate series of determinations made by Thorpe has settled the at. w. to be almost exactly 48 (48.01 if 0=16; 47.9 if 0 = 15.96).

The atom of Ti is tetravalent in the gaseous molecules TiCl, and TiI, Ti s metallic in many of its chemical properties; it decomposes water, giving off H; the oxides Ti₂O₂ and TiO₂ form corresponding salts; the chloride and iodide (and ? also bromide) can be gasified without decomposition; the sulphide TiS₂ does not show any acidic characters so far as it has been examined. The chlorides give pps. of corresponding hydrated oxides by reacting with alkalis, &c. On the other hand, Ti exhibits distinctly non-metallic or chlorous properties; hydrates of TiO, act as feeble acids, producing salts wherein Ti forms part of the negative radicle. The acids H.TiF. and H₂TiO₂F, are known, and also salts derived therefrom. TiCl₄ is very easily decomposed by

water, giving HClAq and TiO, xH,O, &c. As might be expected from the two-sided character of the reactions of Ti, most of the salts obtained by replacing the H of oxyacids by Ti are basic salts. The oxide TiO, has been isolated; it is probably a superoxide. Ti is closely related to Zr, Ce, and Th; these elements, with Ti, form the even-series family of Group IV. (v. TITANIUM GROUP OF ELEMENTS, p. 749). Ti is also closely related to Ge, Sn, and Pb, which form the oddseries elements of Group IV. (v. TIN GROUP OF ELEMENTS, p. 735). Ti also shows distinct relationships to C and Si, which are the first and second members of Group IV. (v. CARBON GROUP OF ELEMENTS, vol. i. p. 682). The similarity between Ti and Si is shown very distinctly in the titanic and silicic acids, the relations between which may be expressed by such a general equation as $nMH_1O_4 - mH_2O = M_nH_{4n-2m}O_{4n-m}$ (M = Ti or Si). Ti is the only element of Group IV. which is known to form compounds of the type $M_2TiO_2F_4 = Ti(OM)_2F_4 = TiX_6$.

Reactions and Combinations .- 1. Heated in air or in oxygen, burns brilliantly to TiO ... 2. Burns when heated in chlorine, forming Ti₁Cl.—3. TiI₄ is formed by passing vapour of iodine over hot Ti.—4. Combines with nitrogen when heated therewith (v. Nitrides, p. 743). -5. Ti is violently oxidised to TiO, by heating with cupric oxide or red lead .- 6. Interacts with water at 100°, forming TiO₂ and H.—7. Dissolves in warm hydrochloric acid, forming TiO₆ (Glatzel, B. 9, 1831; Rammelsberg, B. B. 1874. 490).—8. Ti dissolves easily in hydrofluoric acid (? forming Ti_F_s); also in warm dilute nitric or sulphuric acid, according to Glatzel (I.c.), the solution in H.SO, Aq deposits crystals of Ti_(SO₄), on cooling. Cone hot H.SO, reacts with Ti, giving off SO₂ (? forming Ti(SO₄).); cone. hot HNO₄ oxidises Ti to metatitanic acid

(q. v., p. 747) according to Weber (P. 120, 287).

Detection and Estimation.—Compounds of Ti are not reduced to metal by heating on char-coal in the blowpipe flame. Ti compounds, if not containing elements which give a colour to microcosmic salt, form a colourless glass when melted in the microcosmic salt bead in the outer blowpipe flame; in the inner flame they give a glass which is colourless when hot, but becomes violet on cewling; the delicacy of the reaction is much increased by adding a little zinc to the bead (Riley, C. J. 12, 13). Solutions of TiO₂xH₂O in HClAq or H₂SO₄Aq give white pps. of TiO2.xH2O on boiling; addition of a piece of tin to a solution of TiO_xH_O in HClAq causes evolution of H and produces a violet-blue solution which becomes rose-coloured on dilution with water (von Kobell, P. 62, 599). A solution of TiO,xH,O in HClAq gives a violet-red liquid. (Ti,Cl, solution) by digestion for some time with Cu (Fuchs, A. 56, 319). Ti is estimated as TiO₂, ppd. from solutions by a slight excess of NH,Aq. Insoluble compounds of Ti are generally fused with KHSO,, the fused mass is dissolved in water, and TiO₂-xH₂O is ppd. by long continued boiling.

Titanium, alloys of. The alloys of Ti have not been much examined. Wöhler a. Michel (A. 113, 248; 115, 102) obtained an alloy with aluminium approaching in composition to TiAl,

cryolite, and treating with HClAq. By heating a mixture of Ti and Al with KCl or NaCl in an earthenware crucible in a stream of H, Lévy (C. R. 106, 66) obtained brittle steel-grey crystals which he took to be an isomorphous mixture of TiAl, and JiAl. Ti alloys with iron; it is often present in pig-iron, but rarely in bar-iron or steel (v. Raley, C. J. 16, 387).
Titanium, bromides of. Only one bromide

has been isolated, TiBr,

TITANIC BEOMEDE TiBr. (Titanium tetrabromide.) Mol. w. has not been determined, but the formula is almost certainly molecular from

analogy of TiCl, and TiI.

Prepared by passing Br vapour over a mixture of TiO, and chargoal heated to full redness, collecting the liquid that distils over and solidifies in the receiver, and redistilling it from Hg (to remove free Br) (Duppa, Pr. 8, 42). Also prepared by passing HBr gas over TiCl, kept a few degrees below its boiling-point in a distilling flask connected with an appright condenser; the whole of the Cl of the TiCl, is expelled (Thorne, C. J. 47, 126). Therpe used 350 g. TiCl, and continued the passage of HBr for three days. The HBr is conveniently obtained by the interaction of Br and amorphous P in a little water; it is freed from Br by passing through a U tube containing broken glass and amorphous 12 and is dried by passing through another U tube containing CaCL.

TiBr, forms dark-yellow or orange crystals. S.G. 2 f. melting at c. 40°, and boiling at c. 229° (D., l.c.; T., l.c.). It is very hygroscopics easily decomposed by water, forming a perfectly clear

solution containing HBr and TiO₂ or Li₂O.

Titanium, bromochlorides of. By adding Br to TiCl, (q. v., p. 741) Friedel a. Guérin (A. Ch. [5] 8, 21) obtained a colourless liquid, furning in the air, boiling at 176°, which they said was probably TiBr Cl.; and by the reaction of Br with Ti Cl. they obtained a liquid boiling at 154°. probably TiBrCla

Titanium, carbonitride of, Ti CN. (Titanium nitrocyanide, or cyanonitride Ti, (CN)2N6.) This compound is often found in blast furnaces wherein titaniferous ironstone has been smelted. It was supposed by Wollaston to be Ti (G. A. 75, 220), and was for many years generally mistaken for the metal. In 1850 Wöhler (A. 73, 34) proved it to contain C and N besides Ti.

The compound is found in blast furnaces as luttons, around a contain C.

lustrous, opaque, copper-coloured, prismatic crystals. By treating these crystals with conc. HClAq, then with conc. H.SO, washing, treating with HFAq, and again washing, the compound is freed from admixed Fe, &c.; small leaflets of graphite generally remain mixed with the car-bonitride. Ti.CN, can be prepared by heating a mixture of dry K,FeCy, and TiO, in a closed crucible for an hour or two at c. the melting-point of Ni (1400° to 1450°), dissolving out Fe, &c., by cone. HClAq, washing, and drying. By exami-ning the brown powder thus obtained with a magnifying power of 300 diameters coppercoloured crystals of Ti₅CN₄ can be detected (Wöhler, A. 73, 34). It is also obtained by heating a mixture 1 part C and 5² parts TiO₂, in a closed carbon crucible for some hours at 1400° to 1450°; also by passing N over a mixture of by heating a mixture of TiO2, KCl, NaCl, and C and TiO2 in the ratio 1:53 heated in a carbon boat placed in a carbon tube to the melting-point

oost placed in a carbon tube to the melting-point of Pt (c. 1800°) (W. a. Deville, A. 103, 231).

When Ti, ON, is fused with KQH it gives off NH₂; heated to redness in a stream of water vapour TiO₂ is formed, and H, NH₃, and HCN are given off (W., l.c.); heated in Cl it gives TiCl, and TiCl, 2HCN (W., l.c.; also p. 219); the compound is burnt by heating with PbO, CuO, or HgO, giving off CO₂ and leaving TiO₄ and Pb. Cu, or Hg (much heat is produced in the and Pb, Cu, or Hg (much heat is produced in the reaction) (W., l.c.).

The simplest formula that expresses the composition of Ti carbonitride is Ti, CN, (W., l.c.; cf. Reinhardt, Zeit. für anorgan. Chemie, 1, 121). This formula is generally doubled and written Ti(CN)...BTi,N2, and the substance is regarded as a compound of cyanide and nitride of Ti; Joly (C. R. 82, 1195) regards it as a compound of carbide and nitride of Ti, and writes the formula

TiC.4TiN (or 2TiC.8TiN).

Titanium, chlorides of. Ti and Cl combine to form TiCl,; by the regulated action of H on TiCl, one-fourth of the Cl can be removed and TiCl, produced; and by the further action of H on TiCl, one-third of the Cl can be removed and TiCl, produced. The V.D. of the tetrachloride has been determined, and the formula TiCl, is molecular; from the analogy of C.Cl, and Si,Cl, it is probable that the molecular formula of the trichloride is Ti2Cla; from the analogy of PbCl, and SnCl, the formula TiCl, may be supposed to be molecular, but if the analogy of C2Cl, is to be followed, the molecular formula must be Ti.Cl.

Titakie chloride TiCl, (Titanium tetra-chloride.) Mol. w. 189:38. Melts at -25° (Haase, B. 26, 1052). Boils at 136.41° at 760 mm. (Thorpe, C.J. 37, 329). S.G. $_{45}^{92}$ 176041; S.G. at b.p. 152223 (Thorpe, t.c.). V.D. 98·8 at 143° (Dumas, A.Ch. [2] 33, 388). S.V. 121·47 (Thorpe,

l.c.).

Preparation. - 1. TiO₂ is intimately mixed previously with c. half its weight of lampblack previously heated to redness in a stream of Cl, and the mixture is heated to full redness in a tube of hard glass connected with a receiver, while a stream of dry Cl is passed over it. The TiCl, which collects in the receiver is freed from Cl by shaking with Cu, Hg, or Na amalgam (Merz, Bl. [2] 7, 401), or by boiling for some time (Thorpe, C. J. 47, 119), and is then distilled. Thorpe (l.c.) conducted the final distillation in dry N.— 2. Vapour of CCl,, or a mixture of equal volumes of Cl and CO, is passed over TiO2 in small lumps, heated to bright reduces in a tube of hard glass connected with a receiver. The TiCl, is purified as described above (Watts a. Bell, C. J. 33, 443).

Properties.—A colourless liquid, solidifying at -25° (Haase, B. 26, 1052). Does not conduct electricity (O. v. d. Pfordten, A. 237, 201). Fumes in the air, rapidly absorbing moisture and solidifying to the hydrate TiCl, 5H2O (Demoly, A. 72, 213). (For an apparatus for collecting TiCl, for analysis, v. Thorpe, l.c.) TiCl, is violently decomposed by water, forming HClAq, and TiO2xH2O some of which ppts. (v. Reactions, No. 8).

Reactions.—1. Hydrogen reduces TiCl, at a high temperature, to Ti_Cl, and then to TiCl, (v. trichloride and dichloride) .- 2. Mixed with oxygen and passed through a red hot porcelain tube, Ti,O,Cl, is formed (v. Oxychlorides, p. 748). 3. Heated to 130° in a sealed tube with sodium, the chief product is TiCl₂, according to 0. v. d. Pfordten (A. 237, 201); Robinson a. Hutchings (Am. 6, 74) say that Ti is produced in this reaction. Nilson a. Pettersson (W. 4, 554) obtained Ti by reducing TiCl, by Na at a very high temperature.—4. Sodium analgam produces Ti.Cl. and TiCl. (O. v. d. P., l.c.).—5. Reduced silver gives Ti.Cl. and Ti when heated with TiCl. to 180 (Friedel a. Guérin, A. Ch. [5] 7, 24).—6. By passing vapour of TiCl, over silicon, boron, or several neetals, heated to bright redness, Levy. (C. R. 110, 1368) obtained hard, steel-white, cubical crystals which he supposed to be nearly pure Ti .- 7. Pure, dry, hydrogen sulphide reacts at the ordinary temperature, forming Ti₂Cl₈; at a higher temperature a pp. is produced which is probably a thiochloride of Ti (O. v. d. P., A. 231, 257). -8. Cold water reacts violently with TiCl. with production of much heat and formation of a turbid liquid containing HCl and holding in suspension 2TiO₂H₂O (v. Metatitanic acid under TITANIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 747); after 30 or 40 hours the liquid becomes clear, but ppn. occurs again on heating to c. 85° when about 7 pts. water are present to 1 pt. TiCl, used (v. Thorpe, C. J. 47, 120; and cf. Titanium oxyacius, p. 746). According to Merz (Bl. [2] 7, 401), an oxyadioride, approximately TiCl, 3TiO_16H_O, is obtained by evaporating TiCl₁Aq, or TiCl₁ that has deliquesced in air, over H₂SO₄ and CaO (v. Oxychlorides, p. 748). TiO₂, in the form of brookite, is obtained by passing vapour of TiCl₄ and water, mixed with CO2, through a red-hot porcelain tube (Daubrée, C. R. 29, 227; 39, 153). -9. With hydrochloric acid the compounds TiCl₂OH and TiCl₂(OH)₂ are formed (b. Trianium hydroxyl chiloribes, p. 743). -10. Chlorosulphonic acid (SO₂OH.Cl) reacts with TiCl, at the ordinary temperature to form a yellow, amorphous, deliquescent powder, having the composition TiCl₄·SO₄ (-TiCl₃·OSO₂·Cl) (Clausnizer, B. 11, 2011).—11. By passing vapour of TiCl, mixed with H. through a white-hot tube containing titanium dioxide the oxychloride Ti_O_Cl2 is obtained (v. Oxychlorides, p. 748).

Combinations .- 1. With water to form a pentahydrate and a dihydrate. Demoly (A. 72, 213) obtained TiCl, 5H,O, as deliquescent crystals, by allowing TiCl, to absorb moisture from the air, then adding a little more water, and evaporating under reduced pressure. By drying the pentahydrate over H₂SO₄ in vacuo, D. obtained TiCl₄,2H₂O.—2. With ammonia, to form TiCl. 4NH, according to H. Rose (P. 16, 57), TiCl. 6NH, according to Persoz (A. Ch. [2] 46, 315); easily decomposed in air; heated in a tube gives off NH₃, then NH₃ and HCl, and a yellowish sublimate of TiCl, 3NH, Cl, and leaves Ti; heated in NH, gives Ti, N, (v. TITANIUM NITRIDES, p. 743). 3. With hydrogen phosphide, to form a brown powder, which when heated gives a sublimate of TiCl. 2PH.Cl according to H. Rose (P. 42, 527).

4. With hydrogen cyanide to form TiCl. 2HCN (Wöhler, A. 73, 226); by vaporising this compound through a red-hot tube Ti,N, and C are formed (W. 1.a.). S. With cyanges a hilwide. formed (W., l.c.).—5. With cyanogen chlorids, to form yellow crystals of TiCl, ONCl; sublimable at 100° (W., A. 73, 219).—6. With phosphorus

mentachloride to form TiCl. PCl,; obtained by heating TiCl, and PCl, to 150° in a sealed tube (Bertrand, Bl. [2] 33, 565); also by heating TiO, and PCl_s in the ratio TiO₂:3PCl_s, or by saturating a mixture of TiCl₄ and PCl₅ with Cl (Tüttscheff, A. 141, 111), and removing excess of TiOl, by heating in a stream of Cl (Weber, P. 132, 452). A citron-yellow, loose, semi-crystalline solid; sublimes without melting; deliquescent in air. 7. With phosphorus trichloride to form vellow crystals of TiCl, PCl, melting at 85.5° (Bertrand, 1.c.).-8. With sulphur tetrachloride, to form 2TiCl, SCl,; obtained by saturating a mixture of TiCl, and S,Cl, with Cl, and warming in a stream of Cl (Weber, P. 132, 454).—9. By mixing TiCl. and sulphurous chloride H. Rose obtained large yellow crystals, probably a compound of the two yellow crystals, propaging a compound of the two chlorides (P. 42, 527),—10. With ammoniam chloride, to form TiCl, 3NH, Cl (v. supra, Combinations, No. 2).—11. With phosphoryt chloride to form TiCl, POCl,; obtained by gradually adding POCl, to TiCl, and gently warming (Weber, P. 132, 453); colourless, deliquescent sensitive matters and boilinest 1102. crystals, melting at 110? and boiling at 110 (Wehrlin a. Giraud, C. R. 85, 288).—12. With selenion oxychloride to form a yellow powder, decomposed by heat, having the composition TiCl, 2ScOCl₂; obtained by adding ScOCl₂ to TiCl, and drying the solid that separates on riol, and drying the solid may separates on cooling on a tile over H₂SO₄ (Weber, B. B. 1865, 154).—13. With nitrosyl chloride; obtained by saturating TiCl₁ with NO₂, and subliming (Hampe, A. 126, 47), also by passing the vapours from aqua regia into TiCl, (Weber, P. 118, 476). Hampe (l.c.) gives the composition 3TiCl. 4NOCl, Weber (l.c.) the composition TiCl. 2NOCl. A deep citron-yellow, crystalline mass; decomposes in air; sublimable out of air; with water gives off NO.—14. With sulphur trioxide to form TiCl₁.SO₂ (or TiCl₂.OSO₂.Cl), formed by the interaction of TiCl₄ and SO₂.OH.Cl at the ordinary temperature; a yellow, amorphous, deliquescent powder (Clausnizer, B. 11, 2011). --15. Demarçay (Bl. [2] 20, 127) obtained a great many compounds of TiCl, with esters, mercaptans,

and ethyl sulphide (cf. Bedson, C. J. 29, 309).

TITANIUM TRICHLORIDE Ti.Cl., (Titanium sesquichloride, Titanous chloride.) Mol. w. not determined; but from analogy of C.Cl., and

seguicinoriae. Titanous chloriae.) Mol. w. not determined; but from analogy of C.Cl.sand Si_zCl_s the formula Ti_zCl_s is probably molecular. Formation.—1. By reducing TiCl₁ by H (c. Preparation).—2. By reducing TiCl₁ by H (c. Preparation).—2. By reducing TiCl₁ by Sodium-amalgam (O. v. d. Pfordten, A. 237, 201); or by pure, dry H_zS (O. v. d. P., A. 234, 257).—3. By heating TiCl₁ with reduced Ag to 180°; Ti is also formed, and probably TiCl₂ also (Friedel a. Guérin, A. Ch. [5] 8, 24).—4. A solution of TiCl₂ also obtained by digesting a solution of TiC₂aH_zO in HClAq with Cu at 40°-50° (Fuchs, A. 56, 319); or with Ag ppd. by zinc from AgCl (von Kobell, P. 62, 599). Ti_zCl_s is also probably present in the greenish liquid obtained by adding Na amalgam to K_zTiF_s in HClAq (O. v. d. P., A. 237, 201).

Preparation.—TiCl, is placed in a retort connected with a tube of porcelain or hard glass (if a glass tube is used it should be wrapped in copper-foil) which is placed horizontally in a furnace; the other end of the tube projects considerably out of the furnace and is connected with a receiver to collect undecomposed TiCl.

The delivery tube from an apparatus evolving pure and dry H passes into the retort beneath the surface of the TiCl. H is passed through the apparatus until it is entirely filled with the gas; the tube is then heated to redness, and the retort is gently warmed. Ti_zCl_z is formed and condenses as dark-violet scales on the part of the tube that projects out of the furnace. When all the TiCl_z in the cooler part of the tube retort, the Ti_zCl_z in the cooler part of the tube is gently warmed, while the pusage of H is continued, to remove any adhering TiCl_z; the Ti_zCl_z is allowed to cool in the stream of H (Ebelmen, A. Ch. 13, 20, 385).

Properties.—A dark-violet, very lustrous solid, deliquescing in air, and dissolving in water to form a violet liquid, which gradually decolourises with ppn. of TiO₂xllO. *TiOl, is easily soluble in alcohol, forming a violet or green liquid; it is insoluble in ether, and sparingly soluble in HClAq (O. v. d. P., A. 237, 201).

Reactions.—1. Hented in hydrogen to c. 440°. TiCl, distils over and TiCl, remains (Friedel a. Guérin, A. Ch. [5] 8, 24).—2. Heated in air, TiCl, vaporises and TiCl, remains.—3. Dissolves in water, forming a violet, or green-violet, liquid which slowly becomes colourless with ppn. of TiCl, x40,—4. Alkalis, or alkali carbonates, in solution ppt. Ti₂O₃x41.O from Ti₂Cl₃Aq; ammoutum satphide forms the same pp.: hydrogensulphide gives no pp. (Ebelmen, l.c.).—5. Ti₂Cl₃Aq reduces solutions of gold, siteer, or platinum salts with ppn. of the metals; ferric and cupric salts are reduced to ferrous and cuprous salts; sulphurous acid volution is reduced by heating with Ti₂Cl₃Aq with ppn. of S (F., l.c.).—6. Ti₂Cl₃ reacts with bromine to form a liquid boiling at 154°, probably TiBrCl₁ (F. a. G., l.c.).

Combinations. — With water to form TL₂C_{0.8}H₁O; obtained by Glatzel (B. 9, 1829) by evaporating a solution of Ti in HClAq to the crystallising point, filtering off ppd. TiO_{2.2}H_{2.0} from time to time. The hydrate is a green solid; it dissolves in water, forming an opalescent violet solution containing a little suspended TiO_{2.2}H₂O; the solution becomes colourless on standing, and then gives the reactions of titanic acid.

Therefore TiCl_x (Sometimes called titanous chloride.) Mol. w. is not known. From analogy of SnCl_x and PbCl_x, the formula TiCl, would be molecular; but from the analogy of C_zCl₄ the molecular formula would be Ti_zCl₄.

of C.Cl., the molecular formula would be Ti.Cl.,
Formation.—1. By reducing Ti.Cl. by H
(v. Proparation..—2. TiCl. is probably formed,
along with Ti.Cl., by heating TiCl, with reduced
Ag (Friedel a. Guérin, A. Ch. [5] 8, 24).—3. Along
with Ti.Cl., by the action of Na annalgam on
TiCl.,; also by heating TiCl, with Na to 130° in
a scaled tube (O. v. d. Pfordien, A. 237, 201).

Irreparation.—Ti_Cl_n reacts with H at a red heat to give TiCl_n and TiCl_n. Friedel a. Guérin (l.c.) proceed as follows. The tube containing Ti_Cl_n, prepared from TiCl₁ (v. supra?, while still filled with H, is connected with an apparatus evolving pure, dry CO₂, and the whole of the H in the apparatus is driven out by CO₂. The Ti_Cl_n is then shaken into a small tubulated retort, placed on a sand-tray, and previously filled with CO₂; the CO₂ is displaced by pure, dry H; the retort is then heated to dull red

ness, while a stream of H is passed through it, until TiCl, ceases to distil off; the retort is allowed to cool in the stream of H, and CO, is then passed in until all the H is removed (if this is omitted the TiCl, takes fire in the air), and the black TiCl, in the retort, is quickly shaken into small dry tubes filled with CO, which are at once scaled off.

Properties.—A black, light powder; very rapidly absorbs water, forming a kind of mud; insoluble in CS, CHCl, or Et.O. Volatilised without melting by heating to full redness in II. Shaken with Et,O and KCNSAq, the Et,O becomes dark brown; this is a delicate test for TiCl₂ (O. v. d. Pfordten, A. 237, 201).

Reactions.—1. Takes fire when touched with a drop of water (? with formation of Ti₂O₂Cl₂; v. F. a. G., l.c.); thrown into water, it hisses like red-hot iron, decomposing the water with evolution of H and formation of a yellowish liquid.—2. Decomposes absolute alcohol, giving off H and forming a yellowish liquid.—3. Heated and leaving TiO₂—4. With bromine it forms a liquid boiling at 176°, probably TiCl₂Br₂ (F. a.

Titanium, chlorobromides of, v. TITANIUM

BROMOCHLORIDES, p. 739.

Titanium, cyanonitride of, v. TITANIUM

CARBONITRIBE, p. 739.

Titanium, ferrocyanides of, v. vol. ii. p. 337. Titanium, fluorides of. The only compound that has been isolated with certainty is TiE. There are indications of the existence of Ti₂F_s, and compounds of this fluorido with alkali fluorides are known.

TITANIC FLUORIDE TIF, (Titanium tetra-fluoride). Formula probably molecular, from analogy of TiCl, and TiI, By heating a mixture of TiO, and CaF, with H.SO, Unverdorben (P. 7. 200) extended a solvable distillation which he 7, 320) obtained a colourless distillate, which he supposed to contain a compound of Ti and F. Berzelius (P. 4, 1) obtained crystals (? TiF_i) by dissolving TiO_{2.} xH₂O in HFAq. The crystals were decomposed by water, giving an acid solution (? H₂TiF₆Aq), and an insoluble, 'so to say basic,' compound. TiO₂ is obtained by passing vapour of TiF, mixed with H₂O, through a tube heated to c. 800° or 1000° (Hautefeuille, A. Ch. [4] 4, 131; cf. TITANIUM DIOXIDE, p. 741). Heated to redness in H, perhaps gives Ti₂F₆ (H., l.c.).

Combinations .- 1. TiF, probably combines with hydrogen fluoride to form H. Tilfa. By diswhen hydrogen fatories to folial first of dis-solving TiO_xxH₂O in HFAq, evaporating, adding water to the crystals (? TiF₄) thus formed, and filtering from an insoluble solid (? oxyfluoride). Berzelius (P. 4, 1) obtained an acid solution from which, by neutralisation with KOHAq and exaporation, he obtained the salt K, TiF_s. The said solution probably contained H_sTiF_s. This compound (if it exists) is best called titanifuorhydric acid. It is analogous to H_sSiF_s. HASIF_n, and other acids of the type H₂MX_n, where M = an element of Group IV. (except C), and X = a halogen.—2. With various metallic fluorides to form TiF_n:2MF = M₂TiF_n. These salts were obtained from the K salt, which was got by neutralising the acid solution prepared as described under 1. Salts of NH4, Ca, Cu, Fe, Pb, Mg, and Ni are described (B., Lc.; Weber,

P. 120, 291). These salts are best called titanifluorides; they are similar to stannifluorides.—3. TiF, also combines with ammonium fluoride to form TiF,3NH,F (besides

TiF..2NH,F) (Baker, C. J. 35, 763).

By adding NH,Aq, drop by drop, to warm (NH,),TiF,Aq, Piccini (G. 17, 479) obtained a compound of the form TiO,F,xNH,F; from this he prepared TiO₂F₂Barr, and by carefully decomposing this salt by H₂SO₄Aq he obtained a solution of the acid TiO₂F₂PiF. P. regards this acid as a F derivative of the hypothetical pertitanic acid H.TiO, (the acid of TiO,); he calls the acid fluoroxypertitanic acid, and the cans the acid nuoroxypertianates. Following the plan adopted in this Dictionary, the acid will be called titanoxyftuorhydric acid H_TiO_F, and the salts, M'_TiO_F, will be called titanoxyftuorides. H_TiO_F, Aq is a yellow liquid, not ppd. by Ba salts, giving a pp. of TiO, with alkali carbonates.

TITANIUM TRIFLUORIDE Ti.F. This compound is said to be formed by strongly heating K.TiF. in a stream of H with a little HCl, according to Hautefeuille (C. R. 59, 189; cf. 57, 151). Acradicted (C. 17. 59, 189; cf. 61, 181). According to H., the compound is a purple-red solid, soluble in water. By treating Ti_Cl_Aq with KIHF_0 ro NH_F, Piccini (G. 16, 104) obtained violet pps. of Ti_F_2NF, where M = NH_0 or K; he also obtained Ti_F_3NH_F. The K salt is slightly soluble in water; soluble in dilute acids, forming green liquids, from which alkalis throw down azure-blue pps. that gradually oxidise to TiO_xxH_O on exposure to air. The

salt TiF, 3NH,F, when exposed to air, gradually oxidises to TiO.F..3NH,F.

Titanium, haloid compounds of. Ti combines with the halogens directly to form compounds TiX4; these tetrahalides are generally prepared by passing the halogen as gas over a red-hot mixture of TiO₂ and C. TiI₄ is best-prepared by heating TiCl₄ in HI gas, and TiBr₄ is very conveniently prepared by heating TiCl, in HBr gas; TiF, is prepared by dissolving TiO, xHO in HFAq and evaporating. The two tetrahalides TiCl, and Til, have been gasified. These formulæ are molecular, hence the formulæ TiF, and TiBr, probably also represent the compositions of the gaseous molecules of these compounds. By the action of H, or certain other reducing agents, on TiCl, two chlorides are obtained, Ti_xCl_x and Ti_xCl_x. The V.D. of neither has been determined, but from the analogy of C₂Cl₄ and Si₂Cl₅, the value of x in Ti₁Cl₂* is probably 2; from the analogy of C₂Cl₄, the molecular formula of the lowest chloride is probably Ti₂Cl₄, but from the analogy of SnCl₂ and PbCl₂ the formula TiCl₂ would be of SnCl, and PbCl, the formula TiCl, would be given to it. Ti.F. or TiF, probably exists. No bromide or iodide of either type Ti.X. or Ti.X. has been isolated. Two bromochlorides of the types TiX, and Ti.X. probably exist. TiCl, and TiBr, dissolve in cold water; the solutions contain HXAq and TiO...xH.O; dilution, and more quickly heating, ppts. insoluble TiO...xH.O from the solution of TiCl. FiF, is decomposed by water, giving H.TiF. aq (and? an oxyfluoride). TiI, is also decomposed by water; on heating insoluble TiO...xH.O separates. TiCl. combines insoluble TiO, xH₁O separates. TiOl combines with many non-metallic chlorides and oxychlorides. TiF₄ combines with metallic fluorides,

forming salts M.TiF., and also some more complex salts xTiF.yMF. A few oxylaloid compounds have been isolated, but a great number can doubtless be formed. The acid H.TiO.F. and salts of this acid have been isolated. dissolves in water, and after a time TiO..xH.O separates; the solution is an energetic reducing agent; alkalis ppt. Ti₂O₃.xH₃O. TiCl₂ reacts violently with water, giving off H, and probably

forming an oxychloride.

Titanium, hydroxyl chlorides of. By the reaction of the proper quantity of 36 p.c. HClAq with TiCl₄, the compound Ti(OH)Cl₃ was obmined by Koenig a. O. v. d. Pfordten (B. 21, 1708); using the calculated quantity of 36 p.c. HOIAq, the compound Ti(OH)₂Cl₂ was produced; and the prolonged action of ordinary air on either of the preceding compounds resulted in the formation of Ti(OH), Cl. These compounds are regarded by K. a. O. v. d. P. as derived from Ti(OH), by replacement of OH by Cl; the compounds may be called orthotitanic chlorhydrins. The compounds are yellow or white deliquescent rapidly with a hissing noise, Ti(OH)Cl₂ less violently, and Ti(OH)₃Cl with some difficulty. The aqueous solutions give pps. of TiO_{2...}"1.0 on boiling. When the compounds are heated they give (1) TiO_{1...} and TiO_{2...}"1.0, (2) "iO_{2...}"11.0 and HCl, and (3) TiO, TH,O, HCl, and H.O. By reducing Ti(OH)Cl, by Na analgam, in H, Ti,O, is produced (K. a. O. v. d. P., B. 22, 2070; cf. B.22, 1485).

Titanium, hydroxyl fluoride of. This name may be given to the compound Ti(OH), F4; it is described as titanoxyjluorhydric acid,

under TITANIC FLUORIDE (p. 742).

Titanium, iodides of. Only one compound

has been isolated, TiI,.
TITANIC TODIDE TII,. (Titanium tetraiodide.) Mol. w. 554 02. V.D. at 410° = 261.2

(Hautefeuille, Bl. [2] 7, 201).

Formation.—1. Vapour of I is passed over Ti heated to redness (Weber, P. 120, 287). -2. A mixture of TiCl, vapour, I vapour, and H is passed through a tube heated to dull redness; TiI, mixed with free I, condenses on the colder part of the tube (Hautefeuille, Bl. [2] 7, 201). -3. By decomposing TiCl, by HI.

Preparation. — Dry HI gas is passed into

TiCl, which is gradually heated to its b.p. and kept at that temperature until the reaction is completed; the TiI, is freed from traces of I, which give it a violet tinge, by a few distillations

in H (H., l.c.).

Properties and Reactions .- A reddish-brown, lustrous, brittle solid; when melted and cooled, crystallises in octahedra, changing after some days to tufts of silky, prismatic crystals. Melts at 150°, and boils a little above 360°; can be at 100°, and boils a little above 300°; can 130 distilled without decomposition; metted TiI, remains liquid till cooled below 100°. Furnes strongly in the air. Dissolves easily in water; solution turns brown on exposure to air and ppts. TiO,xH,O. When vapour of TiI, is heated in air it burns to TiO, and I,O, (H., l.c.).

Titanium, nitrides of. Four compounds of Ni and New hear described, but exceedings to

Ti and N have been described; but according to later experiments only two seem to exist.

TRITITANIUM TETRANITRIDE Ti, N4. Mol. w. unknown. This compound is obtained by heating

TiCl. 4NH. (v. TITANIC CHLORIDE, Combinations, No. 2, p. 740), loosely packed in a tube of hard glass, in a stream of dry NH, until the glass begins to melt, and allowing to cool in NH, (Wöhler, A. 73, 43; Friedel a. Guérin, A. Ch. [5] 8, 24). Indigo blue powder, or golden-yellow (? rhomboltedral) crystals; strongly heated in H gives Ti.N., (F. a. G., l.c.).

DITTARIUM INSTRUDE TI.N. Mol. w. unknown. Prepared by placing two porcelain boats, one containing Na and the other K.Tif. in a hard-glass sube previously filled with N, passing a stream of dry N through the tube. heating the K.TiF, to full redness while the Na is volatilised over it, and allowing to cool in N after all the Na has been volatilised; boiling with HClAq, washing, and drying (Wöhler a. Deville, A. 102, 234). Also obtained by heating K₂TiF₄ with K, KCl, NaCl, and Al in №; also by passing TiCl, vapour and II over heated Al, in N; also by passing vapour of TiCl, over heated NH₁Cl (W. a. D., l.c.). F. a. G. (l.c.) obtained the same compound by strongly heating TiO, in a stream of dry NH, for some hours; W. (A. 73, 43) said that TiN, was formed by this reaction. F. a. G. also obtained Ti.N. by strongly heating Ti.N. in II; W. said that Ti.N. was formed by this reaction. An amorphous brown-yellow, very hard powder; S.G. 5.28 at 18° (F. a.

G., l.c.).

The nitrides of Ti are not decomposed by heating, out of air, to c. 950° 1,000°; fused with KOH, or strongly heated in steam (F. a. G., l.c.), they give off NH₃; heated in Cl. TiCl, is produced (F. a. G., Lc.); heated with CaO, Pho, or HgO, the nitrides burn, and Cu, Ph, or Hg is produced (W., A. 123, 34).

TITANIUM DINITRIDE TINg. This compound is formed, according to Wohler (A. 73, 43), by heating TiO, in NII₃ for some time. Friedel a. Guérin (A. Ch. [5] 8, 21) say that the substance obtained by W. contained TiO₃, and that if the heating is continued until a definite nitride is heating is continued until a usually formed the compound so produced is Ti_N_. Formed,

PENTATITANIUM HEXANITUDE Ti,N,. Formed, according to W. (l.c.), by heating Ti,N, to full redness in H; or, mixed with C, by heating TiO₂ in CN or HCN gas. F. a. G. (l.c.) say that the product of either reaction is Ti, N2, in the latter reaction mixed with C.

Titanium, nitrocyanide of, v. TITANIUM

CARBONITHEDE (p. 739).

Titanium, oxides and hydrated oxides of (cf. TITANIUM OXYACIDS AND SALTS AND DERIVATIVES THEREOF, p. 746). Ti burns when heated in O, forming Thy.; by the reaction of reducing agents on TiCl₄Aq, and addition of alkalis, Ti₂O₄ is obtained; when the reduction is carried H₂O₂ is obtained, that TiO.xH₂O is formed. By the feaction of H₂O₂Qq in presence of alkali on salts of TiO₂, a pp. of TiO₂ is obtained. Oxides intermediate between TiO2 and Ti2O2 probably exist. TiO, is a basic oxide, forming salts TiX, where X = NO,, \$SO, &c.; many of the salts are basic. A few salts corresponding with TiO. have been isolated; no salt corresponding with TiO and derived from an oxyacid has yet been obtained. Some of the hydrates of TiO, react as feeble acids.

TITANIUM DIOXIDE TIO, (Titanic oxide. Titanic anhydride.) Mol. w. unknown.

Occurrence.—As rutile, anatase, and brookite; rutile occurs in dimetric prisms, isomorphous with tinstone; anatase in dimetric octahedra; and brookite in trimetric octahedra.

Formation.—1. By burning Ti in air or 0.—
2. By ppg. TiCl, Aq by alkali, and washing, drying, and strongly heating the ppd. TlO₂xH₂O.—

8. By ppg. K₂TiF₄Aq by NH₂Aq, and strongly heating the pp. after washing and drying.—

4. Vapour of TiCl₄, or TiF₄, mixed with steam is paged through a way heat this. passed through a red-hot tube. -5. TiS2 is heated in dry CO_2 (TiS₂ + $2CO_2$ = TiO_2 + 2CO + 2S; O. v. d. Pfordten, B. 22, 2070).

Preparation.-A. Amorphous titanic oxide.—1. Pure TiCl, is added, little by little, to water; sufficient NH₃Aq to neutralise the HCl produced is added, the solution is evaporated to dryness, and the residue is heated to somewhat above 700° until it ceases to lose weight. TiCl, may be obtained from rutile by mixing the finely-powdered mineral with c. half its weight of dry charcoal-powder, making into little pellets with starch-paste, drying the pellets, heating them to full redness in a covered crucible, then heating in a tube of hard glass (to get quite dry), and then passing dry Cl over the pellets while they are heated to bright redness, and a dry receiver is connected with the end of the hard glass tube. The TiCl, may be purified from SiCl₄, FeCl₅. &c.) by repeatedly distilling, best in a stream of N (v. Merz, J. pr. 99, 161).—2. K_TIF₄ is dissolved in water, NH₂Aq is added, the pp. of TiO₂.xH₂O is thoroughly washed, dried, and heated to somewhat above 700 . . (For a and neated to somewhat above 700°. (For a methods of getting K₂TiF₆ from rutile v. Preparation of titanium, p. 738.) For other methods of preparing TiO₂ from Ti ores v. Lévy (A. Ch. [6] 25, 511), Austen a. Wilber (Am. 4, 211), Hempel (Zeit. f. anorg. Chemie, 3, 193), Jones (Fr. 9, 41, 380). B. Crystalline titanic oxide .- 3. By long-continued heating to whitepess TiO₂ is said to become crystalline (n. Rammelsberg, B. 5, 1006).—4. Amorphous TiO₂-xH₂O is heated to incipient redness in HCl gas, at a pressure of three atmospheres; the crystals have the form of anatase (Hautefeuille a. Perrey, C. R. 110, 1038).-5. Crystalline TiO, is also formed, according to Hautefeuille (A. Ch. [4] 4, 127), by passing the mixed vapours of TiF, HF, and HCl—obtained by decomposing molten K. TiF. by HCl gas—through a Pt tube into which a stream of moist H is also passed; at c. 860° (boiling-point of Cd) crystals of anatase are produced, and at temperatures between 860° and 1,000° brookite is formed. 6. Heating amorphous TiO2 in an atmosphere of HF causes crystallisation; at an incipient red heat anatuse forms, at a higher temperature brookite, and at a very high temperature rutile (H_c, l.c.).—7. Crystals of rutile are formed by heating amorphous TiO₂ with microcosmic salt (Ebelmen, A. Ch. [3] 33, 34), or with borax (G. Rose, B. B. 1887, 190; Knou. 4, 157, 355), in a proreclaim 1867. 129; Knop, A. 157, 365), in a porcelain oven. For other methods of producing crystals of TiO₂ v. Deville (C. R. 53, 161, 163), Senarmont (A. Ch. [3] 30, 129), Michel (C. R. 115, 1020), Wöhler (A. 73, 35), Daubrée (C. R. 29, 227; 39, 153), H. Rose (A. 56, 127; 68, 163).

Properties .- TiO, obtained by strongly heating TiO, xH,O forms reddish-brown lumps, more nearly resembling rutile in colour and lustre the

higher the temperature to which it is heated. The dehydration by heat of TiO2.xH2O is ac. companied by the appearance of shades of colour from white, though grey and greenish, to black, according to Wagner (B. 21, 960); these colours are similar to those shown by anatase, brookite, and rutile. Nilson a. Pettersson (Z. P. C. 1, 33 note) prepared TiO₂ as a white powder with faintest yellow tinge, by decomposing TiCl₁ by NH₂Aq, evaporating, and heating to whiteness. NH₄Aq, evaporating, and neating to wniteness. When melted by the O-H flame the colour is blue to black. S.G. TiO₂ increases as the oxide is heated; heated to c. 700° S.G. is c. 3.95 (Karsten, S. 65, 394), after being very strongly heated S.G. rises to 4.25 (Ebelmen, J. 4, 15; 12, 14). S.G. of anatase is 3.75 to 3.9 (Breithaupt, J. 2, 730; Damour, J. 10, 666); S.G. of brookite is 4 to 4.2 (Rammelsberg, J. 2, 730; Beck, J. 3, 704); S.G. of rutile is c. 43 (Scheerer, P. 65, 296; Müller, J. 5, 847). After fusion in the O-H flame and cooling S.G. is 41, according to Hautefeuille (A. Ch. [4] 40, 140). S.H. 0° to 100° = 1785, 0°-211° = 1791, 0°-301° =:1843, 0° -440° =:1919° (Nilson a. Pettersson, Z. P. C. 1, 27; TiO₂ prepared by decomposing TiCl₄ by NH₃Aq, evaporating to dryness, and heating to white heat). TiO₂ crystallises in dimetric prisms (rutile), dimetric octahedra (anatase), and trimetric octahedra (brookite); it is isotrimorphous with SpO₂ (Wunder, J. pr. [2] 2, 206). TiO₂ is somewhat hygroscopic, even after prolonged and intense heating (Thorpe, C. J. 47, 125). It is insoluble in water, and in TiO_x is heated with conc. H_xSO_x until the excess of acid is removed, the solid thus produced dissolves in water. TiO₂ melts in the O-H flame. According to Moissan (C. R. 115, 1034), when heated in an electric furnace to c. 2500° TiO₂ forms black crystals of TiO.

Reactions .- 1. According to Ebelmen (A. Ch. [3] 20, 394), TiO₂ is reduced to Ti₂O₃ by heating to redness in hydrogen; but O. v. d. Pfordten (A. 237, 201) says the product has the composition Ti,O₁₂.—2. A mixture of TiO₂ and magnesium powder heated to redness in H gives Mg/TiO₃, and a brown powder which is probably TiO (Winkler, B. 23, 2657).—3. A mixture of TiO₂ and carbon strongly heated in chlorine gives TiCl. 4. By long-continued heating in dry ammonia Ti2N2 is formed (Friedel a. Guérin, A. Ch. [5] 8, 24).-5. The compound TiCl, PCl, is obtained by heating an intimate mixture of TiO₂ and phosphorus pentachloride, in the ratio TiO₂:3PCl₃, in a retort until the POCl₃ formed is driven off (Weber, P. 132, 452).—6. Heated to redness in carbon tetrachloride vapour, TiCl, is formed (Watts a. Bell, C. J. 33, 443). Demarqay (C. R. 104, 111) says that the first product is TiOCl...—7. TiCl, is formed by heating TiO₂ to redness in a mixture of equal volumes of chlorine and carbon monoxide (W. a. B., l.c.) .-8. Ti2N2 mixed with C is formed by heating TiO2 in cyanogen or in hydrogen cyanide (Friedel a. Guérin, A. Ch. [5] 8, 24).—9. Heating in a nixture of hydrogen sulphide and carbon disulphide forms Ti₂S₂ or TiS₂, according to the temperature (Thorpe, C. J. 47, 491).—10. When TiO₂ is fused with sodium or potassium carbonate the weight of CO₂ expelled corresponds with the formation of M₂TiO₂; on treating the fused mass with water MOHAq is formed, and an acid Na or K titanate which is insoluble in water (v. Hermann, J. pr. 38, 92).—11. Fusion with potassium hydrogen sulphate forms a substance soluble in water; by evaporating the fused mass with conc. H.SO,, and then treating with water, the double salt Ti(SO₄)₂.K.₂SO₄.3H₂O is obtained (Warren, P. 102, 449; Glatzel, B. 9, 1833; Hermann, l.c.).—12. Heating powdered TiO₂ with conc. sulphuric, acid produces a substance that dissolves wholly in water (?forming Ti(SO₄)₂.xH.O or TiO.SO₄; v. Merz, J. pr. 99, 157). For reactions of TiO₂.xH₂O 1, infra, hydrated titunic oxide; and v. also titunic acid under Titanium oxyacids and Salts AND DERIVATIVES THEREOF, p. 746).

HYDRATED TITANIC OXIDE. Hydrates of TiO, are obtained by gradually adding TiCl, or TiBr, to cold NH3Aq; by fusing TiO, with KHSO, dissolving in water, diluting, and boiling for some time; by adding water to TiCl, and boiling; by fusing TiO, with K.CO, washing the fused mass with small quantities of water till all KOII is removed, adding a little conc. HClAq, filtering cold, and allowing the liquid to stand, when it gradually deposits gelatinous TiO_xH₂O_x (O.v. d. Pfordten, B. 17, 727); by decomposing Ti(OEt), by H₂O (Demarçay, C. R. 80, 51); and by other reactions. The isolation of a great many definite hydrates of TiO2 has been announced from time to time. By decomposing TiCl, PCl, (v. Titanic chloride, Combinations, No. 6, p. 740) by the action of moist air, and drying over H.SO., Tüttscheff (A. 141, 111) said that the dihydrate TiO, 2H₂O was formed, and by drying this at 110²-120⁹ he said that the monohydrate TiO, H₂O was obtained. According to Carnelley a. Walker (C. J. 53, 66, 81), dehydration of TiO, xH₂O (obtained by adding TiCl, to cold NEA at a lightly for 14 days prepared some NH₃Aq), air-dried for 14 days, proceeds continuously from 15° to 710° whereat the whole of the water is removed. A very large number of hydrates probably exists, and these pass one into the other as temperature rises without any of them remaining unchanged through more than a few degrees.

a rew degrees.

Two classes of hydrates of TiO₂ exist; one obtained by ppg. TiCl₄ by NH₄A4, or warming TiO₂ with conc. H₂SO₃ dissolving in water, diluting, and ppg. by alkali; the other obtained by dissolving hydrates of the former class in dilute acid, and boiling. Hydrates of the former class dissolve easily in dilute acids, while those of the latter class are insoluble in dilute acids (for more details v. Titanium oxyacids, p. 746).

Hydrated TiO₂, obtained by ppn. by alkali in the cold, dissolves in dilute acids, forming salts TiX₁, where X = NO₃, \(\frac{1}{2}\)SO₃, \(\frac{1}{2}\)Co.; not many salts of this form have been isolated, and most of those that are known are basic salts. TiO₂, xH₂O dissolves in molten H₂PO₄; on cooling crystals of TiO₂P₂O₄(-TiP₂O₂) are obtained (Hautefeuille a. Margottet, C. R. 102, 1017). By heat-TiO₂xH₂O with a little cold conc. HClAq, pouring off the solution after a few days, and evaporating it in vacuo, Koenig a. O. v. d. Pfordten obtained cfystals approximating to Ti(OH)₂Cl₂, but differing from Ti(OH)₂Cl₂ pyepared by the interaction of TiCl₄*and HClAq (B. 22, 1485; cf. TITAMIUM HYDROXYL CHLORIDES, 748)

TITANIUM SESQUINOXIDE Ti.O. (Titanous

oxide.) Mol. w. unknown. By digesting a solution of TiO, xH.O in HClAq with Cu at 40° to 50°. Fuchs (A. 56, 319) obtained a violet solution which gave a brownish black pp. with NH,Aq; the pp. quickly reacted with water, giving off H and forming WiO. xH.O. Von Kobell (P. 62, 599) obtained similar reactions by using reduced Ag in place of Cu. Ebelmen (J. pr. 42, 73) obtained a hearly black pp. by adding alkali to Ti.Cl.Aq. According to Ebelmen (J. pr. 42, 76) Ti_O, can be prepared by heating TiO, to redness in perfectly dry H. Ti.O₃ thus prepared is described as a black solid; unacted on by HNO₅ or HClAq; oxidise to TiO, only by heating to a very high temperature; soluble in H, SO, Aq, forming a violet solution. According to O. v. d. Pfordten (A. 237, 201), the product of reducing $T(O_2)$ in H is not $T(O_3)$ but has the composition $T(O_3)$. Friedel a. Guerin (A. Ch. [5] 8, 38) obtained $T(O_3)$, but not free from other compounds, by passing TiCl, vapour mixed with H over TiO, at a red heat. They describe TiO, as a copper-red, metal-like, microscopically crystalline powder; not acted on by boiling HNO₃Aq, but oxidised to TiO₂xH₂O by boiling H₂SO₄Aq; soluble in HFAq or warm aqua regia; giving off NH, and H with hot alkali solutions; oxidised to TiO, by heating to redness in air.

O. v. d. Pfordten (B. 22, 2070) failed to obtain Ti,O, by the method of F. a. G.

Ti_O, by the method of P. a. O. When Ti is dissolved in hot HClAq, in an atmosphere of H, the solution contains Ti_ZCl_Z Rammelsberg, J. pr. 99, 176); a solution of Ti_{O,x}, H_ZO in HClAq reduced by zine also contains Ti_ZCl_Z (K. a. O. v. d. P., Lc.); in these solutions alkalis give black pps., probably Ti_{O,x}, H_ZO; the pps. soon change in contact w.th H_ZO to Ti_{O,x}, H_ZO, H being given off. According to O. v. d. P. (A. 237, 201), a solution of K, TiF, in a little HClAq gives a pp. of Ti_ZO,xH_ZO on treatment with Na-amalgam.

Sabatier a. Senderens (C. R. 114, 1429; 115, • 236) say that Ti O_z is oxidised to TiO_z by heating to c. 500° in NO_z or to c. 300° in NO_z.

TITANICH MONOXIDE TIO. This oxide has not been isolated with certainty. According to Moissan (C. R. 115, 1034) black prisms, which he took to be TiO, are formed by heating TiO, to c. 2500° in an electric furnace, and at a higher temperature the (?) TiO melts and then volatilises. By heating a mixture of TiO, and Ma powder to reduess, in H. Winkler (B. 28, 2657) obtained a brown powder which probably contained some TiO, mixed with MgTiO. According to Berthier (A. Ch. [2] 54, 374) TiO, lost 6 p.c. O when heated strongly in a carbon grueible, 13 to 16 p.c. O when heated with 12 p.c. C, and 20 p.c. O when heated with 12 p.c. C, and 20 p.c. O when heated with 24 p.c. C (TiO, 405cc 20 p.c. O in becoming TiO); the product may have been a mixture of TiO, Ti₂O₃, and Ti.

HYDRATED TITANIUM MONOXIDE

TiO.H., O. TiO.H., O. v. d. Pfordten (A. 237, 201)
obtained a black pp., said by him to be TiO.H.,
by the continued action of Na-amalgam on a
solution of K.TiF, in a fair amount of HULAq
(if there is little HClAq.Ti_O, is ppd.); the solution became green, then colourless, and then the
black pp. was formed. The black pp. formed by
NH,Aq, alkali carbonates, or (NH,),SAq, in solutions of TiOl, (q. v., p. 741) is TiO,H, according

to O. v. d. P. (l.c.). With Na₂HPO₄Aq, and NaC₂H₄O₂Aq, TiCl₂ is said to give bluish-black and greenish-black pps., which may be salts of TiO (O. v. d. P., l.c.).

TITANIUM PEROXIDE. TiO3. (Titanium trioxide or superoxide.) In 1882 (Atti dei Lincei, 1882. 1) Piccini dropped H₂O₂Aq into solution of TiO₂xH₂O; from the quantity of H₂O₂ that reacted he concluded that an oxide TiO₃ was produced. In the same year (B. 15, 2599) Weller obtained a yellow pp., which reacted with HClAq, giving off Cl, by the interaction of H₁O₂Aq and freshly ppd. TiO₂xH₂O or a solution of TiO₂xH₄O. In 1808, Classen (B. 21, 370) added TiCl₃, drop by drop, to dilutealcohol, the related to this calculation. then added to this solution a very large excess of H₂O₂Aq, and then KOΠΛq, NH₄Aq, or (NH₄)₂CQ₃Aq; in each case he obtained a yellow liquid from which a yellow pp. separated after some time; after syphoning oif the liquid, washing the pp. by decantation, and drying it on a tile, he obtained a yellow solid approximating to the composition TiO, 3H.O. In 1889, Lévy (C. R. 108, 294) approximately determined the composition of the pp. obtained by adding H₂O₂Aq to TiO₂.xH₂O in H₂SO₄Aq, by dropping in H₂O₂Aq of known concentration, and determining the quantity of H2O2 used in the reaction ; L. concluded that the results could be accounted for by supposing the yellow pp. to be TiO₃, TiO₂H₁O₃, or Ti₂O₃H₂O₅ but that probably the pp. was TiO₄. In 1893 Bailey a. Dawson (Studies from the Phys. and Ohem. Laboratoria of the Owens College, vol. i. p. 216) obtained yellow to orange solids, agreeing fairly in composition with the formula TiO,. B. a. D. added (1) H₂O₂Aq, (2) freshly ppd. BaO₂, to TiO₁.xH₂O in dilute H₂SO₄Aq, diluted the deep-red liquids thus obtained with twice their volumes of alcohol, added conc. alcoholic solution of KOH. washed the pps. with alcohol (to remove H₂O and H₂O₂), and then with ether, and, in some cases, dried in the air. According to B. a. D., TiO₃ dissolves in water, forming a deep-red liquid; this solution decolourises KMnO Aq; TiO, dissolves in HClAq, giving off Cl. By allowing ppd. TiO, to stand for some time, B. a. D. say that a modification is formed insoluble in water.

OXIDES OF TITANIUM INTERMEDIATE BETWEEN

TiO₂ AND Ti₂O₃.

I. By heating TiO₂ with HCl gas in a reducing atmosphere, Deville (C. R. 53, 163) obtained a blue, crystalline solid, to which he gave the formula TiO₂ Assimilated (1) and the solid to the solid time of the solid time o mula Ti,O. A similar solid (? same composition) was obtained by Friedel a. Guérin (A. Ch. [5] 8, 44) by passing H and HCl over TiO2 strongly heated in a porcelain tube. This blue solid is said to decompose water, in presence ef strong bases, giving off H and forming TiO.

II. By very strongly heating TiO, in H, O. v. d. Pfordten (A. 237, 228) obtained a dark indigo-blue solid, to which he gave the formula. Ti,O12; according to Ebelmen (J. pr. 42, 76), Ti.O. is formed by this reaction. Heated in air

the compound burns to TiO2.

III. By adding alcoholic solution of KOH to a solution of TiO₂xH₂O in dilute H₂SO₂Aq, after treating the solution with BaO₂, Piccini (Atti dei Lincei, 1882. 1) obtained yellow pps. with com-positions varying from Ti₂O₁₁ to Ti₂O₂.

Titanium oxyacids and salts and derivatives thereof. The hydrates of TiO2 react as feeble acids, besides reacting with the stronger acids as feeble bases. The salts wherein Ti forms part of the acidic radicles are generally obtained by fusing TiO2 with salts of the metals which are to be converted into titanates. Only a very few titanates are soluble in water; several dissolve in HClAq, but on diluting and boiling most, if not all, of the TiO2.xH2O is ppd.

TITANIC ACIDS. Hydrates of TiO, are obtained by various reactions (v. Hydrated titanic oxide. p. 745). By drying under different conditions solids are obtained approximately corresponding with the formula $x\text{TiO}_x y\text{H}_2\text{O}$, where x=1,2, or 3, and y=1,2,3,4, or 5. (For a list of the hydrates obtained by different experimenters v. Tüttscheff. A. 141, 111.) There seems to be a series of hydrates of TiO2, all of which may be classed together under the name titanic acids, none of them being stable through more than a few degrees of temperature (v. Carnelley a. Walker, C. J. 53, 66, 81); the relations of composition of these acids may be expressed by such a general equation as $n \operatorname{TiH}_1 O_1 - m \operatorname{H}_2 O = \operatorname{Ti}_n \operatorname{H}_{4n-2m} O_{4n-m}$

The titanic acids belong to two classes: those which are formed by decomposing TiCl, or TiBr, by dilute cold alkali solutions, or by warming TiO2 with conc. II2SO, dissolving the product in water, and ppge by dilute cold alkali solutions; and those which are formed by decomposing TiCl, or TiBr, by water and boiling, or by dissolving titanic acids of the former classin dilute acid and boiling, or by fusing TiO2 with KHSO, dissolving in much water and boiling. The acids of the former class are generally called titanic acids or ortho-titanic acids, and those of the latter class meta-titanic acids. Orthotitanic acids dissolve easily in dilute acids: metatitanic acids are insol. dilute acids; by prolonged heating with conc. H2SO4 compounds are produced which dissolve on adding water. Metaacids are also formed by heating ortho- acids to c. 100°. Experiments made by Merz (J. pr. 99, 166) show that the meta-acids lose water, on heating, more easily than the ortho- acids.

ORTHOTITANIC ACIDS. According to Wagner (B. 21, 960), a clear solution of an orthetitanic acid is obtained by adding water, a drop at a time, to TiCl,, with constant shaking; HCl and TiCl, are given off (by the heat of the reaction), a solid is produced, then a greenishyellow liquid, and finally a clear solution. By adding 1 pt. TiCl, to c. 6 to 7 pts. water, Thorpe (C. J. 47, 120) obtained an opalescent liquid which became clear after standing for 40 hours. and then contained orthotitanic acid; when this solution was heated ppn. of metatitanic acids began at c. 87°, and at c. 90° most of the Ti was ppd. A solution of TiBr, in water forms a perfectly clear liquid containing orthoacid (T., l.c., p. 126). The white flocoulent solid obtained by adding TiCl, to dilute HClAq, ppg. by NH, Aq when cold, washing with cold water, and drying in the air is TiO₂.2H₂O (=TiO₄H₄), according to Merz (*J. pr.* 499, 166); this composition is also assigned to the solid formed by keeping TiCl₄.PCl₄ under a bell-jar, with water and CaO, for some days, and then drying over H_2SO_4 (Tüttscheff, A. 141, 111). When TiO_4H_4 is dried in vacuo (Tüttscheff, Lc.), or over H.SO.

(Mers, i.e.), the product is said to be TiO2.H2O (Mers, i.e.), the product is said to be 1102.1120 (= H.TiO₂ = TiO.O₂H₂). The composition 2TiO₂H₂O (= H.Ti₂O₃ = Ti₂O₂.O₂H₂) is given to the product dried at .100° (Merz, i.e.; Demoly, O. R. 1849. 325), dried at 140° (Tüttscheff, i.e.), or dried in vacuo over H.SO₄ (H. Rose, A. 52, 268); after drying at 100° or upwards, meta-

acids are probably produced.

mermay kabilah

Orthotitanic acids are insoluble in water or alcohol; but dissolve easily in dilute acids; said also to dissolve in alkali carbonate solutions. The solutions in acids probably contain salts of the type TiX, X = Cl, NO_3 , SO_4 , &c.; but compounds of the form $Ti(OH)_2X_y$, where X is a monovalent acidic radicle, and x is not greater than 3, may be formed, similar to the compounds Ti(OII),Cl, Ti(OH)₂Cl₂, and Ti(OH)Cl₃, obtained by O. v. d. Pfordten by the interaction of HClAq and TiCl₄ (B. 21, 1708; v. TITANIUM HYDROXYL CHLOBIDES, p. 753). By adding a little cone. cold HClAq to orthotitanic acid, allowing to stand for some days, pouring off the clear liquid from undissolved acid, and evaporating in vacuo, Koenig a. O. v. d. P. (B. 22, 1485) obtained a white solid containing Ti and Cl in the ratio 1:147; they regarded this as consisting chiefly either of TiCl. (OH), but different in some properties from TiCl (OII)2 obtained from TiCl,—or chiefly of TiCl(OII), IICl.
White pps. are obtained by adding H₂PO₁Aq. H₂AsO₄Aq, or H₂C₂O₄Aq to solutions of ortho-titanic acids in dilute HClAq, HNO₃Aq, or H₂SO₄Aq, after making nearly neutral by NH₃Aq. When acid solutions of orthotitanic acids are diluted considerably and boiled for some time the whole of the Ti is ppd. as meta-acids. Ortho- acids are also partly changed to metaacids by keeping under water for a long time (Wagner, B. 21, 960), or by washing with hot water. When an orthotianic acid is heated strongly TiO₂ is produced, with vivid incandescence; the change from a meta-acid to TiO. is not accompanied by incandescence. According to Wagner (l.c.), the dehydration of moist ortho- acids by gently warming is accompanied by changes of colour from white to grey, green, and black.

METATITANIC ACIDS. Formed, as white powders, by dissolving ortho-acids in dilute acid and boiling for some time; also by fusing TiO2 with KHSO4 and boiling with much water; also by adding water to TiCl, or TiBr, and boiling; also by adding water to Hol, of This, and dolling, as by oxidising Ti by HNO, S.G. 1.25 (Weber, P. 120, 287). According to Weber (l.c.), freshly prepared dilute TiCl, Aq is not rendered turbid by HClAq, HNO, Aq, or H, SO, Aq, but these acids by HClAq, the second of the second sec at once ppt. metatitanic acids when added to dilute TiCl,Aq that has been boiled even for a few seconds. The pp. obtained by boiling a diluted solution of an orthotitanic acid in dilute diluted solution of an orthotitanic acid in dilute H_SO_sis said to have the composition TiO_21I_2O (=TiO_iH_1) when dried over H_SO_t the composition 3TiO_14H_2O (=Ti_0O_iH_1 - Ti_0O_iO_iI_1) when dried at 120°, and the composition STiO_24H_2O (=Ti_0O_iH_1 - Ti_0O_iO_iH_2) when dried at 140° (Tüttscheff, A. 141, 111); Merz (J. pr. 99, 166) gives the composition TiO_iH_2O (=TiO_iH_2) to the air-dried 120. and the composition 2TiO_iH_2O (=Ti_1O_iH_2) to the pr. dried over H_SO_4, or at 60°. ക്ക Metatitanic acids are white powders, insoluble

in water or dilute acids; after heating with conc. H2SO, the products dissolve in water; when strongly heated TiO. is formed without incandescence

COLLOIDAL TITANIC ACIDS. Graham (T. 1861. 213) obtained a gelatinous, probably orthotitanic, acid, insoluble in water, by dialysing a solution of TiO_.rH_O in HClAq; by dissolving this gelatinous acid in such a quantity of cold dilute HClAq that not more than 1 p.c. titanic acid was present in the solution, and dialysing for several days, G. (C. J. 17, 325) obtained a dilute aqueous solution of colloidal titanic acid. Colleidal, insoluble, titanic acids have also been prepared by Knop (A. 123, 351), Rose (G. A. 73, 76 [1823]), and O. v. d. Pfordten (B. 17, 727).

TITANATES. These salts have not been thoroughly investigated. Those which have been best examined are either derivatives of H.TiO, or II TiO, or are basic salts of the type &MO.TiO, where &>1. Some acid salts MO.xTiO., where a>1, are also known. The older investigations were made chiefly by II. Rose (P. 61, 507) and by Hautefeuille (A. Ch. [2] 4, 129).

Barium titanates. An acid siglt 2BaO.3TiO₂ (=2BaTiO₂.TiO₂ or Ba₂TiO₂.2TiO₂) was obtained by Bourgeois (C. R. 103, 141) in lustrous microscopic crystals, by heating to full redness a mixture of equivalent parts of TiO, and BaCO, with excess of BaCl, and washing with very dilute HClAq.

Calsium titanates. The normal salt CaTiO. occurs native as perowskite. The same salt was formed by heating to bright redness a mixture of equivalent parts of TiO, and CaCO, .ith excess of CaCl., and washing with very dilute HClAq

(Bourgeois, l.c.).

Iron titanates. The mineral titaniferous iron or ilmenite is more or less pure xFe2Ox.yTiO2. By fusing a mixture of 2 pts. TiO, and 5 pts. Felia with a large excess of NaCl, washing with water, and then with very dilute acid, Hautefouille (C. R. 59, 733) obtained dark purple-violet, (G. R. 59, 755) obtained that proposed lustrous crystals of ferrous titanate Fe,TiO, (=2FeO.TiO.); but according to Koenig a. O. v. d. Pfordten (B. 22, 1485) the salt produced of the control of the con is ferric titanate Fe4(TiO4), (2Fe,O4.3TiO2). K. a. O. v. d. P. say that the salt dissolves in water after warming with conc. H2SO, forming a green solution containing Fe2(SO4)2 and titanic acid.

Magnesium titanates. The normal salt MgTiO (= MgO TiO) was obtained (by Haute-The normal salt feuille, i.c.) by heating to whiteness, for a short time in a closed crucible, a mixture of 1 pt. TiO, and 10 pts. MgCl2 with a little NH4Cl, washing with extremely dilute acetic acid, and then with water; lustrous, six-sided (probably trimetric) crystals, S.G. 3-91. The same salt is formed, according to Winkler (B. 23, 2657), by heating a mixture of TiO₂ and Mg powder. By heating a mixture of 2 pts. TiO₂, 1 pt. MgQ, and 40 pts. MgCl, and washing with very dilute acetic acid, the salt Mg.TiO, (= 2MgO.TiO₂) is said to be formed in hard, lustrous, regular octahedra, S.G.

3.42 (H.).

Potassium titanates. When TiO, is fused with excess of K₂CO, the quantity of CO₂ given off corresponds with the formation of the

normal salt K.TiOs; after fusion two layers are obtained, the lower of which is said to consist of K₂TiO₃, while the upper contains the undecomposed K₂CO₃. K₂TiO₃ is described as a yellowish, fibrous, easily fused solid (H. Rose, P. 61, 507). Water resolves it (according to Rose) into an insoluble acid salt, and a soluble basic salt; but according to Hermann (J. pr. 38, 92) no trace of titanic acid goes into Colution in water, but all remains in the insoluble acid salt.

Sodium titanates. The normal salt Na, TiO, was obtained by H. Rose (l.c.) similarly to the K salt; water resolves it into an insoluble acid salt and NaOHAq. By heating Na₂WO₄, and in some cases also WO₃, with mixtures of TiO₂ and Na₂CO₃ previously fused, Cormimbouf (C. R. 115, 823) obtained three acid salts:

(1) 2Na, O.3TiO₂ (= 2Na, TiO₃.TiO₂, or Na, TiO₄.2TiO₄), (2) Na, O.2TiO₂(Na, TiO₃.TiO₃, or $Na_2Ti_2O_3$), (3) $Na_2O.3TiO_2$ (= $Na_2TiO_3.2TiO_3$, or

Strontium titanates. An acid salt
2SrO.3TiO₂ (=2SrTiO₃:TiO₂ or Sr₂TiO₄:2TiO₂)
was obtained, in pale-greenishyellow cubes, S.G. 5.1, by Bourgeois (C. R. 103, 141), by heating equivalent parts of TiO₂ and SrCO₃ with excess of SrCl2, and washing with very dilute HClAq.

Zinc titanates. The normal salt ZnTiO, was obtained by Lévy (C. R. 107, 421), by heating to redness & mixture of 2 pts. TiO₂, 8 pts. ZnSO₄, and 3 pts. K.SO., and washing with dilute HClAq; pale-violet, silky needles, S.G. 3.17, scarcely acted on by boiling conc. acids or cone. KOHAq. By varying the proportion of TiO, ZnSO, and KSO used, L. (l.c.) obtained the normal salt Zn, TiO, which may also be regarded as a basic salt ZnTiO, znO; the basic salt BZnO.2TiO₂ (= 2ZnTiO₃.ZnO); and the acid salt 4ZnO.5TiO₂ (= 4ZnTiO₃.TiO₂).

FLUOTITANATES; v. Titanifluorides, under TITANIC FLUORIDE, Combinations, No. 2 (p. 742).

FLUOROXYTITANATES: v. Titanoxyfluorides, under Titanic fluoride (p. 742).

MOLYBDOTITANATES. A few compounds of the form TiO.12MoO.2M.O.xaq, where M = NH, and K, are described by Péchard (C. R. 117, 788). By shaking with ether a solution of the NH, salt, acidified by HClAq, and allowing the ethereal liquid to evaporate, P. (l.c.) obtained molybdotitanic acid TiO₂-12MoO₂-22aq, in golden yellow octahedra, melting at c. 60°, very soluble in water.

OXALOTITANATES. By dissolving

TiO_xxH_xO in hot KHC_xO₄Aq end cooling, Péchard (C. R. 116, 1513) obtained triclinio crystals of 2KHC₂O₄.TlO₂.H₂O. By treating a solution of this salt with BaCl₂Aq, crystals of Ba(HC,O4)2.TiO2.H2O were obtained; and by decomposing this by an equivalent quantity of dilute H,SO,Aq, filtering, and evaporating in vacuo, long needles of oxalotitanic acid 2H₂C₂O₂.TiO₂.2H₂O were obtained.

SILICOTITANATES; v. this heading,

7. 464.
Titanium, oxychlorides of. Several oxychlorides are known. (1) TiOCl_w. According to Demarçay (C. R. 104, 111), this is the first product of heating TiO₂ and CCl₄ in a sealed tube; it is described as a yellow crystalline solid.

Heated with CCl₄ it gives TiCl₄ and COCl₂.

(2) TiOCI. Obtained by passing a mixture of TiCI, vapour and dry H over TiO₂ in a tube heated white hot; Ti₂O₃ and Ti₂CI_a are also produced in the reaction (Friedel a. Guérin, Bi. [2] 22, 481). Brown, orthorhombic leaflets; heated in air burns to TiO₂ and TiCl₃. (3) Ti₄O₂Cl₃. Formed by passing TiCl₄ vapour through a reduct the containing fragments of provening hot tube containing fragments of porcelain (Troost a. Hautefeuille, C. R. 73, 563). (4) By allowing TiCl, to deliquesce in air, and then evaporating over H₂SO, and CaO, Merz (Bt. [2] 7, 401) obtained a solid approximating in composition to Ti₂O₂Cl₂16H₂O. In connection with expension of Tiranum hydroxyl chlorest IDES (p. 743).

Titanium, oxyfluoride of. By decomposing by water the crystals formed by dissolving TiO_xxH₂O in HFAq and evaporating, Berzelius (P. 4, 1) obtained a white solid, of which he said it was an insoluble, 'so to say, basic,' com-

The titanoxy/luorides TiO,F,.2MF may be regarded as compounds of the oxyfluoride TiO,F.

(v. TITANIC FLUORIDE, p. 742).

Titanium, oxythiochloride of. The compound TiCl, OSO, Cl formed by the reaction of TiCl, with SO, OH.Cl may be regarded as TiO, SCl.

(v. Trranic chiosides, Reactions, No. 10, p. 740).
Titanium, salts of. Not many salts have been prepared by replacing H of oxyacids by Ti; most of those that have been isolated are basic salts derived from the oxide TiO2. One salt, Ti₂(SO₄)₃, corresponding with the oxide Ti₂O₃ has been isolated. For the individual salts v. Nitrates, vol. iii. p. 517; Phosphates, this vol. p. 112, TiP₂O₃, prepared by dissolving TiO₂xH₂O in molten II₂PO₄ (Hautefouille a. Margottet, C. R. 102, 1017) should be added; and SULPHATES, this vol. p. 580.

Titanium, sulphides of. Three compounds of Ti and S have been isolated: TiS, Ti₂S, and TiS, corresponding with the three oxides TiO,

Ti₂O₃, and TiO.

TITANIUM DISULPHIDE TIS, (Titanic sulphide.)
Mol. w. unknown. H. Rose (P. 8, 177) said that
this compound was obtained by passing vapour di CS₂ over very strongly heated TiO₂; but O. v. d. Pfordten (B. 17, 727) and Thorpe (C. J. 47, 421) have found that it is not possible by this method to obtain TiS₂ free from Ti oxides. TiS₄ is prepared by passing perfectly dry H₂S into TiCl, kept somewhat below its b.p., and sending the mixed vapours through a glass tube heated to incipient redness; TiS, deposits in the tube, and HCl is given off (Ebelmen, A. Ch. [3] 20, 285; confirmed by O. v. d. Pfordten, B. 17, 727). According to O. v. d. P. (A. 234, 257), the H₂S should be passed through CrCl.Aq, to remove traces of O, and dried by means of P_2O_3 ; and the tube should be filled with H.S before the mixed vapours are passed into it.

TiS, forms large, brass-yellow, lustrous, metal-like scales.

TiS, is decomposed to Ti2S, and S by heating in hydrogen or nitrogen; it is not changed by heating in hydrogen in presence of excess of hydrogen sulphide; heated to redness in carbon dioxide it is completely oxidised to TiO_2 (O. v. d. P., A. 234, 257). Ebelmen (l.c.) gives the following reactions: with dry chlorine gives TiCl, and S₂Cl₂; heated in air, TiS₂ is burnt to TiO, and SO,; exposure to moist air decomposes TiS, gradually, with evolution of H,S; heated to redness with steam gives TiO, xH,O, H,S, and H; nitric acid produces TiO, xH,O, S, and NO: aqua regia oxidises it to TiO, xH,O and H,SO,Aq; not acted on by hydrochloric acid (H. Rose said that TiS, dissolved slowly in HClAq, giving off H,S); insoluble in potassium sulphide solution; digestion with potash solution produces K titanate and KHSAq (Rose).

TITANIUM SESQUISULPHIDE Ti.S.. Mol. w. unknown. Thorpe (C. J. 47, 401) obtained this compound by passing the vapours of moist H.S and CS2 over powdered TiO2 heated to very bright redness in a porcelain tube; dry H.S and CS2 had no action on TiO2. T. describes Ti.S3 as a greenish-black powder; he did not obtain it quite free from TiS3, as by heating at a lower temperature than full redness in H.S and CS2 it is slowly changed to TiS2. O. v. d. Pfordten (A. 234, 257) obtained Ti.S3 by heating TiS2 to full redness in dry H or N (S being set free); he describes it as a grey, metal-like solid; insoluble in NaOHAq; soluble in HNO3Aq or cone. H.SO4 forming green solutions.

TITANIUM MONOSULPHIDE TIS. Mol. w. unknown. Formed by very strongly heating TiS₂ in perfectly dry II quite free from O (T., lc.; O. v. d. P., lc.). A black powder (T., lc.); forms dark-red crystals (O. v. d. P., lc.). Slowly acted on by HNO₃Aq or aqua regia; insoluble in NaOilAq.

Titanium, sulphochloride of, v. Titanium Thiochloride, infra.

Titanium, thiochloride of. The pp. formed by passing pure dry H.S. into hot TiCl, is probably a thiochloride, according to O. v. d. Pfordten (4. 234, 257). M. M. P. M.

TITANIUM GROUP OF ELEMENTS. The four elements, titanium, zirconium, cerium, and thorium form, with carbon, the even-series family of Group IV. in the periodic classification of the elements. There is yet an element to be discovered between Co and Th; this unknown element will come in series 10 of Group IV. The titanium family of elements is closely allied to the tin family—Ge, Sn, Pb—which, with Si, form the odd-series members of Group IV. Carbon is the first even-series member, and silicon the first odd-series member, of the group; these two elements are more like one another than they are like the rest of the group.

For the properties and relations of C and Si v. Carbon group of elements, vol. i. p. 682; and for the tin family v. Tin group of elements,

this vol. p. 735.

The presence of an element, before unknown, in a Cornish mineral was recognised by Gregor in 1791, and by Klaproth a few years later; the element—called titanium by Klaproth, was isolated by Berzelius in 1824. Klaproth, in 1789, recognised the presence of a new earth in zirconite from Ceylon; the metalezirconium was isolated by Berzelius in 1824. In 1803 the presence of a new earth in a Swedish mineral was announced by Klaproth, who gave the name of cerium to the metal of the earth, he had discovered; Mosander isolated the element in 1826. Berzelius discovered a new earth, in a Norwegian mineral, in 1828, and isolated the metal of the

earth, which he called thorium, in the same year.

None of the four elements Ti, Zr, Ce, or Th occurs native; the compounds of these elements are comparatively rare, especially those of Ce and Th.

The most frequently found compounds are the oxides MO, generally in combination with SiQ, and with alkaline carths. The metals are obtained by reducing their double fluorides by Al, K, or Na; also in some cases by reducing the chlorides by H or Na; Co has also been isolated by electrolysing motten CcCl. The table on the following parapresents some of the physical and chemical properties of the elements.

cal and chemical properties of the elements.

General formulæ and characters of compounds.—Oxides.—MO₃, probably for all (? Th₂O₃); MO₂, for all; M₂O₃, when M = Ti or Ce; perhaps TiO. Hydrates of MO₂ effst.

Sulphides.—MS₃, when M = Ti or Ce; TiS.

Haloid compounds.—MN₃, when X = Br,
Cl. E. or I tonly Cet. Treated: MN₃, when

Haloid compounds.— MX, when X = Br, Cl, F or I (only CeF, prepared); MX, when M = Ti, and X = Cl, also when M = Ce and X = Br, Cl, F or I; Ticl. Salts.— MR, R = NO₃, SO₃, PO₄, &c.; most are basic when M = Ti or Zr, but when M = Ce many are normal, and when M = Th most are normal; several salts Ce₂R₃ are known, and a few TiR₄; the Ce₃R₄ salts are more stablethan the CeR₄ salts. Salts are more salts. Salts are more salts a

The oxides MO, are basic, and also feebly acidic when M is Ti or Zr; they interact with some acids to form corresponding salts, and, when M = Ti or Zr, with alkalis to form salts wherein M forms part of the acidic radicle; no salts of oxyacids with Ce or Th in the negative radicles have yet been isolated. Several hydrates of MO, exist, they easily pass one into the other with small changes of temperature; some of these hydrates react as feeble acids towards strong bases, forming salts of the types Xr₂MO₂, Xr₃MO₂, and, generally, xr₃O₂MO₂; these salts are not referable to such definite forms as the stannals or silicates are, but they resemble these classes of salts fairly closely.

The salts which are derived from the oxides MO, by the interactions of these oxides with acids, are of the form MN, where X=NO, \$500, \$100, &c.; when M=Ti most of the salts that are known are basic, when M=Zr, many are basic, bat a fair number of normal salts is also known; when M · Ce or Th, most of the salts that have been isolated are normal. Little is known of the oxides MO; as they are obtained by adding H₂O₂Aq and an alkali to solutions of salts MX, they are probably superoxides; the formula Th₂O, that is assigned to the oxide of Th formed in this way cannot be accepted as final. The oxides Ti₂O, and Ce₂O₂ are basic; the most definite and stable salts of

_	TITANIUM.	ZIRCONIUM.		1					
		ZIRCORIUM.	. CKRIUM.	Тновим. 232					
Atomic weights.	48	90 ·	139-9						
•	Molecular weights unknown. Mol. weights of one or more com								
	each element, except Ce, have been determined by Avogadro's law; spec. heats								
Maltina mainta	determined directly								
Spec. gravities	Has not been fused	o. 1200°	c. 800°	Hasnot been fused					
(approx.)	3.6	4.20	6.7	11.0					
$Spec.\ heats.$	13	-066	.0448	.0276					
Atomic weight.	10.4								
Spec. gravities	13.4	21.4	. 21.1	21.1					
(approx.) Physical pro-	Obtained only as a	A black amorphous	Steel-grov very lug	Dark-grey, lus-					
perties.	powder; black, lus-	powder; resem-		trous powder;					
-	trous, apparently	bling lampblack,	leable, and duc-	also obtained in					
•\	amorphous. The	but much heavier.	tile. Melts much	microscopic octa-					
	powder has not been fused.	Also obtained as a very lustrous.	more easily than	hedral crystals.					
	been rused.	very lustrous, hard, brittle solid,	any other member of the family.	Has not been fused.					
		resembling Sb.	or the running.	Auseu.					
		Said to melt above m.p. of Si.							
0									
Occurrence and Preparation.	The four metals occur chiefly as silicates, Ti and Zr in moderate quant and the others only in a few rare minerals. The metals are prepare								
z reparation.	reducing the chlor	ides, or alkali salts	of the form K for N	a.lMF by heating					
	with K or Na; Ce a	lso prepared by elect	rolysing molten CeCl	a.					
Chemical pro-	Burns brilliantly	Amorphous Zr	Burns when heated	Burns, when					
perties. 🤏	when heated in air, or in O, forming	burns brilliantly when heated in	in air, or O, to	heated in air or					
•	TiO ₂ . Decomposes	air, or O, forming	CeO. Decomposes cold water, giving	O below redness, to ThO ₂ . Com-					
	H.O at 100°, giv-	ZrO2; Ne crystal-	off H. Combines	bines with Cl, Br,					
	ing off H. Com-	line metal is super-	directly with Cl,	or I when heated;					
	bines readily with	ficially oxidised at	Br, I vapour, S	also with S va-					
	Cl, less readily with Br, and with	a white heat; it burns in O-H	vapour, and P vapour. Dis-	pour when heated therein. Easily					
	I only when va-	flame. Combines	solves easily in	dissolved by					
	pour of I is passed	with Cl, probably	HClAq, HNO, Aq,	HClAq or HFAq;					
	over heated Ti.	also with Br and	H ₂ SO,Aq, or	slowly by hot					
	Dissolves in warm dilute HClAq,	I; compounds	HFAq. Forms two classes of salts,	H ₂ SO ₄ Aq; HNO ₃ Aqhas only					
	H ₂ SO ₄ Aq,	ZrX, are formed by heating ZrO ₂	Ce ₂ X ₆ and CeX ₄ ,	a slight action.					
	HNO Aq, or HFAq.	and C in X. Com-	$X = NO_3$, $\frac{1}{3}SO_0$,	Forms saltsThX.					
	Forms two classes	bines directly with	&c.: salts Ce.X.	$X = NO_3, {}_{2}^{1}SO_4,$					
	of salts TiX_2 and TiX_4 , $X = NO_3$,	S. Dissolves slowly in hot H.SO.,	are more stable	&c. fair number					
	180. &c.: very	HClAq, HNO, Aq;	than CeX, the latter are easily	of basic salts known. Hydrates					
	SO, &c. very few TiX, salts iso-	rapidly in HFA.	reduced to Ce ₂ X ₆ .	of ThO ₂ ,					
	llated, and not	Decomposes mol-	No cerates, where	ThO, 2H,O and					
	many TiX; all	ten KOH; crys-	Ce forms part of	4ThO2.H2O, are					
	salts easily decom- posed. Salts de-	talling Zr is said not to be oxidised	negative radicle, have been isolated.	probably weak acids, but thor-					
	rived from the	by molten KNO,	Salts of form	ates have not					
	acidic hydrates	or KClO _s . Forms	M.CeF, not iso-	been isolated.					
	xTiO_yH_O also	salts ZrX, X=	lated. CeO ₃ , pro-	Oxide higher					
	known. The acids H ₂ TiF ₆ and	NO ₃ , 2SO ₄ , &c. most salts isolated	bably a super-	than ThO, pro-					
	H ₂ TiO ₂ F ₄ , and	are basic.	oxide, seems to exist.	bably Th.O,, iso- lated (? super-					
	salts derived there-	xZrOyR. "Salts	oans.	oxide). ThH.					
	from, are known.	derived from acid		oxide). ThH, perhaps exists.					
	TiO _s , probably a	H ₂ ZrF ₆ are known.							
	superoxide, exists. Combines fairly	Also forms zircon- ates $yMO.zZrO_2$	e	tetravalent in gaseous molecule					
	readily with N.	where Zr enters !		ThCl4.					
	and with N and	into negative radio							
	C. Atom of Ti	into negative radio							
	is tetravalent in gaseous molecules	(? superoxide) exist exists. Atom of Z							
	TiCl, and TiI,	•							
	TION BUG III.	gaseous molecule Zi							

Ce are derived from this oxide. Several of the haloid compounds MX, have been gasified without decomposition, viz. TiCl., TiI., ZrCl., and ThCl. The haloid compounds MX, form many double compounds with other halides; some of these are certainly best regarded as salts of hypothetical acids containing M and X in their acidic radicles; the salts of this class R.MF. acidic radicles; the salts of this class B.MF_a are characteristic of the elements of Group IV.; all the elements of the group, except C and Cc, give these salts B.MF_a. Ce is said to form K_aCe_xF₁₁(= 2CeF_a.3KF), but further examination will most probably lead to the isolation of salts B.CeF_a. Ti and Ce form chlorides MX₁₀ or more probably M_aX_a from the analogy of C.Cl_a and Si_aCl_a; Ce also forms Ce_xF_a, Ce_xF_a, and Ce_xF_a, indeed the only haloid compound of Ce belonging to the form MY, that he yet heap isolated ing to the form MX, that has yet been isolated is CeF4. The sulphides have not been thoroughly examined; Ti is the only member of Group IV. which is known to form three sulphides corresponding with the oxides, TiS, TiS, and TiS,; one sulphide of Zr is known, probably ZrS; ThS₂ is the only sulphide of Th that has been isolated; and the only known sulphide of Co is Ce,S,. So far as investigation has gone, the

sulphides of Ti, Zr, Ce, and Th are basic.

A comparison of the titanium family with the tin family, which comprises the odd-series members of Group IV (C and Si being omitted), shows that Ti, Zr, Ce, and Th are more metallic, on the whole, than Ge, Sn, and Pb. Th is certainly the most markedly positive element of Group IV., and Ti is at least not more negative than Ge; Zr is more metallic than Ge, and Co more metallic than tin. The following formula show that, so far as composition goes, there is about an equal similarity between C and Si and the Ti elements, as between C and Si and the

tin elements:

there is between the two families of Group VI. Considering that the titanium and the tin elements belong to even and odd series, respectively, of Group IV., which group comes midway in the general periodic scheme of classification. we should expect the titanium (even-scries) family to be rather more metallic than the tin (odd-scries) family, but at the same time we should expect these two families to be very like one another; this is exactly what a study of the two families shows to be the case.

In connection with this article v. Tin enough OF ELEMENTS, this vol. p. 735, and CARBON GROUP OF ELEMENTS vol. i. p. 682).

M. M. P. M. TITANOFLUORHYDRIC ACID H.TiF. v. Titanifluorhydric acid, under Trianic fluoride, Combinations, No. 1, p. 742.

TITANOFLUORIDES M.TiF. v. Titanifluorides, under Titanic fluorides, Combinations, No. 2, p. 742.

TITANOXYFLUORHYDRIC ACID HITIO,F. v. Titanic Fluoride, p. 742.

TITANOXYFLUORIDES $M_2\mathrm{Ti}\mathrm{O}_2\mathrm{F}_1$ v. Titanto FLUORIDE, D. 742.

TOLALLYL SULPHIDE C. U.S. [174°]. (350°-360° i.V.). A product of Wistillation of benzyl sulphide (Märcker, A. 136, 75; Forst, A. 178, 370; Baumann a. Klett, B. 24, 3313). Plates (from ether).

TOLANE v. DI-PHENYL-ACETYLENE.

Tolane dibromide v. DI-PROMO-PHENYL-ETHYL-

Tolane chlorides v. Chloro-Phenyletthans and CHLORO-PHENYL-ETHYLENE.

TOLENE v. Tolu balsam. p. TOLENYLAMIDINE $C_aH_{1a}N_a$ 4.6. $C_aH_{1a}N_c$ C(NH)(NH₂). [102°]. Formed by the action of alcoholic NH_a on the hydrochloride of

Oxide s		Sulphides			Chlorides, &c.		
CO ? C ₂ O ₃	CO ₂ .	CS ?SiS	? C ₂ S ₃	$\frac{\mathrm{CS_2}}{\mathrm{SiS_2}}$?SiCl,	C.Cl. Si_Cl.	CCl. SiCl.
? TiO Ti ₂ O ₃	TiO ₂ TiO ₃ ZrO ₄ ZrO ₃	TiS	Ti ₂ S ₃	TiS ₂ ZrS ₂ (?)	$\mathbf{TiCl}_{\mathbf{z}}$	Ti_Cl ₆	TiCl, ZrCl,
$\mathbf{C}e_{2}\mathbf{O}_{3}$		•	Ce ₂ S ₃	\mathbf{ThS}_{2}		Ce ₂ Cl ₆	CeF, ThCl,
GeO SnO 7 Sn ₂ O, PbO Pb ₂ O ₄		GeS SuS PbS	??Sn ₂ S ₃	GeS ₂ SnS ₂ ?PbS ₄	$egin{aligned} \mathbf{?GeCl_2} \ \mathbf{SnCl_2} \ \mathbf{PbCl_2} \end{aligned}$		GeCl ₄ SnCl ₄ PbCl ₄ (?)

A comparison of the odd-series families of the different groups with the even-series families (omitting series 2 and 3) shows that, speaking broadly, the members of the even-series families are more metallic in their chemical properties than the members of the odd-series families, and that the general difference between even and odd families becomes more marked in the higher than in the lower groups (v. Table in vol. iii. p. 811). For instance, the even family of Group VI.—Cr. Mo, W, and U—is decidedly more metallic than the odd family of the same group—S, Se, and Te; but although the even family of Group II.—Ca, Sr and Ba—is more metallic than the odd family of the same group -Mg, Zn, Cd and Hg - there is not nearly so great a difference between these two families as

p-tolenyl-imido-ethyl-ether (Glock, B. 21, 2653). Pearly plates, sol. alcohol and ether.

Reactions .-- 1. CO.Ch, in toluene and NaOH

1422).
Salts.—B'HCl laq. [218°].— B'H.PtCl.
[225°].—B'HNO. [133°]. Needles, v. sol.
water (Kirschnick, A. 265, 167).—B'HNO. 2aq.
[95°].—B'2H.SO. 2aq. [240°], v. sol. water.
o-TOLENYLAMIDOXIM C.H.,N.O. i.e. 1422)

C,H,C(NOH).NH, [149.5°]. Formed by heat-

ing o-toluic nitrile with hydroxylamine hydrochloride, alcohol, and Na₂CO₃ (Schubart, B. 22, 2438). Needles (from hot water), v. sol. alcohol and ether.

Ethyl ether C,H,.C(NOEt).NH. [140°].

Prisms, v. sol. alcohol.

Benzoyl derivative C,H,.C(NOBz).NH2. [145°]. Needles, sol. alcohol. Conc. H.SO. forms С,H,.С<^{N.O}>СРЬ [80°].

o-Toluyl derivative
. C,H,C(NO.CO.C,H,).NH₂. [N.8°]. Converted at 180° into C_1H_1 , $C \leqslant_N^{N,\hat{O}} \geqslant_{\hat{C}} C_1H_1$, [59°] (Stieglitz, B. 22, 8156). Sodium diazobenzene sulphonate forms C_7H_7 . C_7H_7 . C_7H_7 . C_7H_7 . C_7H_7 . C_7H_7 . C_7H_7 .

Reactions.—1. Benzene sulphonic chloride forms C,H,.C NO SO.C,H, [89°] (Pinner, B. 24, 4173).—2. Aceto-acetic ether gives rise to C,H,C N CCH₂Ac [97°] (Schubart, B. 22, 2438) .- 3. Acetic aldehyde forms the compound C,H,.C NO CHMe [127.5°].-4. Hot, HOAC forms $C_{rH,.}C \stackrel{N.O}{\leqslant}_{N}^{N.O} > 0.C_{rH}$, [135°].—5. COCl. produces C,H,.C $\stackrel{N.O}{<}$ CO [220°].—6. ClCO₂Et yields C,H,.C(NH,):NO.CO,Et [130°] .- 7. Phenyl cyanate gives C,H,C(NOH).NH.CO.NHPh [155°].—8. Phenyl thio-carbimide reacts forming Q,H,C(NOH).NH.CS.NHPh.—9. Potassium cyanate acting on the hydrocloride gives rise to C₇H₇.C(NOH).NH.CO.NH₂ [170°]. 10. Ac₂O and NaOAc acting on the hydrochloride form NH(C(NH).C,H₂) [153°] (Glock, B. 21, 2657).—
11. Succinic anhydride forms the compound **C,H,.**O < N.O > C.CH₂.CH₂.CO₂H [138·5°].—12. Boiling Ac₂O forms $C_7H_7.C < N.O > CMe$ [80°].

13. CS. and alcohol form, on long boiling, C,H,,C(NSH)NH.CS.SHH,N.C(NSH).C,H, (Crayen, B. 24, 390).—14. US, and alcoholic potash yield C,H,C(NH,CS). [165*].

Methyl ether C.H. C(NOMe).NH. [85°].

Ethyl ether Eth'. [64°]. Needles. Converted by HBr and NaNO, into O.F. CBr:NOEt, an oil, decomposed at 155° (Schubart, Be 22, 2434), while hydrogen chloride and NaNO, form O,H,.CCl:NOEt (200°).

Bensoyl derivative C,H,.C(NOBz).NH, [178°]. Converted by heat into $C,H,C \stackrel{N.O}{<} CPh$.

References.—Nerso and Oxy-Toluamidoxim.
p.TOLENYL-IMIDO-ETHYL ETHER
C.H., C(NH).OEt. The hydrochloride B'HCl
[1817] formed by the action of dry HCl on p-toluic nitrile dissolved in ether-alcohol forms

prisms, yielding B'₂H₂PtCl₂2aq, converted at 200° into p-toluio amide, by NH₄ into p-tolenylamidine, by aniline into di-phenyl-tolenyl-amidine [168°], and by Ao₂O into the compound C₄H₄Me.C(NH).OAc [147°] (Glock, B. 21, 2650). The free base is liquid and changes on keeping into a polymeride [260°].

TOLENYL-PHENYLENE-DIAMINE

 $C_eH_4 < \stackrel{NH}{N} > C.C_rH_r$. [268°]. Formed by reduction of tolvl-o-nitro-aniline and also from ptoluyl chloride and o-phenylene-diamine in benzene (Hübner a. Hanemann, A. 210, 328). Prisms, sl. sol. water, sol. alcohol.

TOLENYL-PHTHALAMIDONE C, H, N, O i.e.

tolenyl-benzenyl-amidine o-carboxylic acid (Bistrzycki, B. 25, 1984).

TOLENYL-XYLYLENE-DIAMINE C'2H18N i.e. [1:4] $C_0H_4Mo < N_{NH} > C_0H_2Me_2$ $\begin{bmatrix} 5 \\ 6 \\ 1:3 \end{bmatrix}$ [217°]. Formed by reducing the p-toluyl derivative of nitro-xylidine (Brückner, A. 205, 125; Hübner, A. 210, 333). Long crystals (from dilute alcohol).—B'HCl.—B'HNO₃.—B'₂H₂SO₄.

TOLIDINÉ v. DI-AMIDO-DITOLYL. TOLIL v. DI-TOLYL-DIRETONE.

TOLIL-BENZOIN v. BENZOIN, Reaction 9. TOLINDOLE v. METHYL-INDOLE.

TOLISATIN v. Methyl-ISATIN.

TOLU-ACET-ALDEHYDINE C11H14N2 i.e. $C_7H_e(N;CHMe)_2$ or $C_7H_e < \stackrel{N}{N}_{Et} > CMe$ (?) [91° uncor.]. Formed together with a small quantity of ethenyl-tolylene-diamine, by mixing tolylene o-diamine (1 mol.) with aldehyde (2 mols.) in cold HOAc (Hinsberg, B. 20, 1588).

TOLU-AMIDOXIM v. TOLENYL-AMIDOXIM.

TOLU BALSAM. Obtained from incisions

in the stem of Myroxylum toluiferum growing in Columbia, South America. It contains a terpene, tolene $C_{10}H_{16}$ (154°-170°), benzoic and cinnamic acids, benzyl cinnamate and two resins: $C_{18}H_{18}O_4$ [60°] v. sol. alcohol and ether and $C_{18}H_{20}O_{3}$ [above 100°], insol. alcohol and ether (Deville, A. 44, 304; Scharling, A. 97, 71; E. Kopp, A. 64, 372; Busse, B. 9, 830; Baillon, Ph. [3] 4, 385).

TOLUBENZYLAMINE v. METHYL-BENZYL-

AMINE. TOLUENE C,H₈ i.e. C₆H₈,CH₉. Methylbenzene. Retinaphtha. Phenyl-methane. Mol. w. 92. V.D. 3·20 (calc. 3·29). (109°) (R. Schiff, A. 220, 91); (111°) (Wilbrand a. Beilstein, A. 128, 259; Tollens a. Fittig, A. 131, 304). S.G. 20 ·8656 (Brühl); 21 ·8566 (Gladstone, C, J. 59, 290); 13 ·8708 (S.). C.E. (13°-109°) ·001242. S.V. 118 (S.). μ_{B} = 1·4893, (C.). μ_{B} = 1·507 (B.). R_{∞} = 50·06. H.F.p. -3520. H.F.v. -5200 (Thomsen, Th.). H.C. 933,762 (Stohmann, J. pr. [2] 35, 41). Critical temperature 321° (Pawlewski, B.-16, 2634). Occurs in cold tar (Mansfield). Obtained by dry distillation from balsam of tolu (Deville, A. Ch. [3] 3, 168; Muspratta. Hofmann, A. 54, 9), from dragon's 168; Muspratta. Hofmann, A.54, 9), from dragon's blood (Glenard a. Boudault, C. R. 19, 505), from the resin of Pinus maritima (Pelletier a. Walter.

A. Ch. [2] 67, 278), and from wood (Völckel, A.) 86, 334).

Formation .- 1. By distilling vulpic acid with KOH (Möller a. Strecker, A. 113, 69). 2. By the action of sodium on a mixture of bromobenzene and MeI (Fittig a. Tollens, A. 131. 303).—8. By passing petroleum vapour over red hot charcoal (Letny, B. 11, 1210).—4. Beheating petroleum with AlCl, in presence of PbO and air (Friedel a. Crafts, Z. 1878, 1166).— 5. By passing MeCl or CH,Cl, into benzene containing AlCl₂ (Friedel a. Crafts, A. Ch. [6] 1, 460; 11, 264).—6. Together with CH₁ by heating benzene with MeI and I (Rayman a. Preis, A. 223, 317).-7. By distilling cresol with P2S3 (Geuther, A. 221, 58) .- 8. By distilling toluic acid with baryta (Noad, A. 63, 305).

Properties.—Oil, smelling like benzene.

Reactions.—1. When passed through a redhot tube it yields benzene, styrene, naphthalene, diphenyl, anthracene, phenanthrene, and other products (Ferko, B. 20, 661; cf. Berthelot, Bl. 7, 218; Graebe, B. 7, 48).—2. Distillation over red-hot PbO gives benzene, di-phenyl-ethylene, diphenyl, phenanthrene, and anthracene (Lorenz, B. 7, 1097; Vincent, C. R. 100, 908). -3. By electrolysis of toluene to which alcohol and H.SO, have been added benzoic aldehyde and phenose are formed (Rénard, C. R. 92, 965) .--4.—When electric sparks are passed through toluene, acetylene and hydrogen are given off (Destrem, Bl. [2] 42, 267).—5. AlCl, at 200 in sealed tubes forms benzene, and m- and p-xylene (Friedel a. Crafts, C. R. 100, 692; Anschütz, A. .235, 178).-6. Oxygen passed through toluene containing AlCl, forms cresol (Friedel a. Crafts, C. R. 86, 884). -7. A mixture of toluene and ethylene passed through a red-hot tube yields benzene, styrene, and antiracene (Ferko)...
8. CH₂Cl₂ and AlCl₃ yield di-tolyl-methane (280°-290°), di-methyl-anthracene [232°], and m., and p. xylenes (Pricedel a. Crafts, Bl. [2] 41, 322).—9. Bromine acts upon toluene in the dark as readily as in diffused daylight, with production of o- and p-bromo-toluene. The addition of iodine greatly hastens the reaction, but the same products are formed. In direct sum light the substitution takes place entirely in the side-chain, with production of benzyl bromide. But if iodine (even 2 p.c.) is present the effect of the sunshine is entirely counteracted, and the substitution takes place wholly in the nucleus (Schramm, B. 18, 606; cf. Zakrzewski, M. 8, 304).—10. Chlorine, in presence of I, acting even on boiling toluene, forms chloro-toluene and benzyl chlorido (Beilstein a. Geitner, A. 231, 170; cf. Aronheim, B. 8, 1401).—11. Crt) Cl. added slowly to a solution of toluene in CS. ppts.C.H.2CrO.Cl., which slowly absorbs moi; ture, being converted into benzoic add-hyde (Etard. A. Ch. [8] 22, 223).—12. H.SO, yields the o-and p-suphonic acids, converted by potash-fusion into o- and p-cresol (Wurtz. A. Ch. [4] 25, 108).—13. Bz.Q. forms Ci.H.; (c. 260°) isomeric with the di-phenyl-ethylenes, and yielding benzoic acid on oxidation (Lippmann, M. 7, 521).—14. HNO, forms o- and p-nitro-toluene.—15. Parallelyde and conc. H.SO, form ditolylethams and C₂₂H₂₈ (350°-860°) (O.* Fischer, B. 7, 1194). even on boiling toluene, forms chloro-toluene and 1194).

Compounds (C,Hs),AlCls. S.G. 2 1.08 (Gus-

tavson, B. 11, 2151). Oil.— (C.H.), AlBr. S.G. *

Dihydride C,H₁₀. (105° 108°). Formed by heating toluene with PH₄I at 350° (Baeyer, A.

155, 271; Z. [2] 4, 445).

Tetral plride C.H., (104°). S.G. U 797. Occurs in the product of distillation of colophony (Rénard, A. Ch. [6] 1, 231). Oil, sol. alcohol and ether. Rapidly absorbs oxygen. In contact with water it forms crystalline C, H100, H₂SO, forms two polymerides (230 -235°), one only being oxidisable by air.

Hexahydrids C.H., (97°), S.G. § 7741, C.E. (0° 20°) 901 Ø. S.V. 142 (Lossen, A. 225, 109). H.C. 1,092,800 (Longuinine, C. R. 93, 275). Formed by heating tohene with conc. 111Aq at 280 (Wreden, A. 187, 161; cf. Berthelot, Bl. [2] 7, 124; 26, 146). Occurs in oil of resin. Completely oxidised by a hot mixture of

HNO₃ and H₂SO₄, References, - Tri-amido-, Bromo-, Bromo-IODO., BROMO-TODO-NITRO., BROMO-NITRO., CHLORO., CHLORO-TODO., CHLORO-NITRO., LODO., IODO-NITRO., NITROSO., NITRO., and OXY- TOLUENE. TOLUENE ARSONIC ACID r. ARRENIO.

TOLUENE-AZIMIDO-TOLUENE v. AZIMIDO-COMPOUNDS

TOLUENE-AZO- compounds v. Azo- com-POUNDS and DISAZO- COMPOUNDS.

- TOLUENE-AZOXY- compounds v. Azoxy-COMPOUNDS

TOLUENE CARBOXYLIC ACID v. Toluic

Tolpene dicarboxylic acid C,H,O, C₆H₃Me(CO₂H)₂[4:2:1]. Methyl-phthalic acid. Mol. w. 180. [152°]. Formed from (a)-amido-ptoluic nitrile by Sandmeyer's reaction, the resulting nitrile being saponified (Niementowski, M. 12, 623). V. e. sol. water and alcohol. o-amido-phenol it forms C,H,Me(CO),N.C,H,OH [205°], whence boiling aqueous sodium carbonate gives rise to C_dH₃Me(CO₂H).CO.NH.O₄H₄.OH₄ • [200°].

Amide C,H,Me(CONH,), [188°]. Formed . from the imide and NH_3Aq .

102 | Needles

Anhydrida. [92]. Needles. Imida C_uH₃Me.C₂O₂NH. [196°]. Got by fusing the anhydride with urea. Needles.

Nitrite C_bH₃Mc(CN)₂, [120°] (N.); [117°] (Glock, B. 21, 2663). Needles. Converted by alcohol and HCl into C, H, Cy. C(NH, Cl). OEt

[199°]. Toluene dicarboxylic acid (3.11, (3.11, (3.11))C.H.Mc(CO,Hb. 4.33:1]. (B)-Xylidic acid. Methylicophthalic acid. [320°-330°]. Formed by oxidation of m-xylene carboxylic acid (Jacobsen, B. 14, 2112) and of C.H.Mc(CH.OH), (Hielt a. Gadd, B. 19, 868). Formed also by fusing potassium toluene m-disulphonate or the salt C_aH₁Ne(SO₂NH₂),CO₂K with sedium formate (Hakansson, B. 5, 1088; Remsen a. Hes, Am. 1, (Hakansson, B. 5, 1088; Rémsen a. 11es, Am. 1, 119). The same acid (?) is got by oxidation of C_nH₂Mc_nCO₂H [1:4:2] by HNO, (S.G. 1·12) at 150° (Claus a. Wollner, B. 18, 1858). Small crystals, sl. sol. hot water. May be sublimed.—Ag.A": crystals, v. sol. hot water.

Toluene dicarboxylic acid.

C_nH₂Mc(CO₂H₂ [2:4:1]. Methyl-terephthallo acid. (a) Xylidic acid. [c. 282°]. Formed by boiling pseudocumene with dilute HNO₂ (Fittig a. Laubinger, A. 151, 276). Got also by traing

a. Laubinger, A. 151, 276). Got also by fusing

C.H.Me(SO.NH.)CO.K with sodium formate (Remsen a. Iles, Am. 1,114). Needles (by sublimation). Sl. sol. Aq. Oxidised by KMnO, to trimellitic and isophthalic acids (Krinos, B. 10, 1494).—~ZnA". S. 36 at 0°; '735 at 100°, '5 at

130° (Jacobsen, B. 10, 859).

Toluene dicarboxylic acid C,H,Me(CO,H)2 [310°-315°]. Formed by fusing potassium toluone (y)-disulphonate with socium formate (Senhofer, A. 164, 134). Minute needles, v. sl. sol. cold water, v. sol. alcohol and ether. May be sublimed. -BaA" 2aq. -Ag. A": amorphous

Toluene w o-dicarboxyliceacid

CO.H.CH., C.H., CO.H. [2:1]. Homophthalicacid v. o-Carboxy-phenyl-acctic acid.

Nitrile v. o-Cyano-Benzyl Cyanide.

Toluene w m-dicarboxylic acid

CO₂H.CH₂.C₂H₁.CO₂H [3:1]. Formed by oxidation of m-di-ethyl-benzene (Allen a. Underwood, Bl. [2] 40, 100). Needles (from alcohol). Sublimes without melting at 200° 210 .- Ag A".

Toluene ω p-dicarboxylic acid
CO₂H.CH₂,C₃H₂,CO₃H. [285²-288²]. S. 1 at 50°.
S. (alcohol) 14 3 at 30°. Formed by the action 5. (atcono) 14°3 at 30°. Formed by the action of dilute (25 p.c.) HCl on the amide (Mellinghoff, B. 22, 3215). V. sl. sol. ether and benzene.—
Ag_aA": crystalline pp. The same (?) acid formed by oxidation of C₆H, PrPr [1:4] yields

BaA'-14aq /Paterno a. Spica, B. 10, 1740).

Amide CO(NH₂),CH₂,C₆H₁,CO.NH₂. [235°].

Formed from CH₂Cy.C₆H₁,Cy and H₂SO₄. Small

hard nodules.

CO(NH₂).CH₂.C₆H₄.CO₂H₄. acid[261°]. Formed from CH_Cy.C,H,CO_H and H₂SO. Sl. sol. ether, hot water and alcohol.—AgA': crystalline.

Iso amic acid CO2H.CH2.C8H1.CO.NH2. [229°]. Formed from p-cyano-phenyl-acetic acid. Crystalline, v. sol. alcohol and hot water.

-AgA'. Crystalline.

-ARA. Crystamine.
Nitrile CH.Cy.C_aH₄.Cy. p-Cyano-benzyl
cyanide. [100°]. (above 360°). Formed from
CH_Cl.C_aH₄.Cy and KCy (Mellinghoff, B. 22,
3209). Needles, v. sl. sol. hot water, sol. alcohol and ether.

Semi-nitrile CH2Cy.CaH4.CO2H. [201°]. Formed from ω -chloro-p-toluic acid by treatment with KOHAq and alcoholic KCy (Mellinghoff, B. 22, 3213). Crystalline, v. sol. alcohol and ether. -AgA'.

Semi-nitrile CO.H.CH..C.H..Cy. [152] Formed from the nitrile and HCl at 105°.

Prisms, v. sol. alcohol.—AgA'. Crystalline.

Nitrile-amide CH_Cy_C₆H_, CO.NH.

[182°]. Formed from ω-chloro-p-toluic amide

and KCy. Plates. Amide nitrile CO(NH.).CH.,C.H.,Cy. [196.5]. Formed from the nitrile and HCl at 70°. Crystalline, v. sol. alcohol.

Toluene tri-carbaxylic acid C.H.(CO.H).CH,.CO.H. Formed in small quantity by oxidation of s-tri-ethyl-benzene (Friedel a. Balsohn, Bl. [2] 34, 635). Needles. Sublimes before metting.—Ag₃A". Tables (from hot

TOLUENE O-PHOSPHINIC ACID

C.H.Me.P(OH). Obtained by decomposing its chloride with water (Michaelis a. Paneck, A. 212, 223). Oil. Monobasic acid.—CaA' aq. Chloride C.H.Me.PCl2. (244°). Formed

by the action of PCl₃ on mercury ditolyl [107°] and by warming toluene with AlCl. and PCl. Liquid.

Toluene p-phosphinic acid CaH, Me.P(OH)2. [105°]. Formed in like manner. Plates, v. sl. sol. water. Oxidised by HNO₃ to the phosphonic acid. Decomposed on heating into tolyl-

phonic acid. Decomposed on heating into tolylphosphine and toluene phosphonic acid. -KA'.
-NH,A'.-BaA',aq.-FbA',--CuA',4aq.
Ether C₀H,Me.P(OEt)₂. [280°].
Formed from the chloride and dry NaOEt.
Chloride C₀H,Me.PCl₂. [25°]. (245°).
Formed, together with the o-isomeride, from
toluene, PCl₃, and AlCl₃ (Michaelis a. Paneck,
A. 212, 203). Formed also from Hg(C,H,)₂
[235°] and PCl... Needles. v. sol. ether and [235°] and PCl3. Needles, v. sol. ether and benzene.

References .- NITRO- and OXY-TOLUENE PHOS-PHINIC ACID.

TOLUENE PHOSPHINIC ANHYDRIDE v. PHOSPHING-TOLDENE

TOLUENE O-PHOSPHONIC ACID

C_aH₄Me.PO(OH)₂. [141°]. Formed by the action of water on its chloride (Michaelis a. Paneck, A.

212, 231). Crystals, v. sol. water. $-Ag_2A''$.

Chloride C,H.,PCl,
This is formed from
C,H.,PCl₂ and chlorine. Yellow solid.

Toluene p-phosphonic acid CoH, Mc.PO(OH)2. [189°]. Formed from C.H. PCl, and cold water. Woolly needles. Oxidised by alkaline KMnO₄ to CO₂H.C₄H₄.PO(011)₂. Bromine forms bromotoluene. – KH₄A"₂: needles. – BaH₄A"₂—AgHA". – Ag₂A".

Chloride C.H. PCl. [42°]. Formed from H.PCl., and chlorine. Yellow mass, converted C₇H, PCl₂ and chlorine. Yellow mass, comby dry SO₂ into liquid C₇H₇. POCl₂ (285°).

Toluene ω-phosphonic acid

C_aH_aCH_aPO(OH)₂. [166°]. Formed, together with (C_aH_a)₂PO(OH) [191°], from benzoic aldehyde and PH_aI (Litthauer, B. 22, 2145). Stellate groups of prisms (from HOAc).

Reference. - OXY-TOLUENE PHOSPHONIC ACID. TOLUENE & SELINIC ACID C, H, SeO, i.e. C_sH_s,CH_s,SeO.OH. [85°]. Formed by oxidising benzyl disclenide with HNO₃ (Jackson, A. 179, 8). Needles, sl. sol. cold water, v. sol. alcohol, hearly insol. ether. -- AgA': slender crystals (from hot water).

TOLUENE SULPHAMINE v. AMIDO-TOLUENE SULPHINIC ACID.

TOLUENE o-SULPHINIC ACID C, H, SO, i.e. C_zH₁Mc_zSO.OH. [80°]. Formed by boiling C_zH₁N₂H₂SO.C_zH₂ with baryts water (Limpricht, B. 20, 1241). Long needles, v. sol. ether.—BaA'₂ 3aq. Nodules, v. sol. water.

Toluene p-sulphinic acid C_zH₁Mc.SO_zH.

[85°]. Formed in like manner (Limpricht), and also from toluene p-sulphonic chloride and sodium-amalgam, zinc-dust, or Na SO, (Otto, A. 142, 92; 145, 19; B. 9, 1586; Blomstand, 142, 92; 145, 19; B. 9, 1586; Blomskand, B. 3, 965). Plates, v. sol. ether. Fuming HNO₂, Groms crystals [190°]. The Na salt heated with CH_{*}.CHCl_{*} and alcohol at 150° gives a small quantity of 'CH_{*}.CHCl.SO_{*}.C, H. [48°] (Otto, J. pr. [2] 40, 519). The Na salt with ClCO_{*}Et gives the ether (Otto, B. 26, 308).—BaA'₂: 1 lates.—CaA'₂ 4aq.—ZnA'₂ 2aq.—AgA'.

Methyl ether. Formed from the Na salt and ClCO_{*}Et in MeOH. Oil (Otto, J. pr. [2] 47, 1666).

Ethyl ether EtA'. Oil. KMnO, in HOAc to toluene p-sulphonic ether

(Otto a. Rossing, B. 19, 1226)

Toluene exo-sulphinic acid C.H. CH. SO.H. Prepared by reducing C_eH₃.CH₂.SO₂Cl with sodium-amalgam (Otto a. Lüders, B. 13, 1288). Very unstable.-NaA': leaflets, sol. hot alcohol.

Reference .- AMIDO TOLUENE SULPHINIC ACID. TOLUENE o-SULPHONIC ACID C.H.SO, i.c.

C.H.Me.SO3H [1:2].

Formation.—1. In small quantity together with the p-isomeride, by dissolving toluene in hot fuming H.SO. (Engelhardt a. Latschinoff, Z. [2] 5, 617; Anna Wolkoff, Z. [2] 6, 321).-2. Together with the m- and p- isomerides by the action of Cl.SO...OH on toluene (Claesson a. Wallin, B. 12, 1848; Noyes, Am. 8, 176).— 3. From o-toluidine by diazotisation followed by treatment with H.SO, (Müller a. Wiesinger, B. 12, 1348).-4. By reducing p-bromo-toluene sulphonic acid with sodium-amalgam (Terry, .1. 169, 27) .- 5. From (4,1,2) - nitro-toluene sulphonic acid by elimination of NO2 (Jenssen, A.

Preparation.—By adding toluene (60 g.) to CISO₃H (150 g.) in the cold, and pouring the product into water (Noyes).

Properties. -- Thin leaflets (containing 2aq), v.

sol. water. Deliquescent.

Amide C.H., SO., NH... [154°]. S. 1 at 9°; S. (alcohol) 3°5 at 5°. Octahedra, sl. sol. water. Yields a benzoyl derivative [112], which forms C.H., SO, NKBz 1 aq and (C.H., SO, NBz), Ba aq. (Wolkoff, Z. [2] 6, 57). Oxidised by KMuO, in acid solution to o-sulpho-benzoic acid and in

neutral solution to C₆H₄<SO₂>NH (Fahlberg a. List, B. 21, 242).

Anilide C,H., SO,NHPh. [136°].
Toluide C,H., SO,NHC,H., [131°].
Toluene m-sulphonic acid C, H., Mc. SO, H

[1:3]. Formation. 1. By the action of H SO, on m-diazo-toluene salts (Müller a. Wiesinger, B. 12, 1349).—2. A product of the action of CISO H on toluene (Claesson a. Wallin, B. 12, 1848). -3. From o-bromo-toluene m-sulphonic acid and sodium-amalgam (Müller, A. 169, 47). 4. By the diazo-reaction from p-toluidine sulphonic acid and from o-toluidine sulphonic acid (Pechmann, A. 173, 202; Pagel, A. 176, 297; Nevile a. Winther, C. J. 37, 628; Klason, B. 19, 2887).

Properties .- Thin deliquescent scales (con-

Oxidised by 5° (C. a. W.); 17.4 at 14° (V.). Monoclinic tables and octahedra (from alcohol). Melts at 91° according to Noyes. Oxidised by alkaline K₃FeCy₆ to CQ₂H.C₆H₄.SO₂NH₅ (Noyes a. Walker, Am. 8, 187).

Anilida C.H., SO, NHPh. [72°].

m-Toluide C.H.SO., NHC.H., [103°].

Toluene p-sulphonic acid Call, Mo.SO, H [1:4.] The chief product of sulphonation of boiling Tollens, A. 131, 310; Marclor, A. 136, 85; Engelhardt a. Latschiueff, Z. [2] 5, 617; Jaworsky, Z. 1865, 221; Otto a. Grüber, A. 142, 92; 145, 10; Chru tshoff, B. 7, 1167; Fahlberg, B. 12, 1048). -2. From toluene and CISO₂H (Claesson a. Wallin, B. 12, 1848). -3. By the action of H2SO, on p-diazo-toluene salts (M. a. W.).

Properties. -Thick leadlets or flat prisms (containing aq). Deliquescent. Melts at 92° (Norton a. Otten, Am. 10, 140). Fusion with sodium formate yields p toluic acid (Remsen, B. 8, 1412). Potash-fusion gives p-cresol. Hydro-

8,1112). Potash-fusion gives p-eresol. Hydrolysis by steam begins at 150° (Armstrong a. Miller, C. J. 45,148).

Salts. KA' aq. Trimetric crystals; a:b:o=864113:237.—NaA' 3aq. NaA' 2aq.—NHA'.—CaA'_4aq.—BaA'_a, BaA'_aq. S. 21 at 12°.—BaA'_3aq. (Kelbo, B. 16, 621). PbA'_2. —MgA',6aq. ZnA'_26aq. CdA'_26aq.—MhA'_26aq.

CuA'_6aq. AgA': long plates, v. sol. water.

Met hylamine salt 1125°1.—

Methylamine salt [125]... NMc.H.A'. [78"]. NMe.HA'. [92"]. Aniline salt (223"]. ... o Toluidine salt [180"] [125°].---(N. a. O.).

Chloride C.H. SO.Cl. [69°]. Triclinic crystals; a;btc. 768°1:1114; α 97° 24′; β 117° 6′; γ 84′ 28′. Acctoxim and NaOH form C.H. SO.C.N.CMe. [89°] (Wege, B. 24, 3538). In ethereal solution it is reduced by sodium-analgam to toluce sulphinic acid and the compound $C_aH_{10}SO_a$ [76]. In presence of isoamyl ether $(C, H_{10})O$ the compound $C_aH_{10}SO$. [36°] is formed (Otto, A. 143, 216).

2] is formed (Otto, 21, 120), 75, 1867, Bromide C.H. SO.Br. [96°]. adding an alcoholic solution of I to aqueous C.H., SO, Na (Otto a. Tröger, B. 24, 479). Yellow crystalline powder, v. sol. ether, turning brown in air. Heated with water at 100° it forms C.H.S.O., C.H.. Reduced silver acts in like nAnner. ZnEt, forms zinc toluene sulphinate.

Methyl ether MeA'. [6. 30'].

Ethyl ether EtA'. [32']. S.G. 32 1-174.

Thick prissas (Kraft a. Roos, B. 25, 2259).

Phenyl ether C.H. SO.OPh. [95°]. Formed by the action of NaOPi on the chloride dissolved in benzene (Otto, B. 19,1832). Trimetric crystals; a:b:c = 289: 476. Not affected by alcoholic NH, even at 200°.

taining aq), v. sol. water.

Salts.—KA'aq.—NaA'aq.—NH₁A': scales.v.
sol. water.—CaA', 2aq: needles, v. sol. water.—BaA', 2aq.—BaA', 2aq. S. 22·75 at 12° (C. a. W.);
15·5 at 15° (Vallin, B. 19, 29/32).—PbA', 2aq.—DhA', 2aq.—PbA', 2aq.—MgA', 8aq.—ZnA', 26a;
—ZnA', 7aq.—CdA', 2aq.—AgA': v. sol. water.—ZnA', 7aq.—CdA', 4aq.—AgA': v. sol. water.

Chloride C,H,SO,Cl. Oil. Chloride C,H,SO,NH, [108°]. S. 4 at 9° (C. a. W.); 265 at 14° (V.). S. (alcohol) 7·4 at 5°. Leaflets. Yields C,H,SO,NHK aq. BzCl forms C,H,SO,NHB2 [147°-150°], which gives KA', Caz'A', aq, BaA', AgA', and AgA'NH, and is converted by PCl, whence ammonium carbonate solution forms C,H,NO, CCl.C,H, (100°), whence ammonium carbonate solution forms C,H,NO, NC,HC,H, (10°), whence ammonium carbonate solution forms C,H,NO, NC,HC,H,O, converted by NH,Aq into C,H,SO,N,H,(C,H,O), (180°) and

(C,H,SO₂)₂N₂H₂(C,H₁O₂), which crystallises from alcohol (Wolkoff, Z. 1870, 580).

Methylamide C,H,SO₂.NHMe. [75°]. Rectangular plates, sl. sol. hot water. Yields

C,H.,SO,NBzMe [58°].

Ethylamide C,H.,SO,NHEt. [58°].

Antide C,H.,SO,NHPh. [103°].

forms C,H.,SO,NBzPh [149° cor.] (Remsen a. Palmer, Am. 8, 242).

C,H,.SO, NMePh [95°]. Methylanilide

Methylantide C,H,,SO,,MMePh [95°].
Moncelinic crystals (Otto, J, pr. [2] 47, 371).

Ethyl-anilide [88°]. Prigns, insol. water.
p-Toluide C,H,,SO,NHC,H, [118°].

Toluene exo.sulphonic acid C,H,,CH,,SO,H.
Formed by boiling benzyl chloride with aqueous K₂SO₂ (Böhler, A. 154, 50; 221, 215; Mohr, A. 221, 216; Otto a. Lüders, B. 13, 1286). Formed also by oxidising benzyl disulphide with HNO_s (Barbaglia, B. 5, 270, 688), and also, together with acetic acid, by heating benzyl methyl ketone with H₂SO₄ (Krekeler, B. 19, 2625). Very hygroscopic crystals. The K salt heated with KCy yields C₆H₄.CH₂.CN.
Salts.—NH₄A'.—KA'aq. Trimetre prisms.

—BaA', 2aq. Plates, sl. sol. water.—CaA', 2aq.—PbA'(OH): crystals.—PbA',.—AgA'; crystalline.

Chloride C_aH_a, CH_a, SO_aCl. [93°]. De-

omposed by heat into SO₂ and benzyl chloride. A mide C_aH₂.CH₂.SO₂NH₂. [102°] (O. a. L.) [105°] (Pechmann, B. 6, 534). Needles, sol. water and alcohol.*

Toluene (α)-disulphonic acid C₆H₃Me(SO₃H)₂ [1:2:4]. Formed by sulphonation of toluene and

of toluene o- or p-sulphonic acid (Hakansson, B. 5, 1084; Senhofer, A. 164, 129; Gnehm a. Forrer, L. 10, 542; Claesson a. Berg, B. 13, 1170; Klason, B. 20, 354). Formed also by heating toluene p-sulphonic chloride with H.SO. (Fahlberg, B. 12, 1652; Am. 1, 170; 1,280; (Fahlberg, B. 12, 1652; Am. 1, 170; 2, 182).

Thick liquid.— (NH.) A"aq.—K.A"aq.—BaA"aq.

8. 75 at 170. Insol. alcohol.—Ag.A" 2aq.

C n loride C,H.(SO.Cl)... [520].

• A mide C,H.(SO.NH.)... [1867].

Toluene (B)-disulphonic acid C,H.Mc(SO,H).

[1:2:5]. Formed by heating toluene σ -sulphonic acid with fuming H.SO, at 160° (H.), or toluene m-sulphonic acid with H.SO₄ at 180° (Klason, B. 19, 2889; 20, 352).— $K_2\Delta''$ aq.— $Ba\Delta''$ aq. S 3° at 15° (K.).

lb° (K.). Chloride C.H.3Me(SO,Cl)₂. [96° CH Mo(SO,NH.)₂. [224°

Chetriae Callane (SO. 11). [10].

Amide Calla Me(SO.) M1). [224].

Toluene disulphonic acid Calla Me(SO.) H).

[1:2:3]. Formed by the action of sodium-amalgam on p-iodo-toluene disulphonic acid (Limpricht a. E. Richter, B. 18, 2179; A. 230,

[1:2:6]. Formed by reduction of p-bromo-toluene disulphonic acid with sodium-amalgam (Kornatzki, A. 221, 199).—K₂A".—BaA" 4aq. V. e. sol. water.

O'hloride [86.5°]. Prisms (from ligroïn).

Amide [above 250°]. Needles, v. sol. Aq.
Toluene disulphonic acid C.H.Me(SO.H),
[1:3:4]. Formed from p-toluidine sulphonic
acid by conversion into C.H.Me(SH).SO.H and

oxidation of the product (Klason, B. 20, 356). K2A" aq.—BaA" 2aq. S 15. Prisms.

Chloride. [111°]. V. sol. CHCl., Amide. [235°-239°]. V. sol. water V. sol. water.

Toluene-s-disulphonic acid C_eH₃Me(SO₃H)₂[1:3:5]. Formed from o-iodo. (or bromo-) toluene disulphonic acid or o-diazotoluene disulphonic acid by long boiling with cone. HI (Limpricht a. Hasse, B. 18, 2177; A.

conc. HI (Limpriont a., Hasse, B. 18, 2177; A. 280, 295).—K_2A" 2]aq.—(NH.),A".

Chloride [132°]. Long prisms.

Amide [over 240°]. Small plates.

Toluene trisulphonic acid C₆H₂Mo(SO₂H)_s.

Formed by heating sodium toluene (a)-disulf phonate with ClSO₂H at 240° (Claësson, B. 14, 307). Slender needles (containing 6aq), v. sol. water. Salts.—K₃A''' 3½aq.—Pb₃A'''₂ 8aq.— Ba₃A'''

ter. Satts. — A_3A O_2 aq. — IO_3A , A'''_2 14aq. Crystals, v. sol. water. Chloride C_6H , Me(SO,Cl)₃. [153 A mide C_6H , Me(SO,NH)₃. [abc [153°]. [above 300°]. Minute crystals, nearly insol. water.

References .- AMIDO-, BROMO-, BROMO-AMIDO-BROMO-NITRO-, CHLORO-, IODO-, IODO-AMIDO-, NITRO-AMIDO-, NITRO- and OXY- TOLUENE SUL-PHONIC ACID.

TOLUENE p-THIOSULPHONIC ACID

C₁H₁Me.SO₂.SH. Formed by heating a solution of a salt of toluene p-sulphinic acid with sulphur (Otto, B. 15, 129; 20, 2087) or by adding a mixture of Na₂S and C,H,SO₂Na to an alcoholic solution of iodine (Otto a. Tröger, B. 24, 1132). A solution of Na salt gives a white pp. of cuprous salt on adding CuSO,

Reactions.—1. Indine added to an alcoholic solution of the K salt forms the three compounds (C,H,SO₂), S [134°], (C,H,SO₂), S₂ [199°], and (C,H,SO₂), S₃ [182°]. The compound (C,H,SO₂), S is also formed by the action of I on a mixture of C,H,.SO,SNa and C,H,SO,Na, and crystallises from benzene in monoclinic forms a:b:c=2.829:1:3.221; $\beta=60^{\circ}7'$. The compound (C,H,SO₂)₂S₂ is split up by boiling HOAc into (C,H,SO₂)₂S₃ is split up by boiling HOAc into (C,H,SO₂)₂S and (C,H,SO₂)₂S₃ (Otto a. Tröger, B. 21, 1126).—2. Cl.CO₂Et acting on the Na salt forms the cthyl and tolyl ethers and the compound (C,H,SO,)2S, [182°] (Otto a. Rossing,

B. 24, 1148).

Salts.—NaA' 2aq. Trimetric tables.—

KA' 2aq.—AgA' aq: small tables, sl. sol. water.

Ethyl ether C.H., SO., SEt. Tolyl ethyl

disulphoxide. Got from NaA' and Etl. Oil. Ethylene ether C₂H₁A'₂. [77°]. Needles. Decomposed by zinc-dust into the zinc salts of toluene sulphinic acid and ethylene mercaptan

(Otto a. Heydecke, B. 25, 1478).

Tolyl ether C.H., SO, SC, H., Tolyl dissulphoxide. [78°]. Formed by oxidation of p-tolyl mcreaptan (Märcker, A. 136, 83). Formed also from toluene p-sulphonic acid and water at 100° (Otto a. Tröger, B. 24, 480). Mono-clinic prisms (from alcohol). Decomposed on acid and di-tolyl disulphide [41°] (Otto a. Nössing, B. 19, 1240). Reduced by zinc and dilute H.SO. Br. (Otto 2. The C. H.SO.) (C₁₄H₁₄S₂O₂)₂Br₂ (Otto a. Grüber, A. 149, 105). Alcoholic H₂S forms, on wayming, toluene p-sulphinic acid, di-tolyl disulphide, and tolyl tetrasulphide.

Reference. - AMIDO-TOLUENE THIOSULPHONIC

TOLUBNYL- v. TOLENYL-.

o-TOLUIC ACID C.H.Mc.CO.H.[1:2]. Mol. w. 136. [104°]. H.C.v. 928,800. H.C.p. 929,400. H.F. 98,600 (Stohmann, J. pr. [2] 40, 133).

Fornation.—1. By oxidation of oxylene with dilute HNO₃ (Bieber a. Fittig, Z. [2] 6, 496; A. 156, 242).—2. From toluene o sulphonic acid vid C.H.,CN (Ranysay a. Fittig, Z. [2] 7, 584; A. 168, 246).—3. By the action of sodiunt amalgam on a mixture of ClCO.Et and o-iodotoluene and saponification of the resulting C,H,.CO,Et (Kekulé, B, 7, 1007). 4. By boiling phthalide (3 mols.) with HIAq (127°) and yellow P (2 at.), the yield being 97 p.c. (Hessert, B. 11, 238; Racine, A. 239, 72). -5. From o-toluidine via the nitrile (Cahn, A. 240, 280).

Properties.—Plates (containing 2ng), volatile with steam, sl. sol. cold water. Oxidised by alkaline KMnO, to phthalic acid (Weith, B. 7, Bromine-vapour above 100° forms phthalide; in the cold Br forms bromo-toluic

platande; hand could be form acid C₆H₃MeBr.CO₂H [167°]. Salts.—NaA' 2aq. [228°]. plates.—CaA'₂ 2aq. BaA'₂ 2aq. Ethyl ether EtA'. (220°). Efflorescent

Amido-ethyl ether Amido-ethyl ether
C,H,CO.O.CH,Edh.,NH,... Formed from o-tolyloxazoline and HClAq. Oil. Yields B'HBr
[156°], B'C₈H₈N₃O, [188°].
Amido-propyl &ther
C,H,CO.O.CHMe,CH,NH,... Formed by evapo-

rating tolyl-methyl-oxazoline with HClAq. Yields B'HBr [140°], B'C, H, N, O, [192°], and a platinochloride [211°].

Benzyl ether C.H.A'. (315°). S.G. 17 112. Oil (Hodgkinson, C. J. Proc. No. 103, p. 167). Chloride C.H.OCl. (211° at 733 mm.).

Anhydride (C,H,.CO) O. [c. 38°]. (Ebove 325°). Formed from the Na salt (6 mols.) and POCI. (1 mol.). Insol. water, sol. ether and

Amide C,H,.CONH... [140°] (Hutchinson, B. 24, 174; G. J. 57, 957; cf. Weith, B. 6, 420). On reduction in acid solution it yields o-tolyl alcohol and a small quantity of the dihydride C,H_s.CO.NH₂ [156°], which on boiling with water yields an acid [68°]. The dihydride is also formed by reducing the amide in alkaline solution.

Anilide C,H, CO.NRPh. [125]. Formed from anti-phenyl-o-tolyl ketoxim and PCl_a followed by water (Smith, B. 24, 4047).

Xylide C.H., CO.NHC, H.Me₂ [1:2:3]. [165°].

Formed by heating o-tolyl xylyl ketone with hydroxylamine at 120° (Smith).

Bromo-ethylamide C.H., CO.NH.CH., CH.Br. [71°] (Salomon, B. Landolt, B. 8, 720), and in other ways (Buchka 26, 1322).

Chloro-ethylamide C,H,.CO.NH.CH, CH,Cl. [73°]. White needles.

Bromo-propyl-amide Needles . C,H,,CO.NH.CH,,CHBr.CH3. $(86^{\circ}).$ (from benzene-ligroïn) (Salomon B. 26, 1323).

Chloro-propyl-amide C,H,.CO.NH.CH,.CHMeCl. [84°]. Formed by evaporating o-tolyl-methyl-oxazoline with excess of HClAq. Needles (from ligroin). .

o-Nitro-benzyl-amide C.H.,CO.NH.CH.,CH.,NO, [195]. Needles (from alcohol). May be reduced to the o-amido-

benzyl-amide [116°], which yields B'HCl [214°] (Wolff, B. 25, 3034).

(Woin, B. 20, 3034).

Imide (Q,H,CO)₂NH. [148°].

Nitrile C,H,CN. (204° cor.). V.D. 4·03 (obs.). H.F. -34,800 (Berthelot a. Petit, A. Ch. [6] 17, 12:3). Formed by heating KCy with potassium toluene o-sulphonate or with tri-otolyl phosphate (Heim, B. 16, 1776), by heating o-tolyl thiocarbimide with finely-divided copper (Weith, B. 6, 419), by boiling o-tolyl carbamine (Weith, B. 7, 722), by heating o-iodo-toluene with AgCy at 350° (Merz a. Weith, B. 10, 751), by boiling the formyl derivative of o-toluidine with zinc-dust (the yield being 18 p.c.) (Gasiorowski a. Merz, E. 17, 74; 18, 1004), and by Sandmeyer's reaction from a-toluidine (Cahn, B. 19, 756). Liquid. H.SO, at 60° to 70° forms C.H. C(NH).NH.CO.C H. [103°], which is converted, by warming its acid solution, into the imide (C.H., CO), NH (Krafft a. Kerstens, B. 25, 455). Cone. HIAq forms C.H., CI_, NH_ [98°] (Biltz, B. 25, 2510).

Hexahydride v. Methyl-nexamethylens CARBOXYLIC ACID.

M-Toluic acid C_cH₁Me,CO_cH [1:3]. [110^o] (Jacobsen, B. 14, 2347; Bornemann, B. 20, 1382). (263°). H.C.v. 928,500. [1.C.p. 929,100] H.F. 98,900 (Stohmann, J. pr. [2] 40, 134). S. 09 at 15°; 1·66 at 100°.

Formation. 1. By oxidising bromo-xylene. and reducing the resulting bromo toluic acid with sodium-amalgam (Ahrens, Z. [2] 5, 106; Richter, B. 5, 421; Böttinger a. Ramsay, A. 168, 255). 2. By distilling uvitic acid with lime (Fittig, B. 5, 268). 3. By oxidation of m-xylene with dilute HNO₄ (Taxildaroff, B. 4, 410; Bruckner, B. 9, 406; Reuter, B. 17, 2028).—

4. By saponifying the nitrile. Preparation. 1. By boiling \(\omega\)-chloro-xylene with HNO, (4 vol. of S.G. 14) and water (3 vols.) (Senff, A. 220, 247).—2. By suphonating crude xylene, then preparing C₃H_Me₂SO₂NH₂, oxidising by KMnO₃, heating the resulting C₃H_Me(SO₂NH₂).GO₂H with HCl at 230°, and

distilling with steam (Jacobsen, B. 14, 2347). Properties. - Long needles, volatile with steam, v. sol. alcohol and other. Oxidised by chromic acid mixture to isophthalic acid.

Salts.—CaA' 3aq. S. 3.17 at 15°; 8.2 at 100°.—BaA', 2aq: trimetric plates or tables.—

AgA'.

Ethyl ether EtA'. (226°).

Chloride (218' at 724 mm.) (Ador a.

Rilliet, B. 12, 2300).

Nitrité C.H.CN. (200°). Formed by heating m-tolyl thiocarlimide with Cu (Weith a

a. Schachtebeck, B. 22, 841).

—Tofnic acid C.H.Mc.CO₂H [1:4]. [179].

(275° cor.) (Fischli, B. 12, 415). H.C.v. 926,800.

H.C.p. 927,400. H.F. 100,600 (Stohmann, J. pr.

[2] 40, 134). Formation.—1. By the action of dilute NHO₃ on cymene (Noad, P. M. [3] 32, 19; A. 63, 289) on p-xylene (Beilstein, A. 137, 302; Bruckner, A. 205, 113), and on terpenes (Hirzel, Z. 1866, 205).—2. By saponification of the nitrile.—3. By heating p-bromo-toluene with ClCO₂Et and sodium-amalgam and saponifying the product (Wurtz, C. R. 68, 1238).—4. From p-bromo-toluene, CO, and sodium (Kekulé, 4,

187, 184). - 5. By the action of POCl₂ (40 g.) on 1 a mixture of toluene (40 g.), HOAc (80 g.) and ZnCl, (80 g.) at 110° (Frey, J. pr. [2] 43, 116). 6. By reducing bromo p-toluic acid with sodiumamalgain (Reinsen a. Morse, Am. 1, 138) .-7. From the chloride which is formed by the action of COCl2 on toluene in presence of AlCl3 (Ador a. Crafts, B. 10, 2176) .- 8. From the amide which is formed by the action of AlCl, on a mixture of toluene, CS₂, and NH₂,CO.Cl (Gattermann a. Schmidt, B. 20, 859).—9. By fusing C,H,.CO.Cl,II,.CO,II with potash (Friedel a. Costte, Bl. (19) 35, 50(8), and she have the continuous and the cost of the Crafts, Bt. [2] 35, 508), and also by passing gaseous evanic acid and HCl into Sluene at 100° containing AlCl, (Gattermann a. Rossolymo, B. 23, 1195).

Properties.—Needles, v. sol. hot water, v. e. sol. alcohol and ether. Volatile with steam. Oxidised by CrO, or KMnO, to terephthalic acid. Yields a di-nitro-derivative [158].

Salts.—KA'.—BaA', 2aq: needles (Buchka a. Irish, B. 20, 1764).—CaA', 2aq.—MgA', 2aq.—

Cul', - AgA'.

Methyl ether McA'. [322]. (217°).

Ethyl ether Eth'. (228"). Oil.

Amido-ethyl ether C, H, COO.C, H, NH.,

Yields B'HBr (167°) and B'C, H, NO, I(80°).

p-Amido-propyl ether C,H,,CO.O.C,II,,NH2. Th The hydrobromide B'HBr is formed by evaporating a solution of the bromo-propyl-amide. It yields B'C, H, N, O, [186°] and B',H,PtCl,

[186°] and B'Haltuch.
Phenyl other PhA'. [72°].
Chloride (225° at 720 mm.).
Amile C.H., CO.NH... [159°]. Formed by heating the NH, salt in scaled today at 230° (Hallemann, R. T. C. 6, 79).
Methylamide C.H., CO.NHMe. [143°].

Formed by the action of NHMe.COCl on toluene in presence of AlCl₃ (Gattermann a. Schmidt, B. 20, 120; A. 244, 51). Tables.

Ethylamide C,H,CO.NHEt. [96°].

Bromo-ethyl-amide

C,H, CO.NH.CH, CH, Br. [129°] (Salomon, B. 26, 1325). Formed from p-toluic chloride and bromo-ethylamine. Plates. Converted by boiling water into the amido-ethyl ether.

Chloro-ethyl-amide C,H,.CO.NH.CH,.CH,Cl. [122°]. Needles (from ligroin).

Bromo-propyl-amide C,H,CO.NH.CH,CHBr.CH₃. Melts at 74°. becomes solid, and melts again at 158° (B. 26, 1326)

Chloro-propyl-amide C,H,CO.NH.CH.,CHMeCl. [78°]. Anilide C,H,CO.NHPh. [145°]. Formed, from toluene, phenyl cyanate, and AlCl, (Leuckart, J. pr. [2] 41, 306).

o · Nitro · anilide. [110°]. Yellow prisms.

p - Toluide C,H,.CO.NHC,H,. [160°]. Formed by the action of sodium-amalgam and HOAc at 60? on an alcoholic solution of di-p-tolyl ketoxim (Goldschmidt a. Stöcker, B. 23, 2747; 24, 2799). Needles. Nitro-toluideC,H,CO.NHC,H,Me(NO2)

[4:1:8]. [166°].

Diphenylamide C.H., CO.NPh., [1559]. Prisms (from alcohol) (Lellmann a. Bonhöffer, B. 20, 2118).

Xylide C.H., CO.NHC, H.Me., [1396]. Yields C.H., CO.NH.C, H.Me. (NO.) [1876].

Phenyl-methyl-amide C.H., CO.NPhMe. [70°] (Lellmann a. Benz, B. 24, 2114).

o-Nitro-benzyl-amide C.H.,CO.NH.CH.,C.,H.,NO2. [142°] (Wolff, B.

25, 3036).

Nitrile C.H.Me.CN. ſ28·5°1. Formed by distilling potassium toluene p-sulphonate with KCy (Merz, Z. [2] 4, 33), by heating C.H. N.CS with Cu (Weith, B. 6, 421), by heating tri-p-tolyl phosphate with KCy (Heim, B. 16, 1775), and by passing C.H..NH.CHO over heated zinc-dust (C. a. M.). Obtained also from p-toluidine by Sandmeyer's reaction (Glock, B. 21, 2650). Sodium added to its boiling alcoholic solution forms a small quantity of ω -amido-p-xylene, the greater part being saponified (Bamberger a. Lodter, B. 20, 1710). ILSO, gives C.H.,C(NII).NH.CO.C.H. [145°]. Easily converted into the imide (C.H.,CO).NII [155°] (Kruff a. Karstens, B. 25, 454). Conc. HIAq forms C.H. Cl. NH. [115°-120], decomposed by

forms C.H.,CL,NH₂ [115 - 120], account fusion (Biltz, B. 25, 2539).

Tetrahydride C₃U_{1,0}O₂, (252°). Formed by reduction of CH₂:CCCH₂CH₂CH₂CO₂H with sodium-amalgam (Einhorn a. Willstälter, B. 26, 2009). Needles, melting below 0°. Yields CaA'₂4aq, CuA'₂2aq, McA'. (210°-220°), and an amide [158°]. Boiling NaOHAq converts the acid into a solid isomeride [47°] (254'-260°) which yields CaA', 4aq and an amide [135°]. Hexahydride (Screbojakoff, B. 25, 3355).

References .- Amido-, Bromo-, Bromo-nitro-, CHLORO-, NITRO-, NITRO-AMIDO-, OXY-, OXY-AMIDO-, and SULPHO- TOLUIC ACID.

a-Toluic acid is PHENYL-ACETIC ACID

o-TOLUIC ALDEHYDE C.H.Mc.CHO[1:2]. o-Toluylic aldchyde. (200°). Prepared by boiling ω-chloro-o-xylene with lead nitrate solution (Lauth a. Grimaux, Bl. [2] 7, 233; Rayman. Bl. [2] 27, 498). Prepared also from o-xylene by the successive action of CrO,Cl, and water Bornemann, B. 17, 1467), and by oxidising C_nH,Mc.Cll,OH with chromic acid mixture (Kröber, B. 23, 1029). Oil, smelling like bitter almonds. Yields a crystalline compound with NaH&O3. Reduced by sodium-amalgam to o-tolyl-carbinol.

oxim. White crystals (from ether), v. solalcohol. Yields a crystalling had Oxim C.JI, Me.CH: NOH. [49°]. Is an anti-Yields a crystalline hydrochloride. Ac₂O yields an acetyl derivative [56°]. AcCl acts in like manner. The acetyl derivative is decomposed by alkalis with regeneration of the oxim, no nitrile being formed (Dollfus, B. 25, 1921). The oxim is converted in ethereal solution by PCl, into the nitrile (204°).

"m-Toluic aldehyde C_cH₁Mc.CHO[1:3]. (199°). S.G. 2 1·037. Formed by boiling ω-chloro-m-xylene or ω-bromo-m-xylene with lead nitrate solution (Gundelach, Bl. [2] 26, 44; Müller, B. 20, 1913) and select by the action content. 20, 1213), and also by the action of water on C,H,CrO,Cl, obtained from m-xylene (Etard, B. 14, 848; Bornemann, B. 47, 1464). Oil, smelling like almonds. Combines with NaHSO. Aniline forms C.H., CH:NPh. (314°).

Phenyl-hydraside C.H., Me.CH:N2HPh. [91°]. (B.); [88°] (Rudolph, A. 248, 100).

Prisms (from ligroin), v. sol. ether.

n-Toluic aldehyde CaH.Me.CHO[1:4]. (205°). Formed by distilling calcium p-toluate with calcium formate (Cannizzaro, A. 124, 254). Formed also by the action of water on the product of com-bination of p-xylene with CrO.Cl. (Bornemann). Oil, with peppery smell. Oxidised by air to toluic acid. Alcoholic potasts forms potassium toluate and tolyl-carbinol.

Reference .- NITRO- and OXY- TOLUIC ALDE-

TOLUIC CHLORIDE v. Chloride of Toluic

TOLUIDES. Compounds derived from toluidine by displacement of H in NH, by an acid radicle

o-TOLUIDINE $C_8H_4Me.NH_2[1:2]$. Mol. w. 107. (198°). S.G. ²⁰ 9986 (Brühl, A. 200,189). H.C.p. 964,700. H.C.v. 963,750. H.F. 3,800 (Petit, C. R. 107, 266). μ_B 1-5895. R_{∞} 57:56. S.V. 126:6. Formed from o-cresol, ZnBr., NH₀, and NH₀Cl at 335° (Merz a. Müller, B, 20, 547). Prepared by reduction of o-nitro-toluene. May be senarated from p-toluidine by means of the acidoxalates (Bindschedler, B. 6, 448; Ihle, J. pr. [2] 14, 449; Miniati, Booth a. Cohen, S. G. I. 6; 418), by freezing (Rosenstiehl, Bl. (2) 17, 7), by means of the nitrates (Schad, B. 6, 1361), hydrochlorides, sulphates, or phosphates (Lewy, Fr. 23, 269; B. 19, 1717, 2728; cf. Wülfing, B. 19, 2132). o-Toluidipe can be prepared from C.MeHBr(NH.)(NO) H. vid. C.MeHBrI(NO)H, C.MeHBrl(NH.)H, C.MeHBrlBrH, followed by C.Me(NO.)BrIBrH, and C.Me(NH.)BrIBrH. It can also be got from C.Me(NH.)BrIBrH vià can also be got from Cate(N1)167116711 that CaMelBriBrH, followed by C_MelBriBr(NO) and C_aMelBriBr(NH_2) thus proving that the toluidine C_H_Me(NH_2) [1:2] is identical with C_aH_Me(NH_2) [1:6] (Wroblewsky, A. 192, 213).

Properties.—Oil. A solution in H_SO_H_O is coloured orange by HNO₄ and blue by CrO₃, the

solution in the latter case becoming reddishviolet on dilution. Forms a crystalline com-pound with liquid CO₂ at 8° (Bitte, C. R. 105, 614). With PbO, and aqueous acetic acid gives a green colour, while PbO, and alcoholic acetic acid gives a reddish-violet colour (Lauth, C. II. 111, 975). Unlike p-toluidine, it forms a crystalline compound with alloxan (Pellizzari, C. C. 1887, 1288, 1396). If an ethereal solution of o-toluidine is shaken with very dilute blacking. powder solution the aqueous layer becomes yellow or brown, and the ethercal layer, if decanted and shaken with dilute H SO, colours A solution of p-tolylene this reddish-violet. diamine hydrochloride mixed with a little otoluidine gives a green colour on addition of

rougaine gives a green colour on addition of FeCl, or K_Or₂O, (Nietzki, B. 10, 1157).

Reactions.—1. POCl, forms PO(NHC,H.) e [225°] (Michaelis a. Rudert, B. 26, 505), v. sol. water, whence Br forms PO(NHC,H.,BrM), [253°]. Another product of the action of POCl. no-toluidine is POCI(NHC, H, Me)₂, whence water forms HO.PO(NHC, H₂)₂ [95⁻²]. PSCI, forms PS(NHC, H₃)₂ [95⁻²]. PSCI, forms PS(NHC, H₃)₃ a whitegranular powder (Harden C. J. 51 40)₁ = 8 Deating with mathematical states. C. J. 51, 40).—3. On heating with matter acid it yields the mono-toluide [178°], di-toluide [181°], and a tolyl-imide [116°] of malic acid (Bisa) off, B. 23, 2043).—4. Chloro-citryl chloride forms C,H,N CO.C.H (214°) (Skinner

a. Ruhemann, C. J. 55, 289) .- 5. SO, alcohol, and nitrous acid give rise to the 'sulphazide C₁₁H₁₂N₂SO₂ [142°] (Limpricht, B. 20, 1241).— 6. On nitration of o-toluidine or its acetyl derivative NO₂ enters the p- and o- positions, but in presence of H.SO₄ (10 pts.) the compound C.H.Mc(NO₂)(NH₂) [1:4:6] [107°] is formed (Nölting a. Collin, B. 17, 265), together with the (1,2,6)-isomeride (Green a. Lawson, C. J. 59, 1018). -7. Benzoic aldehyde forms C_sH₂CH:NC₇H₇, an oil (316°) (Etard, Bl. [2] 39, 530; Pictet, B. 19,1063). 8. Hydrobenzamide or warming forms the same body (310°) (Lachovitch, M. 9, 695). 9. Toluidine heated with toluidine hydrochloride and benzoic aldehyde in scaled tubes at 120 forms $C_nH_nCH(C_nH_nMe,NH_n)_n$, a crystalline powder turning blue in the air (Ullmann, J. pr. [2] 36, 251). - 10. The methyl derivative of p-oxy-benzoic aldehyde at 120 produces the compound CaH (OMe).CH;N.C H [32°] (Steinhart, A. 241, 310). Il. Bromo-propiolic acid reacts, forming C_{1.}H₁₈N₂O₂ [185°] (Mabery a. Krause, B. 22, 3308). –12. aB-Di-brory-acrylic acid produce pale-yell-w needles [15°] (M. a. K.). –13. The hydrochloride heated with MeOH at 250°–300° xvlidine gives rise to di-methyl-toluidine, xylidine $C_0H_3Me_2(NH_2)$ [4:3:1] and mesidine (Limpach, B. 21, 640).—14. Cyanagan passed into an alcoholic solution forms crystalline C_nH_nN_n which yields B"H_Cl_n and B"2HNO₁ (Bladin, I^H, [2] 41, 128).—15. On heating with S it yields C_nH_nN_nS [120] crystallising from alcoholic realization and the control of the con in yellow plates and yielding a dibromide *C₁,H₁,Br₂N₂S₁[190] (Gattermann, B. 22, 425).— 16. CISO₂H in CHCl₂ forms C₂H₂NH₂SO₂H₃, which yields BaA', 2aq. Both the acid and as salts reproduce o-toluidine when treated with hot water (Traube, B. 23, 1656).

Salts (Beilstein a. Kuhlberg, A. 156, 66; Rosenstieht). B'HClaq. S. 374 at 15.5°. S. (alcohol) 100. - B', H PtCl_o. Decomposed by boiling water (difference from p-toluidine) (De Coninck, Bl. [2] 45, 131). B' H₂ZnCl₁. White tables (Bibanoff, Montt. scient. [3] 4, 925).— B',ZnCl, 2aq (Lachovitch, M. 9, 513). B',HgCl, [115°]. Prepared by shaking an alcoholic solu-[115°]. Prepared by shaking an alcoholic solution of the base with HgCl, (Klein, B, 11, 743). Crystalline powder, sol. alcohol and ether. B'.MuCl., B' H CuCl, Yellow crystalline pp. got by adding CuCl, to a solution of the hydro-chloride (Pomey, C. R. 104, 365).—B'HBr. Trichleride (Ponicy, C. R. 101, 303).—B 11Bt. Trimetric prisms.—B H.B.R. 11Bt.] Locaflets (Klein, B. 13, 835).—B Z.B.B.; (Leeds, J. 1882, 503).—B H.L. Trimetric prisms (Städel, B. 16, 28).—B H.B. White needles.—B Z.B.B. B Call...—9B H.B.Cy.,—B H.FeCy.; crystals.—B H.G. (SO₂)... Formed by adding aqueous cupric sulphate and NaBSO, to a solution of the bars in surface and Chemica. B 112–270. base in acetic acid (Deniges, C. R. 112, 870) .base in acetic acid (Denigis, C. R. 112, 870).—
B'Hg'M(\$\oldsymbol{G}_{\partial_2}\), aq. B'H_{\partial_2}\), Crystals (Wellingtoff a. Tollens, B. 18, 3343).—B'_{\partial_2}\), B. 78
at 22?—S. (89 p.c. alcohol) 1:6 at 21:5°.—B'HNO_{\partial_2}\), S. 10 at 19°. S. (89 p.c. alcohol)
23:5 at 16:5°.—B'H_{\partial_2}\), Crystals, v. sol. water
(Lewy, B. 19, 1717). The salts B'_\partial_2\), P. H_{\partial_2}\), could not be prepared. Aniline sets
free o-toluidine from B'H_{\partial_2}\), p. Toluidfie also
sets free o-toluidine from the property of B'HSCyCr(SCy),2NH. Red plates, v. sol. hot water (Christensen, J. pr. [2] 45, 362).—Oxalate: small plates. S. 238 at 21°. S. (84 p.s.

alcohol) 2.68 at 21°. S. (ether) .65 at 21°.— Chloroacetate B'C.H.ClO. [95°] (Bischoff, R. 21, 1257).—(\$?)-naphtholate [81°] (Dyson, C. J. 48, 470).

Formyl derivative C,H, NH.CHO. [58°]. (288°). 'Plates (Ladenburg, B. 10, 1129; Tobias, B. 15, 2446). The crystalline polymeride [211° is v. sol. hot HOAc, nearly insol. ether and cold alcohol.

Thioformyl derivative C.H.NH.CSH: [96°]; yellow needles; bitter taste; sol. alcohol and ether, insol. water. Formed by heating the formyl derivative with P.S. It dissolves unformyl derivative with P₂S₃. It dissolves unaltered in cold aqueous NaOH, and is reprecipitated by an acid. By distination in vacuo it

forms di-tolyl-formamidine $\overset{\leftarrow}{C_2H_1,NH} \gg CH$ with

evolution of H₂S and CS₂. By heating for 7 hours at 190° under pressure a crystalline compound

at 190° under pressure a crystaline compound $C_{14}H_{18}N_{2}$ S [160°] is formed with evolution of H_{2} S (Senier, B. 18, 2292; C. J. 47, 762).

Acetyl derivative C.H., NIIAc. [109°] (Bedson a. King, C. J. 37, 753). (296°). S. 85 at 19°. Formed from the base and HOAc (Bedl-19°). stein a. Kuhlberg, A. 156, 77; Alt, A. 252, 318), or by shaking it with water and Ac.O (Hinsberg, B. 28, 2962). Converted by PCl, into the compound C,H,N:CClMe, which when carefully heated gives a base C,H,N:CMe.CH₂.CCl:NC,H, [53°], and when treated with excess of o-toluidine gives · di-tolyl-acetamidine [69°]. Br in HOAc forms $C_{a}H_{3}MeBr(NHAc)$ [1:6:2] [157°].

Chloro-acetyl derivative C,H,NH.CO.CH_Cl. [112]. Formed by the action of chloro-acetyl chloride on o-tolulline dissolved in benzone (Widman, J. pr. [2] 38, 299). Needles (from dilute al-conol). Converted by alcoholic potash into a pyrazine derivative

[160°].
Di-ntoro-acetyl derivative C, H, NH.CO.CHCl2. Needles, volatile with steam • (Bügheimer a. Hoffmann, B. 18, 2987).

Tri-chloro-acetyl derivative
C,H,NH.CO.CCl₃. [67°]. Formed from hexachloro-acetone and o-toluidine (Cloez, A. Ch. [6] 9, 215). Needles, sl. sol. cold alcohol. Bromo-acetyl derivative

C,H,.NH.CO.CH,Br. [113°]. Formed from o-toluidine and bromo-acetyl bromide (Widman, J. pr. [2] 38, 298). Needles. Converted by alcoholic potash into C₁₀H₁₈N₂O₂ [160°].

Thio-acetyl derivative

C,H,NH.CS.CH,. [68°] (Wallach, B. 13, 529; 16, 147). Converted by NaOEt and EtBr into oily C,H,N:CMe.SEt (262°).

Propionyl derivative C.H..NH.COEt. [87°]. (299° at 730 mm.)! Formed from o-toluidine and propionic acid (Pictet a. Duparc, B. 20, 3421). Needles, sl. sol. hot water. (Avidised by KMnO, to propionyl-o-amido-benzoic acid €117°].

a-Bromo-propionyl derivative C,H,NH.CO.CHBr.CH₃. [131°]. Needles, insol. ligroin (Tigerstedt, B. 25, 2920). Bensoyl derivative C,H,NHBz. [131°]

(Gudeman, B. 21, 2553); [143°] (Brückner, A. 205, 130). Long braad needles. Vields benzoylo-amido-toluic acid on oxidation by KMnO.
PCl. forms C,H.,N:CCl.C.,H. (Just, B. 19, 982).

Oxaly! derivative C,O./(NH.C.H.).

Plates (from alcohol) (Bladin, Bl. [2] [181°]. 41, 130).

Phthalyl derivative C,H,N:C,O,:C,H, [182°]. (near 360°). Needles, sol. hot HOAc (Frehlich, B. 17, 2679).

Phenacyl derivative C,H,NH.CH,.CO.C,H₃. [89°]. Formed from the base in alcohol and ω-bromo-acetophenone (Bischler, B. 25, 2865). Needles. Yields B'HCl and an acetyl derivative [92°].

m-Toluidine C_oH₁Me.NH₂ [1:3]. (197°) (Beilstein a. Kühlberg, A. 156, 83); (201°) (Buchka a. Schachtebeck, B. 22, 840); (202°) (Lorenz, A. 172, 180; Morz a. Müller, B. 20, 548). S.G. 25; 998. S.N. 128:1. H.C.v. 964,600. H.C.p. 965,600. H.F. 2,900 (Petit, A. Ch. [6] 17, 155). Formed by reduction of m-nitro-toluene. Obtained also from p-toluidine by successive acetylation, nitration, saponification, diazotisation, boiling with alcohol, and reduction (Lorenz, B. 7, 448). Formed also by heating m-cresol with ZnBr, ammonia, and NH, Br at 300° (M. a. M.). Prepared from benzoic aldehyde by nitration, conversion into m-nitro-benzylidene chloride and reduction of this body by zinc and HClAq in the cold (Vienne a. Steiner, Bl. [2] 35, 428; Widman, B. 13, 676; Bl. [2] 36, 216; Ehrlich, B. 15, 2011; Harz, B. 18, 3398). m-Toluidine can be shown to exist in commercial toluidine by means of the nitroso- derivative of di-methylm-toluidine, since o- and p- di-methyl-toluidines do not give nitroso- derivatives (Wurster a. Riedel, B. 12, 1796).

Properties. -Oil. Its solution in H2SO4H2O is coloured yellowish-brown by CrO, and blood-red by HNO3. Its ethereal solution, shaken with water and a little bleaching-powder, is coloured reddish, the aqueous layer being brownish yellow. HNO, added to its solution in a mixture of H₂SO, and HOAc below 0° forms nitro-toluidine [134°] and some of its isomerides. Cyanogen passed into its alcoholic solution gives the compound (C,II, NH₂), C₂N₂ [200°] which forms B'₂HCl, B'₂ZlNO₃, and B'₂Zl₂SO₄ (Clève a. Bladin, Bl. [2] 41, 129). Yields (4,2,1)-xylidine when its hydrochloride is heated with MeOH at

200°-300° (Limpach, B. 21, 616). Salts.—B'HCl. S. 96·3 at 12°. alcoho) 61-9 at 9 - B'_1H_PtCl_-B'HNO_ 18 20-1 at 23-5°. S. (94 p.c. alcohol) 46 at 15°.— B'HBiI₃ (Kraut, A. 210, 323).—B'_1H_SO_ 8 6-25 at 14°. S. (94 p.c. alcohol) 41 at 15°.— B'H BiC. (Fiscahola 4. 200. 370). 5'25 at 14°. S. (94 p.c. alcohol) '41 at 15°.—
B',H,FcCy, (Eisenberg, A. 205, 270),—B'H,2C,Q,
Silky needles. S. 2'65 at 13°; S. (94 p.c. alcohol)
1.77 at 15°; S. (ether) '13 at 15°,—
B',2H,2C,Q, White plates, S. 1.45 at 15°;
S. (94 p.c. alcohol) '96; S. (ether) '128 at 15°5°,
—B',2H,2C,Q, aq. Very unstable.

Formyl derivative C,H,NH.CHO. (278° at 724 mm.) (Niementowski, B. 20, 4892). Converted by long boiling into C,H,N:CH.NHC,H, [123°].

Acetyl derivative C,H,NHAc. (303°). S. 44 at 13°. [659].

Di-chloro-acetyl derivative C.H.,NH.CO.CHCl., [106°]. Silky (Rügheimer a. Hoffmann, B. 18, 2988). Bensoyl derivative C.H.,NHBz. plates

(Just, B. 19, 983). Phthalyl derivative C,H,N.C.O.:C,H. [168]. Needles, v. sol. HOAc (Frohlich, B. 17. 2679).

2679).
p - Toluidine C.H.Me(NH.)[1:4]. [45°]
(Städeler); [42:8°] (Mills). (198°) (M. a. H.);
(206°) (Städeler, J. pr. 96, 65). S.G. 1'046.
S. 35 at 11:5°. H.C.p. 958,800. H.C.v.
957,800. H.F. 9,700 (Petit, C. R. 107, 266).
S.V. 128,700. Formed by reduction of p-nitrotoluene (Muspratt a. Hofmann, A. 54, 1; 66, 144; Noad, A. 63, 305: Hugo Müller, Z. 1864, 161; Sell, C. J. 16, 186; v. also o-TOLUTDINE). Formed also by heating p-cresol with ammoniacal ZnOl₂ (Buch, B. 17, 2637; Merz a. Müller, B. 20, 545) and by treating methylaniline hydrochloride at 350° (Hofmann, B. 5, 720). On sulphonating a mixture of o- and ptoluidine the o-toluidine is first attacked and

the p-toluidine can then be distilled off.

Properties.—Plates (from ligroin or dilute alcohol). Its solution in H₂SO₄H₂O is turned yellow by CrO, and blue by HNO, in the latter case changing to red and finally brown (Rosenstichl, Bl. 10, 200). Bleaching-powder does not colour its solution in water or ether. PbO, and HOAc diluted with water or alcohol give a bright red colour (Lauth, C. R. 111, 975). When boiled with water, crystals of an efflorescent hydrate

separate on cooling (Lewy, B. 19, 2728).

Reactions.—1. Oxidised by KMnO₀ alkaline R₃FeCy₉, or chromic acid to C_uH₂₁N₃ or C₆H₂Me(NC₁H₁)₄(NH₂) [1:2:5:4], which may be readily reduced to C_uH₂Me(NHC₁H₁)₄(NH₂) readily reduced to C₁(1.34(NIC,11.34(NI₂) crystallising from alcohol in colourless plates [166°], readily re-oxidised to C₂(11.3N, (Barsilovsky, A. 207, 102, 118; J. R. 1887, 132; Perkin, C. J. 35, 728; 37, 546; Klinger a. Pitschke, B. 17, 2439; Green, C. J. 63, 1395). The compound $C_{cl}H_{21}N_3$ crystallises from xylene in dark-red plates [227°], dissolving in acids, forming maroon-red liquids, quickly decomposing with separation of p-toluidine. Conc. composing with separation of p-tolindine. Cone. H₂SO₄ dissolves C₂₁H₂N₃, forming a greenish-blue liquid which on warning becomes winered with production of p-toluidine. – 2. Oxidised by CrO₃ and HOAc to toluene-azo-toluene C,H₂,N₂,C,H₃. — 3. Nitrons acid forms C,H₂,N₂,NHC,H₃. When NaNO₂ is added to a solution of the hydrochlorides of o and p-toluidine, the activation is first attacked. toluidine, the o-toluidine is first attacked, yielding C₂H₂N₂,C₂H₆NH₄ and can thus be removed when mixed with p-toluidine (Wülfing, D. P. J. 263, 260).—4. Substituents usually enter positions 3 and 5 [Me 1] but when p-toluidine or its acetyl derivative is dissolved The Hard of the compound C₄H₄Me(NO₂)(NH₂) [1:2:4] is formed instead of the (1,3,4)- isomeride (Nölting a. Collin, B. 17, 263).—5. Bromine in conc. HClAq at 0° forms C₄H₂Br₂Me(NH₂) [5:3:1:4]; but C₄H₃BrMe(NH₂) C₂H₂Br₂Me(NH₂) [5:3:1:4]; but U₄II₃DrMe(NH₂) [2:1:4] is formed in presence of conc. H₂SO₄, (Hafner, B. 22, 2538, 2902).—6. ICl forms C₂H₂H₂Me(NH₂) [5:3:1:4] (Michael a. Norton, B. 11, 107).—7. Chlorine passed into p-toluidine dissolved in H₂SO₄ at 0° forms C₂H₂MeCl(NH₂) [1:3:4] and larger quantities of its [1,2,4] · isomeride. In HClAq (40 p.c.) the chief product is C₂H₂MeCl₂(NH₂) [1:3:5²A] (Hafner).—8. Cyanogen respective an electric solution forms C₂H₂MeCl₂(NH₂) [1:3:5²A] (Hafner).—8. Cyanogen passed into an alcoholic solution forms CieHisN. or (C,H,N),C,N, crystallising in planty scales [322°-280°] and yielding the crystalline salts B',2HCl, B',2HNO, B',H,SO, 6aq, and B',H,C,O,

(Hofmann, C. J. 1, 170; A. 66, 144; Clève a. Bladin, Bl. [2] 41, 125). The mother-liquor contains C_{.1}H_{.2}N_{.3} [182°] which yields the salts B'HCl 3aq (a_sred powder) and B'_{.2}H_{.3}PtCl_. The compound C₁₆H₁₈N_{.4} is also formed when p-toluidine is heated with oxalimido-ether at 100° (Vorländer, B. 24, 805).—9. Cyanurio chloride forms C₈N_{.3}(NHC.H.), [288°] (Klason, J. pr. [2] 33, 294).—10. Chloro-acetic acid (½ mol.) forms C,H,NH.CH.,CO,H, while chloro-acetamide forms C,H,NH.CH.,CO,H, (P. F. Meyer, B. 8, 1158). An alcoholic solution of Meyer, B. 8, 1458). An alcoholic solution of chloro-acetic acid and HCyS yields C₁₀H₁₂N₁SO₂ [176 · 182 ·] (Nenchi, J. pr. [2] · 16, 1).—11. Dichtoro-acetic acid forms tolylamido-methyloxindole.—12. Chlorat reacts, with formation of CCl₃CH(NHC,H₁), [115 ·] (Wallach, A. 173, 278). When chloral is warmed with an alcoholic architect for the Line of the color. alcoholic solution of p-toluidine there is also formed CCl_xCII(OEt).NIIC, II, [77°]. = 18. Aldehyde forms crystalline CH_xCH(NIIC, II,) [c. 60°] .-- 14. Furfuraldchyde added to a hot alcoholic solution of / coluidine and its hydrochloride forms brown amorphous $C_{19}H_{22}N_2O_{29}$ which yields B'HCl and B'HNO₃ both crystallising in purple needles (Stenhouse, A. 156, 203). 15. Nascent formic alaichyte produces a base $C_{17}H_1,N_2$ [134] which is converted by nitrous acid with evolution of CO_2 into $C_{18}H_{18}N_2O_3$ acid with evolution of CO, into Charling Vg. [260° 264°] (Tollens, J. pr. [2] 36, 225).— 16. Bensoic all hlyde at 100° reacts, forming C_hH₂CH(NHC,H₁)₂ [100°] (326° i.V. at 723 mm.), which changes at 160° into an isomeride [120°-125] and is converted by Br in CS₂ into C₁₁H₁₁B₂N [160 -165°] (Schiff, Z. 1865, 400; Mazzara, J. 1880, 566; Pictet, B. 19, 7063). In the action of p-toluidine and its hydrochloride on benzoic aldehyde at 120 there is produced on benzoic aldehyde at 120° there is produced $C_2\Pi_{\rm BN}$, [178] and $C_2\Pi_2$, $C_2\Pi_2$ ($C_2\Pi_2$ [Me,NH₂)₂ [186°] (c. 430°), which yield a di-acetyl derivative [218°] and a di-benzoyl derivative [198°] (Ullmann, J. pr. [2] 36, 267). 17. p-Methoxylebrasic aldehyde forms $C_2\Pi_2$ (OMe), CHI(NC,H.) (1992) (Steinheyst 4, 111, 2001). [92°] (Steinhart, A. 241, 332). 18. p-Methoxy [92] (Steinmart, A. 241, 533).—18, p-Methoxybenzophenone chloride yields the compound C₆H₁(OMe).CPh:NC,H, [96] Hantzsch a. Kraft, B. 21, 3520).—19. An ethereal solution of C₆H₂.CCl:NSO₂Ph, obtained from benzene sulphonic antilde and PCl₈, forms the compound C₆H₂.C(NHC,H.):N.SO.Ph, which separates in second-line and the compound C₆H₂.C(NHC,H.):N.SO.Ph, which separates in second-line and the compound compound the c monoelinic crystals; a:b:c = 650:1:533; $\beta =$ mononinic crystais; a:00 = 000(1:055; B=69° 16′, insol. water (Wallach a. Gossmann, A. 214, 216).—20. Alcohol, SO, and nitrous acid form the sulphazide C₁₄H₁₆N₂SO₂ [140°] (Limpricht, B. 20, 1241).—21. Heated with persulphocytnic acid it gives p-tolyl-thiobiuret (B. 17, 584).—22. On heating with sulphur it. (B. II, 584).—22. On seating with surprise 1, yields dehydrothiotoluidine and primuline; v. Pransulane.—23. Diazobenzan chloride yields C₃II., N_x. AHC, H₁. (85°) which is identical with the product of the action of p-diazotoluene chloride on aniline (Nölting a. Binder, B. 20, chloride on annihe (Mothing L. Brider, B. 20, 3005),—24. Brono-propiolic acid forms di-tolyl-acetamidine C₁₆H₁,N. [120°] (Mabery a. Krause, B. 22, 3307), which is also formed by the action of HOAc and PCl, on p-toluidine (Mot-mann, Pr. 15, 55).—25. Hacquic acid in boiling aqueous solution forms C,H,N<CH,CH,CO,H
[185°] (Scharfenberg, A. 254, 150).—26. Acetyl-

citric anhydride dissolved in chloroform forms

C₃H₅O(CO₂H)(CO.NHC,H₇)₂ [189°] Klingemann, C₄H₁O(CO₂H)(CO.NHC,H.)₂ [189°] Ringemann, B. 22, 987).—27. Malic acid at 160° yields C.H₂O(CO.NHC,H.)₂ [208°] (Bischoff, B. 23, 2045).—28. The hydrochloride heated with MeOH yields C₄H₂Mc₄(NH₂) [1:3:4] (Limpach, B. 21, 640).—29. Elihylene oxids forms oxyethyl-p-toluidine (Demole, B. 7, 635).—30. SOCl₂ forms thionyl-toluidine (q. v.).—31. 30. SOCI, forms PO(NHC,H.), [192°]; which yields PO(NHC,H.,Br.), [180°] and PO(NH.C.H.,NO.), [247°] (Rudert, B. 26, 569). Another product of the action of POUI, is POCI(NHC,H.)., whence water forms HO.PO(NHC,H.), [124°]. — 32. PSCI forms PS(NHC,H.). [185°]

PO(NHC,H_BP)₈ [180"] and FO(NHO,H_A)₂ [247°] (Rudert, B. 26, 569). Another product of the action of POUl₃ is POCl(NHC,H₁)₂, whence water forms HO.PO(NHC,H₁)₂ [121°].—32. PSCl₃ forms PS(NHC,H₁)₃ [N85°].

Salts.—B'HGI. S. 22°9 at 11°; S. (89 p.c. (alcohol) 25 at 17°. B'HAuCl₁.—B',H,PtCl₂. Not decomposed by boiling water (De Coninck, Bl. [2] 31, 499).—B',H,PtCy, (Scholz, M. 1, 905).—B',PtCl, Et,PO₃ (Saillard, Bl. (2] 18, M. 1, 905).—B',PtCl, Et,PO₃ (Saillard, Bl. (2] 18, M. 1, 905).—B',PtCl, Et,PO₃ (Saillard, Bl. (2] 18, M. 1, 905).—B',PtCl, Et,PO₃ (Cochin, Bl. 1878, 315).—B,ZnCl, 3aq (Lachovitch, M. 9, 513).—B,H,ZnCl, (Gräfinghoff, Z. 1865, 599).—B',HgCl, [125°]. Thick needles, sol. alcohol and ether (Klein, B. 11, 743).—B',NiCl,2E(OH. Green pp. (Lippmann a. Vortmann, B. 12, 81).—P',CoCl₂. Blue needles.—B',Hl,SnCl₄. Monoclinic crystals (Hjortdahl, J. 1882, 535).—B',H,CuCl, (Pomey, C. R. 104, 800).—B',MnCl, (Leeds, J. 1882, 503).—B',UrO,Cl₂.—B',HB. Plates (Städel, B. 16, 28).—B',HgBr. [121°]. Plates (Klein, B. 13, 835).—B',ZnBr,.—B',CdBr,.—B'HH.—B',HgI, [81°].—B',HgH, (Jörgensen, J. pr. (2] 14, 386).—B',MI,Sol,HH, (Jörgensen, J. pr. (2] 14, 386).—B',MI,Sol,HH, (Jörgensen, J. Pr. (2] 14, 386).—B',MI,Sol,HH, (Jörgensen, J. Pr. (2] 14, 386).—B',MI,Sol,D,B',HB, O, S. 5°6 at 22°; S. (84 p.c. alcohol) 1°3 at 23°.—B',HSO, Crystals, converted into B',H,Sol, by water (Tollens, B. 18, 3312).—B',Ag,Sol, 2aq (Mixter).—B',HP,O, J. Thick needles, v. sl. sol. oold water (Lewy, B. 19, 1717).—B',(NH,Ph)H,CoCy, 14aq (Weselsky, J. 1869, 314).—B',H,ChO, [102°] (Baralis, J. 1884, 699).—B',CH,Clo, [141°]. (B.) [136°] (Disiberg, B. 18, 194).—B',CH,Clo, [137°].—Mu cate B',C,H,Glo, Ycllowish crystals, sol. hot water.—Piorate B'C,H,Clo, [141°]. (B.) [136°] (Disiberg, B. 18, 194).—B',C,HClo, [137°].—Mu cate B',C,H,Glo, Ycllowish crystals, sol. hot water.—Piorate B'C,H,N,G, [141°]. (B.) [136°] (Disiberg Brown laters.—B',HgH,N,H,CHO, [45°] (Hühner a. Ru,lolph, A. 200, 371); [52°] (Tobias, B. 15, 244(9)).

heating with P.S. into C.H., NH.CHS [174°]

(Senier, B. 18, 2294; C. J. 47, 766). Yields C,H,.NNa.CHO aq.

Acetyl derivative C.H.,NHAc. [1470] (Hübner a. Wallach, A. 154, 302; Kelbe, C., L. 44, 915). (307°) (Beilstein a. Kuhlberg, A. 156, 74). S. 089 at 22°. Dimorphous, crystallising in monoclinic forms; a:b:c=1.216:1:.788; $\beta = 106^{\circ}$ 7', and also in trimetric crystals; a:b:c = .651:1: 329 (Panebianco, G. 9, 362). Oxidised by KMnO, to acetyl-p-amido-benzoic acid (Hofmann, B. 9, 1299). Oxidised in like manner in the animal body (Jaffe a. Hilbert, H. 12, 295). PCl, forms a liquid product which solidifies when strongly cooled, the crystals doubtless being C,H,NH.CCl,,CH,. This readily splits up into HCl and C,H,N:CCl.CH,. This is a colour-less solid which is converted by Aq into acetyl-toluidine; by toluidine into di-tolyl-acetanidine. The chloro-innide C,H,N:CCl.CH, at 100° forms a base $C_{11}H_{10}N.C[1(72^3]]$, which may be crystallised from alcohol. It is probably C.H.N.C.Mc.C.H...C.C.I.N.C.H.. It is decomposed by moist air or water with production of McC(N.C.H.)N.C.H.H., H.O.C.M.C.H.. M.C.H.. M.C.MeC(NC,H,)NC,H,H, HOAC and MeCONHC,H,
and by heat with production of an amorphous
base C_bH₁₈N₂ (Wallach a. Fassbender, A. 214,
202). Nitrous acid converts acetyl-p-toluidin
into C,H,NAC.NO [80°] (O. Fischer, B. 10, 959).
Chloro-acetyl derivative
C,H,NH.CO.CH,Cl. [162°]. Needles (Tommasi,
Bl. [2] 19, 400; Meyer, B. 8, 1154).
Di-chloro-acetyl derivative
CH NH.CO.CHC. [163°] (Bigheimer a. Hoff.

C,H,NH.CO.CHCl. [153°] (Rügheimer a. Hoffmann, B. 18, 2980).

Tri-chloro-acetyl derivative C,H,NH,CO.CCl₂. [80°] (C.); [102°] (J.). S. (alcohol) 12·5 at 14°. Formed from p-toluidine and (CCl₃), CO (Cloez, A. Ch. [6] 9, 145), and also from p-toluidine and CCl3.COCl (Judson, B. 3, 784).

Bromo-acetyl derivative C, Π , NH.CO.CH, Br. [164°]. Needles (Abenius, J, pr. [2] 40, 433) converted by alcoholic potash into an azine and C.H.NH.CO.CH.OEt [32°] which is v. e. sol. alcohol.

Thio-acetyl derivative Theo-acetyl derivative C.H., NILCS.CH₂, [131°]. Formed from the acetyl derivative and P₂S₅ (Jacobsen a. Ney, B. 22, 206). Got also by heating tolyl-acetamidine with CS₅ at 100° or di-tolyl-acetamidine with ILS (Bernthsen a. Trompetter, B. 11, 1759; Wallach a. Pannes, B. 13, 529). Converted by NaOEt and EtBr into oily C.H.,N:CMc.SEt (272°) (Wallach a. Wüsten, B. 16; 147).

a-Bromo-propionyl derivative C.H.NH.CO.CHBr.CH₂. [125°] (Tigerstedt, B. 25, 2921). Plates, v. sol. CHCl₃.

Benzoyl derivative C,H,NHBz. (322). Formed from p-toludine and BzCl (Jaillard, Z. 1865, 440; Kelbe, B. 8, 875; Hübner, A. 208, 310; Wallach, A. 214, 217; Gudeman, B. 21, 2553; Müller, B. 22, 2404). Needles, vo. 8. alcohol. Converted by PCl, into C.H.N.CCl.C.H., [522] [Just, B. 19, 980) crystallising from ligroin in prisms.

using from ligroin in prisms.

p.Nitro-benzoyl derivative
C₅H₄(NO₂).CO.NHC.H., [197°]. Formed from
p-toluidine and p-nitro-benzoyl obloride. Yellow
needles (Gattermann, B. 25, 1082). Converted
by PCl₅ into C₅H₄(NO₂).CCl₄NHC.H., [119°]
crystallising in golden prisms.

Phenacyl derivative O,H,NH.CH,.CO.C,H,. [127°]. Formed from w-bromo-acetophenone and p-toluidine in alcohol (Bischler, B. 25, 2866). Yellow prisms, yielding B'HCl and an acetyl derivative [89°] crystallising in white needles (from alcohol).

Phthalyl derivative C,H,N:C2O2:C4H. [205°] (Fröhlich, B. 17, 2679).

References .- Bromo-, DIBROMO-10DO-, BROMO-NITRO-, CHLORO-, TRI-CHLORO-NITRO-, IODO-,

NITRO-, and NITROSO- TOLUIDINES.
TOLUIDINE SULPHONIC ACID v. AMIDO-TOLUENE SULPHONIC ACID and also NITRO- and IODO- TOLUIDINE SULPHONIC ACID

TOLUIDINE THIOSULPHONIC ACID v.

AMIDO-TOLUENE THIOSULPHONIC ACID.

TOLUIDO- v. TOLYL-AMIDO-TOLUIDYL-CYANURAMIDE v. CYANIC ACIDS. TOLUIDYL-MELAMINE v. CYANIC ACIDS. TOLUISATIN v. DI-TOLYL-OXINDOLE.

TOLU-(αβ)-NAPHTHAZINE C1, II 12N2 i.e. $C_{\mathfrak{s}}H_{\mathfrak{s}}$ $C_{\mathfrak{s}}H_{\mathfrak{s}}$ $C_{\mathfrak{s}}H_{\mathfrak{s}}$ $C_{\mathfrak{s}}H_{\mathfrak{s}}M_{\mathfrak{s}}$ $\begin{bmatrix} 3\\4 \end{bmatrix}$. [180°].

Formed by oxidation of a mixture of tolylene-odiamine (1 mol.) and (β)-naphthol (1 mol.) with K_sFeCy_s. Formed also, together with the isomeride [169°], by the action of (β)-naphthoquinone on tolylene-o-diamine (Witt, B. 20, 577). Dissolves in conc. H.SO, with violet-red colour. Forms with its isomeride a molecular compound

[142°]. Tolu- $(\alpha\beta)$ -naphthazine $C_1, H_{12}N_2$ i.e.

$$C_eH_1$$
 $CH:CH.CN$
 C_vH_2Me
 $\begin{bmatrix} 41\\ 3 \end{bmatrix}$. [169°].

Formed as above, and also, together with amidobenzene p-sulphonic acid, by boiling sulpho-benzene azo-(β)-naphthyl-p-tolyl-amine with dilute H.SO, and by boiling wood black' C₈H₄(SO₃H).N. C₆H₃(SO₄H).N. C₆H₄(SO₄H).N. C₁₀H₁.NHC.H. with dilute H.SO₄ (Witt. B. 20, 577). Yellow erystals, v. sl. sol. alcohol. Conc. H SO₄ forms a brownish-red solution.

TOLUNITRANILIC ACID v. NITRO-DI-OXY-TOLUCUINONE

TOLUOIN v. DI-METHYL-BENZOIN.

TOLUOL v. TOLUENE.

TOLUPHOSPHINIC ACID v. PHOSPHOTOLUIC ACID.

TOLUQUINOL v. HYDROTOLUQUINONE. TOLUQUINOLINE v. METHYL-QUINOLINE. TOLUQUINONE C.H. O. i.e.

C.H.,MeO. [24:1]. [69°]. Formation.—1. By exidation of tolylenep-diamine or of o-toluidine (Nietzki, B. 10, 832, 1934; A. 215, 158; Ladenburg, B. 10, 1128).—
2. By boiling crude crossol with MnO₂ and dilute H₂SO₄ (Carstanjen, J. pr. [2] 23, 425). Separated from accompanying xyloquinone by related with SO₂ caustallicing the hydrother. reduction with SO2, crystallising the hydrotoluquinone from benzene, and re-oxidising by fuming HNO₂.—3. By oxidation of m-xylidine (Nölting a. Baumann, B. 18, 1151).

Preparation.—20 g. of o-toluidine are dis-

solved in 600 c.c. of water containing 160 g. of H.SO.; 20 g. of finely powdered potassium bichromate are added by degrees, with continual agitation, keeping the temperature at 10°-15°. After standing over night, 33 g. more K, Cr, O, are added; the quinone is then extracted with ether, dried over CaCl. and the ether removed by dis-

tillation. The yield is about 86 p.c. of the theoretical quantity (Schniter, B. 20, 2283).

Properties—Golden-yellow plates smelling like quinone. Very volatile. M. sol. hot water, v. sol. alcohol and ether. Its aqueous solution is turned brown by alkalis. SO₂ reduces it to hydrotoluquinone. Dilute (50 p.c.) H₂SO₄ changes it to isotoluquinone (C,H,O₂), a powder not melted at 300° (Spica, G, 12, 225). An aqueous solution of toluquinone mixed with one of hydrotoluquinone deposits steel-blae needles of the quinhydrone [52°], v. e. sol. water. o-Nitro-aniline forms [2,2:4:6] C_sH_sMcO_sNH_sO_gH_sNO_g erystallising from alcohol in red crystals decomposing at 200° (Leicester, B. 23, 2796). Nitrop-toluidine CallaMe(NO2).NH2[1:3:4] forms a homologous body.

Chlorimide $C_0 \Pi_3 \mathrm{Me} < \frac{O}{\mathrm{NGI}} \left[1\frac{\mathbf{y}}{2}\right]$. [88°] (Hirsch, B. 18, 1514). Formed by the action of a solution of bleaching-powder on the hydrochloride of amido-o-erciol. Yellow prisms (from alcohol) volatile with steam. Decomposes violently at 100 '-115°. By digestion with NaIISO, for several hours it is converted into amidocresol sulphonic acid.

Chlorimide $C_0H_3Me < \stackrel{NCI}{O} \begin{bmatrix} 1\frac{5}{2} \end{bmatrix}$. [75°]. Made in like manner from anyido-m-cresol

(Staedel, A. 259, 218). Yellow prisms (from. alcohol), volatile with steam.

Oxim C.H.McO(NOII)]2:1:4). Nitroso-ocresol. [135]. Formed by the action of nitrous acid on oscresol (Nölting a. Kohn, B. 17, 370). Formed also by the action of hydroxylamine hydrochloride on toluquinono (Goldschmidt a. Schmid, B. 17, 2063). Needles (from water), decomposed by fusion. V. sol, alcohol and ether. Yields nitro-cresol [95"] on oxidation. NaA'3aq.

KA': brown needles, v. sol. water. $Ox im = C_8H_4MeO(NOH)$ [2:4:1]. Nitroso-mcresol. Formed by boiling nitroso-di-methyl-ni-toluidine with dilute (10 p.c.) NaOHAq (Wurster a. Riedel, B. 12, 1799). Formed also by the action of NO.SO, II on m-cresol and water at 0° (Bertoni, G. 12, 303). Small needles (from water). Decomposes at 145°-150°. Sl. sol. hot water. Gives Liebermann's reaction. Forms an acetyl derivative C.H.MeO(NOAc) [92] crystallising in large prisms.

Di-oxim C₆H₄Me(NOH)₄[2:1:4]. Formed by the action of hydroxylamine on either monooxim (Nietzki a. Guitermann, B. 21, 430) or by oxim (Nictzki a. Guitermann, B. 21, 439) or by boiling nitroso-o- or m-toluidine with hydroxyl amine hydrochloride (Mehne, B. 21, 729). Yellow needles, exploding at 220° 234°, v. sl. sol. benzene, sol. hot water, alcohol, and other. Reduced by tin and HClAq to tolylene-p-diamine. Alkalino K. FeCy, forms di-nitroso-toluene. According of Mc(NOA) [1102] exceptibilizing from C. H. Mc(NOA) [1102] exceptibilizing from forms CaH, Me(NOAc), [120°], crystallising from alcohol in colourless needles.

Ditolylimide C, H, Me(NC, H,)2. Formed by oxidation of tolylene-di-tolyl-diamine in alkaline solution (Green, C. J. 63, 1409). Red prisms, v. sol. alcohol, v. e. sol. benzene.

References .- DI-BROMO-, CHLORO-, IODO-, and OXY TOLUQUINONE.

. TOLUQUINOXALINE v. METHYL - QUIN-

o-TOLURIC ACID C., H., NO., i.e. C., H., CO.NH.CH., CO.H. Toluyl Toluul - alucocoll the second of th

[162.5°]. Formed from toluyl chloride, amido-acetic and, and NaOH (Gleditsch a. Möller, A. 250, 376). Found in the urine of dogs that have

zou, 5/0). round in the urine of dogs that have taken o-toluic acid. Thick plates, sol. water.

m. Tôluric acid. [139°]. Formed as above, and also when m-xylene or m-toluic acid is administered to a dog (G. a. M.; of. Schultzen a. Naunyn, Z. 1868, 29). M. sol. water.—ZnA', 4aq.—CuA', 6aq.

p. Toluric acid. [161°]. Formed from actions hallowide acid. [161°].

p-toluyl chloride, and glycocoll (G. a. M.) and also by passage of p-xylene or p-toluic acid through the animal body (Kraut, A. 98, 360). Plates (from water), sl. sol cold water, v. sol.

alcohol.—CaA', 3aq.—BaA', 5aq.—AgA'.

TOLUYL. The radicle CH_x,C_yl₁,CO. The same name has been given to the radicle CH₂.C₄H₄.CH₂, which is isomeric with xylyl, and has also been called tolyl, but may be more conveniently named methyl-benzyl. Tolyl

is CH₂.C₄H₄.
o-TOLUYL-ACETIC ACID
Ethyl ether C₄H₄Me.CO.CH₂.CG₂Et₄ got by boiling the nitrile with alcohol and HCl.

Gives a violet colour with FeCl,.

Nitrile C, H, CO. CH, CN. [74.4°]. Formed

by boiling o-toluyl-cyano-acetic ether with water (Haller, C. R. 108, 1117). Prisms, sol. alcohol and alkalis. Diazobenzene chloride and NaOH form C,H,CO,CHCy,N,C,H, [125°]. Cold alcoholic HCl forms the hydrochloride of C,H,CO,CH,C(NH).OEt [116°].

TOLUYL-ACRYLIC ACID C,H,O, i.e. C

CaH,(CH₂).CO.CH:CH.CO₂H. [138°]. Formed by the action of AlCl₃ on a mixture of maleic anhydride and toluone (Pechmann, B. 15, 888). TOLUYL ALCOHOL v. TOLYL-CARBINOL.

TOLUYLAMIDE v. Amide of TOLUIC ACID. p-TOLUYII-o-BENZOIC ACID C₁₃H₁₂O₃ i.e.

[1:4] C₄H₄Me.CO.C₄H₁CO₂H [1:2]. Principle tolyl ketone carboxylic acid. Mol. w. 240. [146°].

Hormed by the action of phthalic anhydride on toluene in presence of AlCl₃ (Friedel a. Crafts, A. Ch. [6] 14, 447; C. R. 92, 833). Prisms (containing aq) (from alcohol-toluene), v. sl. sol. hot water. Its dilute aqueous solution tastes sweet. Potash-fusion yields benzoic and p-toluic acids. Warm cone. H_2SO_4 forms (β) -methylanthraquinone. — BaA', 4aq. — CdA', 1aq. -

CuA', 4aq.

Methyl ether MeA'. [53°].

Ethyl ether Eth'. [69°].

Toluyl-benzoic acid C,H,.CO.C,H,.CO.L. [222°]. Formed by oxidation of di-tolyl-methane Ador a. Crafts, C. R. 85, 1163; O. Pischer, B. 7, 1184; Ador a. Crafts, C. R. 85, 1163; O. Pischer, B. 7, 1195; Anschütz, A. 235, 316). Slender needles (from MeOH), sl. sol. hot water.—KA':

tufts of long needles.—AgA.

Reference.—DI-CHLORO-TOLYI-BENZOIC ACID.

TOLUYLENE: v. Tolylens...
p.TOLUYL-PROPIONIC ACID C₁₁H₁₂O₃ i.e.
C.H.,CO.CH.,CH.,CO.H. [127°] (C.); [120°] (B.). Formed by the action of succinyl chloride or succinic anhydride on toluene and AlCl, (Claus, B. 20, 1878: Burcker, Bl. [2] 49, 448). Plates B. 20, 1878; Burcker, Bl. [2] 49, 448). Plates or needles (from water), v. sol. ether.—BaA', 4aq: sol. hot water.—AgA': small needles, insol. Aq. .-TOLUYL-TOLUIC ACID. Lactons

C.H. CO,H, [93°]. Got from nitro-tolyl-

methylene-phthalide, HIAq, and P (Heilmann, B. 23, 3166). Thin prisms. Converted by alcoholic NH₂ into C₀H₄. CH:C.C.7H₇ [196°].

oo-DITOLYL C₁H₁₁ i.e. [1:2] C₁H₁Me.C₂H₁Me [1:2]. Mol. w. 182. (272°). S.G. 102 9945. Formed from o-bromo-toluene and Na (Fittig, A. 139, 178). Liquid.

mm-ditolyl [1:3] C₂H₁Me.C₃H₁Me[1:3]. (280°)

(Schultz, B. 17, 468); (288°) (Perrier, C. R. 114, 481); (280°) (Stolle, B. 21, 1096). S.C. 49 9993. Formed by diazotising diamide diditolyl and boiling the product with alcohol. Formed also by the action of Na on m-bromotoluene (P.), and by reduction of di-oxy-m-ditolyl and di-chloro-m-ditolyl. Oil; yields diphenyl di-m-carboxylic acid and isophthalic acid on exidation.

pp-ditolyl [1:4] C₆H₄Me.C₆H₄Me [1:4]. [121°]. S.V. 198 0. Formed by adding Na to a solution of p-bromo-toluene in toluene (Zincke, B. 4, 396; Louguinine, B. 4, 514). Monoclinic prisms (from ether). Yields on oxidation p-tolyl-benzoic acid [244°] and diphenyl di-p-carboxylic acid (Carnelley, C. J. 32, 653). SbCl, at 360° forms CCl, and per-chloro-diphenyl.

om-Ditolyl [1:2] C_0H_1Me, C_0H_1Me [1:3]. (270°). Formed from [2:4:1] $C_0H_1Me(NH_2), C_0H_2Me(NH_2)$ [1:3:4] by elimination of amidogen by the diazoreaction (Schultz, B. 17, 471). Yields isophthalic

acid on oxidation by CrO.

op-Ditolyl [1:2] C₆H₄Me.C₆H₄Me [1:4]. (272° 280°). Formed from crude brome-toluene and Na. It is also one of the products of the passage of a mixture of behzene and toluene through a red-hot tube (Carnelley, C. J. 37, 707; 47, 587). Oxidised by CrO, and HOAc to o-tolylp-benzoic acid [180°] and terephthalic acid.

Ditolyls have also been obtained by Barbier (C. R. 78, 1769) and Varet a. Vienne, Bl. [2] 47,

919).

References .- DI-AMIDO-, DI-BROMO-, DI-IODO-, NITRO-AMIDO-, OXY-AMIDO-, and OXY-DITOLYL.

p-TOLYL-ACETAMIDINE C₉H₁₂N₂

 $C_9H_{12}N_2$ i.e. [96°]. Formed CH₃.C(NII).NHC₆II₄Me [1:4]. from p-toluidine hydrochloride and acetonitrile (Bernthsen a. Trompetter, B. 11, 1757). Prisms. Alkaline in reaction.—B"₂H₂PtCl₆.—B"H₂C₂O₄. Prisms, v. sol. water and alcohol.

Di-o-tolyl-acetamidine [1·2] C.H.Me.NH.CMe:NC₆H.Me [1:2]. [136°] (W.); [140°] (L.). Formed by the action of PCl₃ on o-toluidine and HOAc (Ladenburg, B. 10, 1262), and also by the action of o-toluidine on CMc(SEt):NC,II, or on CMcCl:NC,H, (Wallach a. Wüsten, B. 16, 148; A. 214, 208). Needles.

Di-p-tolyl-acetamidine [1:4] C.H.Me.NH.CMe:N.C.H.Me [1:4]. tolyl-imid-tolyl-amide. [120°]. Formed from p-toluidine and CMeCl:NC,H,, which is the proproduction and Catelline, H, which is the product of the action of PCl, on acetyl.—toluidine (Wallach a. Fassbender, A. 214, 203; B. 9, 1214; 16, 148). Formed also from p-toluidine and bromopropiolic acid (Mabery a. Krause, B. 22, 3307). Prisms (from benzene). Formed also from the production of the from p-toluidine, HOAc, and PCl, -B'H.PtCl, -B'HCl. [200°].

op-Di-tolyl-acetamidine C₆H,Me.NH.CMe:NC₆H,Me. [142°]. Formed from o-toluidine and the product of the action of PCl, on acetyl-p-toluidine, and also from

p-toluidine and the product of the action of PCI on acetyl-o-toluidine (Wallach a. Pannes, 4.214, 209). Formed also from p-toluidine and [1:2] C.H.MEN:CMC.SEt, and from o-toluidine and [1:4] C₆H₄MeN:CMeSEt; the compounds obtained, [148°] and [140°] respectively, being perhaps isomeric and not identical (Wallach, B. 16, 148)

o-TOLYL-ACETIC ACID C₀H₁₀O₂ i.e. [1:2] C₂H₁Me.CH...CO₂H. |89° f. Formed by c. TOLYL-ACETIC ACID C.11., 102, i.e. [1:2] C. H., Me.C.H... CO.H... [80°]. Formed by saponification of its nitrile (Radziszewski a. Wispeck, B. 15, 1747; 18, 1281). Needles, sl. sol. cold water. Yields phthalic acid on oxidation.—CaA'₂ 4aq.—AgA'. Plates, sol. bot water A mide [161°]. Plates, sl. sol. ether. Nitrile C., H., N. (244°). S.G. 2² 10156.

Formed from w-bromo-o-xylene and KCy. Oil. m-Tolyl-acetic acid [1:3] C6H4Me.CH2.CO.H. [61°]. Formed by saponifying its nitrile, which is obtained from ω-bromo-m-xylene (R. a. W.).

Needles, sol. hot water.—CaA', 3aq.—AgA'.

Amide [141°]. Sl. sol. cold water.

Nitrile (241°). S.G. 2° 1.0022. Oil.

Methyl other MeA'. (228°). S.G. 2° 1.041.

Liquid (Senkowski, M. 9, 854).

Ethyl ether Eth'. (238°). S.G. 175 1.018.
p-Tolyl-acetic acid [1:4] C₂H₁Me.CH₂CO₂H.
[94°]. Formed in like manner from ω-bromo-pxylene (R. a. W.; Strassmann, B. 22, 1230). Got also by reducing p-tolyl-klyoxylic acid with Hr (Claus a. Kroseberg, B. 20, 2051). Needles, sl. sol. cold water. Phthalic anhydride and

NaOAc yield $C_6H_4 < CO_{C(CH,C_6H,Me)} > O$ [151°], whence HNO2 at 0° forms the compound $C_6H_4 < CO \xrightarrow{\bullet} C(NO_2).CH(NO_2)C_7H_7 > O$ [140°], which

is converted by treatment with boiling alcohol into C₈H₄<CO (CNO₂)C,H,>O [207°], and is reduced

by HI and P to C₆H₄ CO.O (Ruhemann, B. 24, 3965).—NaA': needles, sol. water.—

CaA', 3aq.—AgA': needles, sol. hot water. Ethyl ether EtA'. (240°). Amide C,H₁₁NO. [185°]. Plates. Formed from the acid, and also by the action of yellow ammonium sulphide on p-tolyl methyl ketono (Willgerodt, B. 21, 534).

Nitrile C,H,.CN. [18°]. (243°). S.G. 82 ·9922.

Reference. - Nitro- and Oxy-Tolyl-Acutic

ACID. m-TOLYL-ACETYLENE [1:3] C.H.Me.C:CH. Methyl-styrene. (164°). Formed by distilling barium m-tolyl-propiolate with lime (Müller, B. 20, 1215). Formed also by saturating a solu-20, 1210). Formed also by saturating a solution of m-tolyl-acrylic acid with HBr at 0° and treating the product with NaOHAq. Oil, becoming solid on standing. Gives an explosive red pp. with animoniacal Cu₂Cl₂. Br forms C,H,CHBr.CH₂Br [45°].

Di-tolyl-acetylene C,H,C:C.C,H, [136°]. Formed by heating C,H,CHBr.CHBr.CHBr.CH, with alcoholic potach at 140° (Goldschmiedt a Hern

alcoholic potash at 140° (Goldschmiedt a. Hepp, B. 6, 1505). Needles (from alcohol).

DI-TOLYL-ACIPIPERAZINE OXY-DI: TOLYL-PYRAZINE

Di-tolyl-di-aci-piperasine DI-OXY-DI-TOLYL-PYRAZINE.

m-TOLYL-ACRYLIC ACID C, H, O, i.e. [1:3] C.H.Me.CH:CH.CO.H. Methyl-cinnamic acid. [111°]. Formed by heating m-toluic aldebyde with Ac.O and NaOAc (Bornemann, B. 17, 1474; 20,1382; Von Miller, B. 20,1213; 23,1899). Silky needles v. sol. alcohol, al. sol. ligroin. FeCl, gives a bright-yellow pp. in neutral solutions. Reduced by sodium-amalgam to m-tolyl-propionic acid [43°]. KMnO, oxidises it to m-toluic acid. Br forms C,H.C,H,Br,CO,H [167°].—

BaA'_AA'. Crystalline powder.
p-Tolyl-acrylig acid
[1:4] C_hH_Me,CH:CH,CO_H. [197°]. Formed from p-toluic aldehyde, NaOAe, and Ac.O (Von Miller, B. 23, 1897; cf. K. bber, B. 23, 1033). Needles (from benzene), sl. sol. hot water. Reduced by HI and P to p-tolyl-propionic acid. Br forms C.H.Me.CHBr.CHBr.CO.H.

TOLYL ALCOHOL v. TOLYL-CARBINGL.

p-TOLYL-ALLYL-HYDRAZINE C10H11N2 i.e. C,II,N(C,H₂),NH₂. (160°-170° at 90° mm). Got from tolyl-hydrazine and allyl bromide (Michaelis, B. 26, 2175°). Oil. Yields B'HCl, [129°] Bonzoic aldchyde forms the compound C,H,.N(C,H,).N:CHPh -[61°], while cinnamic aldehyde forms the corresponding hydrazide [118°]. Ferric chloride gives the tetrazone (C,H,(C,H,)N),N, [104°],

o - TOLYL-ALLYL-THIO-SEMI-CARBAZIDE C,H,NH.NH.CS.NHC,H,. [105°]. Formed by warming o-tolyl-hydrazine with allyl thiocarbimide (Avenarius, B. 24, 268). Needles, insol. water, v. sol. alcohol and CS.

p - Tolyl - allyl - thio - semi - carbazide [128°]. •Formed in like manner (A.). Needles

o-TOLYL-ALLYL-THIO-UREA C, H, N, S i.e. C, H, NH.CS.NHC, H, J. Tolyl-thiosinamine. [98]. Formed from o-toluidine and oil of mustard (Jaillard, Z. 1865, 441; Maly, Z. [2] 5, 258; Weith, B. 8, 1259. Decar B. 29, 2002). Englyparytals med 1528; Prager, B. 22, 2998). Pearly crystals, m.sol. ether, v. sol. HOAc. According to Dixon (C. J. 55, 622), it melts at 76°. Converted by heatings with HClAq into tolyl-propylene-ψ-thio-urea [126°]. Cyanogen passed into its alcoholic solution forms C₁₃H₁₄N₄S, which on warming with dilute H2SO, and alcohol gives a pp. of oxalyl-tolyl-allyl-thio-urea CS<NC,H,>C,O, [157°].

Reference. -- OXY-TOLYL-ALLYL-THIO-URFA.

o-TOLYL-AMIDO-ACETIC ACID C.H.1NO. i.e. C.H.1Me NH.CH.2CO.H. Tolyl - glycocoll. [150]. Prepared by the action of chloro-acetic acid and aqueous NaOAc on o-toluidine (Staats, B. 13, 137; Cosack, B. 13, 1091; Ehrlich, B. 16, 201; Bischoff a. Nagtvogel, B. 22, 1787).— GuA', 2aq. Small needles .- CaA', 3aq: needles,

m. sol. water (Mauthner, M. 11, 377).

Ethyl ether Eth.'. (281'). S.G. 30 1058.

Oil (Bischoff, B. 25, 2270).

Acetyl derivative C,N,NAc.CH,CO,H. [212]. Tables (from dilute alcohol).

• Chloro-acetyl derivative C,H,N(CO.CH,Cl).CH,.CO,H. [117] from the acid and chloro-acetyl chloride, in ether (Widman, J. pr. [2] 38, 304). Rectangular plates, v. sol. hot alcohol, sl. sol. water.

Bromo-acetyl derivative C.H.N(CO.CH.Br).CH.,CO.H. [124]. Bectangular plates.

Glycolyl derivative C,H,N(CO,CH,OH),CH,CO,H. [144°]. Formed. by boiling the chloro-acetyl derivative with conc. Na_CO_Aq (Abenius, J. pr. [2] 40, 503). V. e. sol. water. Yields KA' aq, BaA'2'/aq, and AgA', and is converted by heating at 160° into C,H,N CO.CH, O [109°], whence alcoholic NH, produces C,H,N(CO.CH₂.OH),CH₂.CO.NH₂ [152°], crystallising in plates (from attohol).

o Toluide C,H,NH.CH₂.CO.NHC,H,

o. Toluide C,H,NH.CH,CO.NHC,H,. [92°]. Formed by boiling chloro-acetic ether with o-toluidine (Ehrlich, B. 16, 205). Needles,

insol. water and HClAq.

m-Tolyl-amido-acetic acit [1:3]C,H,Me,NH.CH,CO,H. Formed from chloro-acetic acid and m-toluidine in ether (Ehrlich, B. 15, 2011). Solid mass.—CuA'₂2a₄. Ethyl. ether Eth'. [68]. Formed from

chloro-acetic ether and m-toluidine. Six-sided plates, v. sol. alcohol and ether, sl. sol. Aq.

p-Tolyl-amido-acetic acid [1:4]C₈H, Me.NH.CH, CQ H. [119°]. Formed, together with a compound [168°], from p togener with a compound [1687], Iron ptoluidine chloro-acetic acid and NaOAc (dissolved in a little water) at 100° (P. J. Meyer, B. 8, 1158; 14, 1323; Staats, B. 13, 137; Schwebel, B. 10, 2047; Bischoff, B. 23, 1997; 25, 2281). Got also by saponifying its ether. Needles (from water). When fused with potasit it yields a product which, when dissolved in water is oxidized by air to an dissolved in water, is oxidised by air to an indigo-derivative (Heumann, B. 24, 1346). When fused with p-chloro-acet-toluide it yields methyl-indigo (Eckenroth, B. 24, 693). methyliming (Eckenton, B. 24, 503). In compound [1689], formerly supposed to be p-tolyl-amido-acetic acid, ought, according to Bischoff a. Hausdörfer (B. 25, 2281) to be represented as CO_H.CH_N(C, H)_CH_CO.ONH_C, H_E thyl ether Eth'. [49]. Formed from

chloro-acetic ether and p-toluidine. Monoclinic

plates, v. sl. sol. hot water.

• Amide C_pH₁₀N₂O. [163°]. Formed by heating p toluidine with chloro - acetamide. Plates, v. sl. sol. cold water.

Anilide C,H,NH.CH,.CO.NHPh. [83°].
Formed by heating chloro-acetic acid with

aniline. Needles (from hot water).
p-Toluide C.H., NH.CH., CO.NC, H.,. [136°]. Formed in like manner, and also by heating toluidine with the compound of glyoxal with NaHSO₃ (Hinsberg, B. 21, 112). Plates, v. sl. sol. hot water. Yields a chloro-acetyl derivative

Nitrile C,H,NH.CH,CN. [126°]. A product of the action of heat on the amide.

Acetyl derivative C.H., NAc.CH., CO.H. [175°]. Formed from chloro-acetic ether and C.H., NAcNa, the product being saponited with O.A., NACKA, the Product being saportime with potash (Paal a. Otten, B. 23, 2006). Plates (from water).—NaA'3aq: plates, v. sol. water.

Imids (C.H.,NH.CH₂.CO),NH. [210°].

Imide (C.H., NH.CH., CO), NH. [210°]. Got by heating the acid at 200° and adding NH,Aq to the product. Needles, sl. sol. waters and NH,Aq (Bischoff).

Dio-tolyl-di-amido-acetic acid (C,H,NH),CH.CO,H. [240°]. Formed by heating di-chloro-acetic acid with o-toluidine (P. Meyer, B. 16, 925). Needles, insol. water, sl. sol. alcohol, v. sol. aqueous acids and alkalis. Reference.—NITRO-TOLYL-AMIDO-AGETIC ACID.

[1:4]C,H,Me.NH.CH,.CO.C,H,. Phenacyl-ptoluidine. [134°]. Formed from p-toluidine and

p-TOLYL-AMIDO-ACETOPHENONE

bromo-acetophenone in alcohol (Lellmann a. Donner, B. 23, 167). Tables, v. sol. benz. ene, m. sol. alcohol. Yields, on nitration, [1:3:4]C₀H₃Me(NO₂).NH.CH₂Bz [165°] and a dinitro- derivative [156°]. Forms B'HNO, and

B'HCl.

, p-TOLYL-AMIDO-ACRYLIC ETHER [1:4]C_aH₁Me.NH.CH:CH.CO₂Et. [116°]. Formed from p-toluidine and formyl-acetic ether (Von Pechmann, B. 25, 1053). Yellow plates, insol. water and ligroïn. Alcoholic potash yields plates [144°]. Ac.O forms acetyl-toluidine. TRI-p-TOLYL-TRI-AMIDO-BENZENE

C₂,H₂,N₃ i.e. C₀H₃(NHC,H₁)₂. [187°]. Formed by heating phloroglucin with p-toluidine at 210° (Minunni, B. 21, 1984). Needles, v. sl. sol. cold alcohol. Conc. H₂SO₄ forms a bluish-green solution, turning black on heating.—B"HCl: amorphous; decomposed by water.—B"2HCl: small needles.—B",H₂PtCl₃.

Tri-acetyl derivative [1989]. Plates.

Tri-benzoyl derivative [282°]. Minute

prisms.

p-TOLYL-AMIDO-BENZOYL-(a)-NAPHTHO-INONE C_6H_3 -CO. C_6H_3 -CO.Ch- H_6 -CO.Ch

[197°]. Formed by boiling p-toluiding with benzoyl-(α)-naphthoquinene in alcoholic solution for 15 minutes (Kegel, A. 247, 185). Red

needles (from HOAc), v. sl. sol. alcohol.

p-TOLYL-o-AMIDO-BENZYL-AMINE [4:1] C₆H₄Me.NH.CH₂·C₆H₄·NH₂ [1:2]. [80.5°]. (söderbaum a. Widman, B. 23, 2187). Thin leastets (from alcohol). Ac.O yields a di-acetyl derivative [186°]. The mono-acetyl derivative C,II,NAc.CH₂.C₆H₄NH₂ [99°] may be got by reducing C,H,NAc.CH₂.C₆H₄NO₂.

O-TOLYL-a-AMIDO-n-BUTYRIC ACID

C,H,,NH.CHEt.CO,H. [84°]. Long prisms. Forms an acetyl derivative [116°] and yields

propyl-o-toluidine on distillation.

Ethyl ether EtA'. (278°). S.G. 29 1.019. Got by heating o-toluidine with a-bromo-butyric

ether at 100° (Bischoff a. Mintz, B. 25, 2314). ο-Tolyl-α-amido-isobutyric acid C.H. C.H. C.M. C. H. [629]. Formed together with the 3 isomeride [110°] by the action of KOH and a current of steam on the ether [57°], which is got by heating o-toluidine with a-bromoisobutyric ether (Bischoff a. Mintz, B. 25, 2334). The acid [110°] yields an acetyl derivative [219°], sl. sol. ether. On distillation it forms a lactone [95°].

p-Tolyl-a-amido-n-butyric acid C.H.NH.CHEL.CO.H. [153°-156°]. Got from the ether Eth' (279°) S.G. 32 1-011, which is produced when p-toluidine is heated with a.bromo-n-butyric acid at 105°. Leaflets. Yields Got from propyl-p-toluidine on distillation.

Acetyl derivative C,H,NAc.CHEt.CO.H.

[149°]

p-Tolyl-a-amido-isobutyric acid [1:4] C_bH₄Me.NH.CMe₂.CO₂H. [150°]. Formed together with the \$- isomeride, by the action of hot potash in a current of steam on the ether EtA' [36°], which is got by heating p-toluidine with a-bromo-isobutyric acid. Yields an acetyl derivative [146°]. Forms isopropyl-p-toluidine on distillation.

p-Tolyl-8-amido-isobutyric acid C,H,NH.CH,CHMe.CO,H. [196°]. Formed as above. Gives an acctyl derivative [206°] and decomposes on distillation into p-toluidine and

a lactone C,H,N<CH,CHMe
CO .CMe,O
CO (?) [170°].
o-TOLYL-AMIDO-CROTONIC ACID

[1:2] C₆H₄Me.NH.CMe:CH.CO₂H.

Methyl ether MeA'. [31°]. Formed by the action of o-toluidine on methyl aceto-acetate (Conrad a. Limpach, B. 21, 523). Prisms (from alcohol).

Ethul ether EtA'. Yellowish oil.

p-Tolyl-amido-crotonic acid.

Methyl ether MeA'. [60°]. Prisms.

Ethyl ether EtA'. [29°]. Formed from acetoacetic ether and p-toluidine.

TOLYL-AMIDO-CYANURIC ACID Cyanuric acid, described under Cyanic acids. p-TOLYL-AMIDO-METHENYL-BENZAMID-

OXIM CPh \ll N.O \gg C.NH.C, H, Me [1:4.]. [135]. Formed by heating p-tolyl-thiocarbimide with benzamidoxim (Koch, B. 24, 398). Plates

(from alcohol), v. sol. ether.
DI-p-TOLYL-AMIDO-METHYLENE-0-PHE-

NYLENE DIAMINE C₁H₂N₄ i.e.

C₄H₄NH CNH1.C H, [186°]. (above 400°).

Formed by heating C(NC,11.), with e-phenylene-diamine at 135° (Moore, B. 22, 1639; 3188). Tables (from alcohol), v. sl. sol. boiling water.
—Salts: B'_3HCl. Needles,—B'_3H_PCl_8aq.
—B'H_SO, Needles, insol. ether, v. sol. hot Aq. Nitrosamine

 $C_{_{0}}H_{_{4}} < \stackrel{N(NO)}{\underset{N(NO)}{\langle NO, H_{7}, NO \rangle_{2^{*}}}} C(NC, H_{7}, NO)_{2^{*}} \quad [130^{\circ}]. \quad Yellow$ needles, v. sol. alcohol.

Di-acetyl derivative [143°]. Needles. Di-benzoyl derivative [185°]. Prisms. Tetra-benzoyl derivative [274°

Tetra-p-tolyl-tetra-amido - di - methylene - ophenylene-diamine $\mathbf{C}_{0}\mathbf{H}_{1}:\mathbf{N}_{2}(\mathbf{C}(\mathbf{NHC}_{1}\mathbf{H}_{7})_{2})_{2}$. [116°]. Formed by heating C(NCH₂), with ophenylene-diamine at 200° (Moore, B. 22, 3195). phenylene-diamine at 200° (atome, 17, 22, 31, 57). Needles, v. sol. alcohol. Decomposed by dilute HClAq at 150° into di-p-tolyl-urea and o-phenylene-diamine. B'2H,SO, Needles, sl. sol. cold water.—B'3HCl.—B'3H,PtG, 15aq.

Tetra-acetyl derivative [1152].

Tetra-benzoyl derivative [1460]. DI-p-TOLYL-AMIDO - METHYLENE-o-PHE-NYLENE-PHENYL-GUANIDINE

 $C:NPh > C(NHC, H_1)_x$ [187]. Formed

by boiling C(NC,H,), with o-phenylene-phenyl-guanidine (Keller, B. 24, 2508). Needles (from

pushing alcohol), sl. sol. ether.

DI - p - TOLYL - AMIDO - METHYLENE - o.

PHENYLENE -p-TOLYL-GUANIDINE
C₂H,:N₂(CNC,H,):C(NHC,H,)₂. [1,88°]. Formed
by heating o-phenylene-p-tolyl-guanidine with
C(NC,H,)₂ at 220° (Keller, B. 24, 2513). Prisms (from benzene).

DI - p - TOLYL - AMIDO - METHYLENE - 04 TOLYLENE-p-TOLYL-GUANIDINE C,H,:N₂(C:NC,H,):C(NHC,H,), [210°]. Formed by heating tolylene-tolyl-guanidine together with C(NC,H,), at 220° (Keller, B. 24, 2521). Needles, sl. sol. alcohol.
o-TOLYL-AMIDO-METHYL-MALONAMIC

ETHER CO.Et.CMe(NHC.H.,).CO.NH. Formed by dissolving a evano-tolyl-a-amido-propionic cher in cont. H.SO, (Gerson, B. 19, 2966). Long needles, sol. hot water. Converted by boiling NaOHAq into tolyl-amido-propionio

p-TOLYL-AMIDO p METHYL-OXINDOLE

 $C_{10}H_{10}N_{2}O$ i.e. $C_{0}H_{0}Me < \frac{NH}{CH(NDCH)} > CO.$

[167]. Formed by heating di-chloro- (or di-bromo-) acetic acid, with p-toluiding (Duisberg, B. 18, 190). Needles, y. sol. hot alcohol. Reduces ammoniacal AgNO, forming a mirror. Readily absorbs exygen from the air, forming C₆H₃Me < N11 CO. Alcoholic KOH forms a blood-red solution. BIICI: crystalline

powder. Di-acetyl derivative C16H11Ac2N2O. [117°].

Nitrosamine C, H, N,O... [c. 220°]. p-TOLYL-AMIDO METHYL-THIAZOLE

ĊН CMe. [125°]. Formed S C(NHC,H):N oxy-methyl-thiazole and p-toluidine (Hantzsch a. Weber, B. 20, 3130).

TRI-p-TOLYL-TRI-AMIDO NAPHTHASENE $C_{s}H_{i} < \stackrel{C(NHC,H):C(NHC,H_{i})}{C(NHC,H):CH}. \quad [160^{\circ}]. \ \, \textbf{Formed}$

by heating nitroso-ethyl-(a)-naphthylamine with 7-toluidine at 150 (Pischer a. Hepp, A. 256, 244). Needles (from alcohol). Readily axidised to di-methyl-phenyl-rosinduline.

O-TOLŸL-AMIDO-(a)-NAPHTHOQUINONE C₁₇H₁₃NO₂ i.e. C₁₀H₂O₂(NHC₃H₂). [142°]. Formed from o-toluidine and (a) naphthoquinone (Elsbach, B. 15, 689). Red needles, sol. NaOHAq.

p-Tolyl-amido (a)-naphthoquinone C., H.O. (NHC, H.). [2027]. Formed from (a) naphthoquinene and p-toluidine in hot alcoholic solution (Plimpton, C. J. 37, 638). Formed also by the action of p-toluidine on (β) -oxy- (α) naphthoquinone, and by heating p-tolyl-amido-(B) naphthogumone with HOAc at 150° (Elsbach, B. 15, 687). Red needles. Forms a crimson solution in conc. H2SO4. Insol. NaOHAq.

 $Ditoluide = C_0H_1 < \frac{C(NC, H_1):C.NHC_1H_2}{C(NC, H_1):CH}$ [1476]. Formed by oxidation of tri-p-tolyl-amidonaphtbalene (Fischer a. Hepp, A. 256, 246). Orange plates.

o.Tolyl.amido (β)-naphthoquinone C₁₀ H₂O₂(NHC H₂) or C₁₀ H₂(OH)O(NC,H₂). [240°]. Formed from (B) naphthoquinone and o-toluidine (Elsbach, B. 15, 689). Red needles, sol. dilute NaOHAq. Not affected by heating with HOAc at 150°. On heating with dilute HClAq it yields

(β) oxy-(α)-naphthoquinone and o-toluidine p - Tolyl - amido - (B) - naphthoquinone [246°]. Formed from (β) -naphthoquinone and p-toluidine (Elsbach, B. 15, 686). Red needles, sol. hot al-cohol and NaOHAq. On heating with HClAq at 130 it is split up into p-toluidine and (8)naphthoquinone.

Methyl ether MeA'. [150°]. Red crystals (Zincke a, Brauns, B. 15, 1969). Ethyl ether Eth'. [137'].

Isopropyl ether PrA'. [139].

p-Toluide C,0H, (NHC,H,)O(NC,H,). [188° cor.]. Formed by heating di-bromo-(a)-naphthol with p-toluidine (Meldola, C. J. 45, 159). Formed also from (B-naphthoquinone oxim, p-toluidine, and HOAc (Bromme, B. 21, 391). Orange crystals with green lustre.

DI-o-TOLYL-DI-AMIDO-OIAZTHIOLE

C₁₆H₁₆N₄S i.e. S<C(NHC,H₁):N. [135°]. Formed by boiling an alcoholic solution of o-tolyl-thiourea with dilute HClAq and H₂O₂ (Hector, B. 23, 368). V. sol. alcohol. Cya 10gen passed into its alcoholic solution forms C₁₆H₁₆N₄SCy₂(89°).—B'HClaq. [219°].—B'2H,PtCl_c. [192°].—B'AgNO₂. White pp.—B'2H,HgCl_c. [232°]. Needles.—Picrate: B'C₆H₃N₃O₇. [201°]. Acetyl derivative C₁₆H₄,RaN,S. [211°]. Bensoyl derivative C₁₆H₄,RaN,S. [214°]. Nitrosamine C₁₆H₁₆(N),S. [135°].

Nitrosamine C₁₆H₁₆(N),S. [135°].

Formed in like manner from n-tolyl-11. by boiling an alcoholic solution of o-tolyl-thio-

Formed in like manner from p-tolylhio-urea (Hector, B. 23, 364). Thick yellowish prisms, v. sol. alcohol. Cyanogen forms B'Cy₂ [190°].—B'HCl. [233°]. White needles, becoming reddish in air.—B'_2H_PtCl₈ 1\(\frac{1}{2}\)aq. [109°].—B'AgNO₄ 1\(\frac{1}{2}\)aq. [177°].—B'_2H_1\(\frac{1}{2}\)L(1\(\frac{1}{2}\)aq. [14°_2]. Pi or \(\frac{1}{2}\)steel [238°]. Yellow prisms, sl. sol. alcohol.

Acetyl derivative C₁₆H₁₅AcN₁S. [166°].

Bunzoul derivative C₁₆H₁₅BzN₄S. [186°].

Nitrosamine C₁₆H₁₅(NO)N₁S. [247°].

o-TOLYL-m-AMIDO-PHENOL C₁₆H₁₅NO i.e.

O,H,NH.C₆H₄OH. (c. 373° cor.). Formed from resorcin, o-toluidine, and CaCl₂ at 270°, (Philip, J. pr. [3], 34, 70). Oil. Reduced by hot zincodust to hydro-acridine and acridine.

Formul designation (LiGe). Tables

Formyl derivative. [169°]. Tables.
o-Tolyl-p-amido-phenol C,H,NH.C,H,OH.
[90°]. (86°° cor.). Formed from hydroquinone,
o-toluidine and CaCl, at 240° (Philip, J. pr. [2] 34, 57). White lamine (from light petroleum). Reduced by distilling with zine to hydro-acridine and acridine. Converted by heating with conc. HCl into hydroquinone and o-toluidine.

Salt .- B'HCl : crystalline powder. Mono-formyl derivative [136.5°]. Di-acetyl derivative [106°]: needles.

Di-benzoyl derivative [1019]: needles.

Di-benzoyl derivative. [1719].

p-tolyl-m-amido-phenol C₁₄H₁₄NO i.e.
C,H,NH.C,H,OH. [929]. (350° cor.). From
resorcin, p-toluidine and CaCl₂ at 260° for 8
hours (Hatschek a. Zega, J. pr. [2] 33, 20°).

Prisms or needles (from benzene mixed with petroleum ether). Distilled over zinc-dust, it gives C.H.NHPh.

Salts .- B'HCl; decomposed by water.

Formyl derivative.

C.H., N(CliO).C., H., OH. [14°]. V. sol. ether. Di-benzoyl derivative.—
C.H., NBzC., H., OBz. [c. 105°]. Gives with tuning HNO, a di-nitro-derivative, [110°].

Nitrosamine.—C.H., N(NO).C., H., OH. Onyphenyl-tolyl-nitrosamine. [105°]. Yellow readles (term ill electron) phenyl - tolyl - nitrosamine. needles (from dil. alcohol).

needles (from dil. alcohol).
p-Tolyl-p-amide-phenol C,H.,NH.C,H.,OH.
[122°]. (350°-360°). From hydroquinone, ptoluidine, and CaCl., 8 hours at 260° (Hatschek
a. Zega, J. pr. [2] 33, 224). Plates. Heated
with zinc-dust it gives phenyl-p-tolyl-amine.
Salt.—B'HCl. Powder, decomposed by Aq.
Di-acetyl derivative. [101°]. Tables.

Di-bensoyl derivative. [1697]. Nitroso-derivative O.H.,N(NO).O.H.,OH [130°]; needles. Very unstable.

o-TOLYL-a-AMIDO-PHENYL-ACETIC ACID NHC,H,CHPh.CO₂H. [143°]. Formed from abromo-phenyl-acetic acid and o-toluidine (Stöckenius, J. 1878, 781). Plates, almost insol. water

p-Tolyl-a-amido-phenyl-acetic acid. Formed in like manner, using p-toluidine. Insol. water. Ethyl ether EtA'. [90°]. Yellowish prisms.

o-TOLYL - AMIDO-TRI-PHENYL-METHANE CPh₃.NHC,H₇. [142°]. Formed from CPh₃Br and o-toluidine (Wittich, B. 17, 705). Prisms

(from ether). p-Tolyl-amido-tri-phonyl-methane Crystals (from ether).

CPh.,NC.H.,NO. Nitrosamine f145°-

p-TOLYL-AMIDO-DI-PHENYL-NAPHTHO-QUINOXALINE. Phenylo-chloride

Got by heating C₁₀H₃(OEt) < N=CPh with ptoluidine at 120° (Witt a. Schmidt, B. 25, 2005). Bronzed plates, v. sol. alcohol, forming a crim-son solution. Con. H.SO, forms a slate-blue solution, becoming first blue and then violet on dilution.

TRI-p. TOLYL - TRI - AMIDO - DI-PHENYL-TOLYL-CARBINOL C41H30N3O. Tri-tolyl-rosaniline. The salts are formed by heating rosaniline salts with p-toluidine (Hofmann, A. 132, 290) .-C41H38N3Ci. Small blue crystals (from alcohol), insol. water.

TOLYL-AMIDO-PIPITZAHOIC Toluido-PIPITZAHOIC ACID.

o-TOLYL-a-AMIDO-PROPIONIC ACID

CH₃.CH(NHC,H₇).CO₂H. [116°]. Formed by saponification of the nitrile (Tiemann a. Stephan, B. 15, 2038; C. C. 1886, 470). Got also by boiling o-tolyl-amido-methyl-malonic acid with NaOllAq (Gerson, B. 19, 2963). White crystals. Ethyl ether Eth' (2786). S.G. \$\frac{20}{26}\$ 1.047. Hormed from a-bromo-propionic ether and o-toluidine (Bischoff a. Hausdörfer, B. 25, 2298).

Actyl derivative C,H,NAc.CHMeCO,H.
[177°]. Leaflets.

Amide. [125°]. "Minute needles.

Nitrile CH,CH(NHC,H).CN. [78°]. Formed by digesting the cyanhydrin of acetic aldehyde (lactonitrile) with o-toluidine.

p - Tolyl - α -amido - propionic acid. Formed in like manner. Plates, sl. sol. water and ether. May be sublimed.

Ethyl ether EtA'. [35°]. Acetyl derivative [166°]. Tables.

Amids. [145°]. Needles, sol. hot Aq. Nitrile. [82°]. Plates, sl. sol. hot Aq.

p. Tolyl-8 amido-propionic acid C.H.Me.NH.CH.CH.CO.H. [86°]. Formed from \$-iodo propionic acid and p-toluidine (Bischoff a. Mintz, B. 25, 2352). Pearly scales, v. e. sol. ether.

Reference. — DI-BROMO-TOLYL-AMIDO-PROPIO-NITRILE.

o-TOLYL-AMIDO-PYROTARTRIMIDE CH, CO NH [181°]. Obtained by saponi-

fication of o-tolyl-amido-pyrotartramic ether, which is formed by the action of H.SO, upon the a-cyano-a-o-toluido-butyric ether (Schiller-Wechler, B. 18, 1050). White needles. alcohol and benzene, sl. sol. ether and hot water, insol. cold water and ligroin. Has both acid and basic properties.
DI-p-TOLYL-DI-AMIDO-SUCCINIC ACID

CO.H.CH(NHC.H.).CH(NHC.H.).CO₂H. [c. 200°]. Formed, together with 'di-toil succin' C₁₈H₁₆N.O₂ [228°], by boiling di-bromo-succinic acid with p-toluidine (Junghahn a. Reissert, B. 26, 1766). V. sol. alcohol, insol. water. Yields 25, 1700). V. Sol. alcolol), fiscol. water. Tields a di-nitroso-derivative [125°], and a di-netyl derivative $C_{22}H_{21}N_{2}O_{q}$ aq, which yields CaA'' aq, BaA'' aq, and anhydrides $C_{21}H_{21}N_{2}O_{5}$ [232°], and $C_{22}H_{30}N_{2}O_{7}$ [222°]. Na,A''.—CaA''.—CuA''.

Ethyl ether Et,A''. [169°]. Needles.

DI-p-TOLYL-TRI-AMIDO-TOLUENE

C₆H₂Me(NHC,H₁)₂(NH₂)[1:2:5:4], [166°], Formed by reducing amido-toluquinone ditoluido with zine-dust and HOAc (Green, C. J. 63, 1403; cf. Barsilowsky, B. 6, 1209). Plates (from dilute HOAc). A very feeble base.

DI - p - TOLYL - DI - AMIDO - TOLUQUINONE C_bHMeO₂(NHC,H₂)₂[1:2:5:4:6]. [178*]. Formed from azotoline, MeOH, and conc. H₂SO₄ (Fischer a. Hepp, A. 262, 251). Brownish-red needles. Di-p-tolyl-di-amido-toluquinone

C₆HMeO₂(NHC,H₇)₂ [122;5;3;6]. [241°]. Formed by boiling toluquinone with p-toluidine and alcohol (Fischer a. Hepp, A. 256, 259). Yellow

TOLYLAMINE is TOLUIDINE (q.v.)

(312)Di-o-tolyl-amine NH(C,H,Me[1:2]) i.V.) at 728 ram. (Graebe, A. 238, 363). Obtained, together with diphenylamine by heating o-toluidine with aniline hydrochloride at 280 (Girard a. Willin, Bl. [2] 25, 248). Formed also by heating o-cresol with ZnBr., ammonia, and NH.Cl at 335° (Merz a. Müller, B. 20, 547). Oil.

Di-m-tolyl-amine NH(C,H)₂. (322°). Formed in like manner (Cosack B. 13, 1091; Merz a. Müller, B. 20, 519). Oil, volatile with steam. Sl. sol. acids, v. sol. alcohol.

Nitrosamine (C,H,),NNO. [103°]. Dip-tolyl-amine NH(C,H),... [79]. i.V.) (Graebe, A. 238, 363). Formed by heating p-toluidine with its hydrochloride (Girard, A. 140, 346; Gerber, B. 6, 446). Formed also by heating p-cresol with ZnCl₂ ammonia, and NH₂Cl at 335° (Merz a. Müller, B. 20, 516). White needles. Its salts are decomposed by

Nitrosamine (C,II,),N.NO. [103] Yellow trimetric crystals (Lehne, B. 13, 1514 Cosack).

Acetyl derivative (C,H,),NAc. [85°]. $[125^{\circ}].$ Benzoyl derivative (C.H.), NBz. References. - TETRA-BROMO- and NITRO- DI-TOLYL-AMINE

DI.p-TOLYL-ISOAMYL-AMINE C, H,N i.e. (C,H,),NC,H₁₁, (290°-800° at 15 mm.). Formed by heating di-p-tolyl-amine with isoamyl alcohol and HCl in sealed tubes (Girard, Bl. [2] 24,

120). TOLYL-ANILINE v. PHENYL-TOLUIDINE. Vol. IV.

TOLYL-ARSINE v. ARSENIC.

TOLYL-AURAMINE C, H, N, i.e.

C,H,Me.N:C(C,H,NMe,), Formed from auramine
hydrochloride and p-toluidine (Fehrmann, B. 20, 2853). Decomposed by H₂S in alcoholic solution at 50° inte CS(C₆H,NMc₂), and p-toluidine.—
B'₂H,PtCl₈. Red flakes, v. sl. sol. water.

TOLYL-AZIMIDO-TOLUENE v. COMPOUNDS ...

DI - 2'- TOLYL - TETRAZINE Ciellien, i.c. $C_{c}H_{i}Me.N < \stackrel{N=CH}{CII:M} > N.C_{c}H_{i}Me.$ [185°]. Mole w. 269 (obs.). Formed by the action of chloroform and alcoholic potash on p-tolyl hydrazine (Ruhemann, C. J. 55, 218; 57, 51). Yellow plates (from hot alcohol). Yields a nitroderivative C18H15(NO2)N1 [144°].

TOLYL - DISAZO - compounds v. DISAZO-COMPOUNDS.

TOLYL BENZAMIDE v. Benzoyl derivative of TOLUMBINE.

p - TOLYL - BENZAMIDINE $C_{14}U_{14}N_{2}$ i.e. $C_{6}U_{5}$ (NC, U_{1}), NH, [99°]. Formed from benzonitrile and toluidine hydrochloride (Bernthsen, B. 8, 1319; 9, 429). Forms a crystalline nitrate

and oxalate. Di-p-tolyl-benzamidine

C.H., C(NC,H.).NHC,H., [131°]. Formed by the action of p-toluidine on benzonitrile, and on w-chloro-benzylidene-p-toluidine C,H,N:CCl.C,H, (Bernthsen; Just, \hat{B} , 19, 981). May be sublimed.

Reference. -- AMIDO-TOLYL-BENZAMIDINE. needles. Di.p-tolyl-di-amido-toluquinone p-toluide p-to Calla CS.NHC, H, and Na CO, at 100° (H. Müller, B, 22, 2406). White needles, sl. sol. hot water. B'HCl: white needles, sl. sol. water. ClCO,Et converts it into C_0H_3 . $C < N_{C_1H_2}^{N.O} > CO$. [163°].

TOLYL-BENZENE v. METHYL-DIPHENYL. Tri-p-tolyl-benzene C2,H2, i.e. C6H3(C,H7)

[171°]. Formed by passing dry HCl into p-tolyl methyl ketone for some days (Claus, J. pr. [2] Al, 402). Needles. Oxidised by Cr0, to C_pII,(CO.H). Yields C_pII,(Br. 212°). P-1014L-BENZIMIDO PHENYL ETHER C_pII,C(NC,H.).OPh. [120°). Formed from

C.H., C(NC, H.). OPh. [120°]. Formed from CaH, CCl: NC, H, and NaOPh (Hantzsch, B. Formed from 26, 927).

om-TOLYL-BENZOIC ACID [1:3] C. H., Mc.C. H., CO. H. [1:3]. [204°]. Formed by oxidation of [1:3] C. H., Mc.C. H., Me [1':3'] with dilute HNO. (Perrier, C. R. 114, 484). Silky needles, sol. alcohol, m. sol. Aq.

pp-Tolyl-benzoic acid [1:4] C₆H, Mc.C₆H, CO₂H [1':4']. [244']. Formed by oxidation of pp-ditolyl by CrO₂ and HOAc (Camelley, J. 1877, 384). Sl. sol. hot water.—

op-Tolyl-benzoic acid. [180°]. Formed by oxidation of [1:2] C₄H₄Me.C₄H₄Me [1':4'] (Carnelley, C. J. 37, 707). Insol. water, sol. hot alcohol.

TOLYL-BENZYL-AMINE v. BENZYL-ADLU-

p-TOLYL-BENZYL-ISOBUTYL-UREA O. H., N.O. [41°]. Got from p-tolyl-benzylcarbamic chloride and isobutylamine (Hammerich, B. 25, 1824). Crystals (from ligroin).

p-TOLYL-BENZYL-CARBAMIC CHLOBIDE (C.H.Me)N(CH.Ph).COCl. Formed from p-tolylbenzyl-amine and COCl, (Hammerich, B. 25,

1822). *Oil.

p-TOLYL-BENZYL-CARBINOL C, H, O i.e. C, H, Mc.CH(OH).CH,Ph. [66°]. (above 360°). Formed by reducing p-tolyl benzyl ketone in alcoholic solution by Na (Mann, B. 14, 1646). Small concentric needles, sol. alcohol and ether. p-TOLYL-BENZYLENE-ACETAMIDINE

C₁₀H₁₀N₂ i.e. C₀H₄ < CH₂.NC,H₇. [79°]. Formed by reduction of the acetyl derivative of o-nitrobenzyl-p-toluidine in acetic acid solution with tin and HCl (Lellmann a. Stickel, B. 19, 1610). Small glistening plates. V. sol. alcohol, ether, and chloroform.

and chloroform.

p.TOLYL BENZYL KETONE C₁₃H₁,O i.e.
C₄H₁Me.OD.CH₄Ph. [109°]. (above 360°). Formed
by the action of AlCl₃ on a mixture of phenylacetyl chloride and toluene (Mann, B. 14, 1646;
Strassmann, B. 22, 1229). Plates, sol. alcohol
and ether. Na added twiss alcoholic solution forms the carbinol and an acid C19H20C2 ["3"].

Oxim [131°]. Plates, insol. water. o-TOLYL BENZYL OXIDE C,H,O i.e. [1:2] C.H.Mc.Q.CH.Ph. (2859-290°). Oil (Standel, B. 14, 899). Converted by HNO, (S.G. 1.5) into a tri-nitro- derivative [145°]. mrTolyl benzyl oxide. [43°]. (300°-305°).

Tables (from alcohol), v. sol. ether.

p-Tolyl benzyl oxide [41°]. Formed from C,H,Me.OK and CH,PhCl (Frische, A. 224, 154). Crystals. Converted by HNO, (S.G. 45) into di-nitro, η -cresol [84°]. **TOLYL-BENZYL-ISOPHOSPHINE** $C_{11}H_{13}P$

or C₂₇H₂₈P₂. [187°]. An indifferent body formed by the action of zinc on a mixture of benzyl chloride and CoH, MePCl2 (Michaelis a. Gleichmann, B. 15, 1963)

p. TOLIVI BENZYL SULPHONE C.H.Me.SO., CH.Ph. (145°). Formed by the action of benzyl chloride on sodium tolucne p-sulphinate (Otto, B. 13, 1278). Needles, sol. hot alcohol.

p.TOLYL.BENZYL.THIO.SEMICARBAZIDE C,H,N,S. [121°]. Formed from benzyl thiocarbimide and p-tolyl-hydrazine (Dixon, C. J.

61, 1022). Prisms, sl. sol. cold alcohol. o-TOLYL-BENZYL-THIO-UREA C o-TOLYL-BENZYL-THIO-UREA C_{1.}H_{1.}N₂S i.e. C₂H₄MeNH.CS.NHCH₂Ph. [139°]. Formed by boiling o-tolyl-thiocarbimide with benzylamine in alcohol (Dixon, C. J. 59, 556). Tufts of prisms, m. sol. hot alcohol.

m-Tolyl-benzyl-thio-urea. [114°]. Formed from benzyl-thiocarbimide and m-toluidine.

Vitreous crystals, v. sl. apl. hot Aq. p-Tolyl-benzyl-thio-urea [121°]. p-TOLYL-BENZYL-UREA

[181°]. CH,Ph.NH.CO.NHC,H,Me. from p-tolyl cyanate and benzylamine (Kühn a. Henschel, B. 21, 505).

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p-Tolyl-di-bensyl-urea C₂₂H₄, N₂O i.e.

(CH_Ph)₂N.CO.NHC₄H, Me. [169°]. Got from (O,H.)₂N.CO.U and p-toluidine (Hammerich, B. 25, 1820). Needles (from alcohof), insol. ether.

p-Tolyl-di-bensyl-ures C₂₂H₂₂N₂O i.e.

CH_PhN(O,HTMe).CO.NH.CH₂Ph. [85°].

Formed from tolyl-bensyl-carbamic chloride and

Formed from tolyl-benzyl-carbamic chloride and benzylamine (H.). Prisms, v. sol. alcohol.

Di-p-tolyl-benzyl-urea C₁₂H₁₂N₂O. [115°].

Formed from p-tolyl-benzyl-carbamic chloride and p-toluidine. Needles, v. sol. hot alcohol.
Di-p-tolyl-di-benzyl-urea

CH.,PhN(C,H,Me)),CO. [93°]. Got from ptolyl-benzyl-carbanic chloride and p-tolyl-benzyl-amine. Crystalline, sol. alcohol.

DI.-p.TOLYL-BIURET (C,H,MeNH.CO),NH.

[c. 220°]. Formed from p-tolyl-urea and p-tolyl cyanate at 160° (Kühn a. Henschel, B. 21, 506). White needles (from alcohol).

Tri-p-tolyl-biuret (C₈H₄MeNH.CO)₂NC₈H₄Me. ſ156°7.

from di-p-tolyl-urea and p-tolyl cyanate.

p-TOLYL-BORIC ACID C₈H₄Me.B(OH). [240°]. Formed by the action of water on boronp-tolyl-dichloride (v. vol. i. p. 531). Needles, sol. hot water. HgCl₂ gives a white pp. of C,H,HgCl.

TOLYL-BROMO-ETHYLENE v. BROMO-TOLYL-

ETHYLENE.

TOLYL BROMO METHYL KETONE

C.H.Me.CO.CH.Br. [55°]. Formed by the action of hot water on di-exo-bromo-eso methylatrolactic acid (Böttinger, B. 14, 1598). Crystals, volatile with steam, sol. water and ether.

p-TOLYL BROMO-METHYL SULPHONE

C.H.Me.SO.CH.Br. [92°]. Formed by the action of bromine on an aqueous solution of Thin monoclinic needles, sol. hot alcohol.

p-Tolyl di-bromo-methyl sulphone CaH.Me.SOa.CHBr2. [117]. Form Formed tolyl-sulphono-acetic acid and Br (O.). Monoclinic prisms, v. sol. hot alcohol.
TOLYL-BUTANE v. BUTYL-TOLUENE.

m-TOLYL-BUTYLENE C.H., Me.CH., C.H., (195°). Formed from C.H., Me.CH., Cl., allyl iodide, and Na (Aronheim, B. 9, 1790). Oil. Yields a liquid dibromide.

p-TOLYL-p-BUTYL-PHENYL-THIO-UREA C₈H,Me.NH.CS.NH.C₈H,C₄H₂. [137°]. Formed from isobutyl-phenyl-amine and p-tolyl-thiocarbimide (Mainzer, B. 16, 2024). Plates, sol. alcohol and ether.

DI-p-TOLYL-ISOBUTYL-UREA 119°]. Formed from (C,H,)2N.COCl and isobutylamine (Hammerich, B. 25, 1822). Prisms, v. sol, alcohol and ether.
m-TOLYL-ISOBUTYRIC ACID

C₄H₄Me.CH₂.CHMe.CO₂H. [92°]. Formed by oxidation of m-isobutyl-toluene by dilute HNO₄ (Kelbe, B. 16, 620). Needles (from ligroin).-

AgA: pp.

Reference.—Nitro-tolyl-isobutyric acid. o-TOLYL-CARBAMIC ACID C.H.NO. i.e. C,H,Me.NH.CO,H.

Ethyl ether EtA'. [42°] (C.); [46°] (L.). Formed from o-toluidine and ClCO2Et (Cosack, Formed also from C.H., Mc.CCl:NCl and alcoholic potash (Lachmann, B. 12, 1349). Tables, sol. alcohol and benzene. Volatile with steam. alcohol and benzene. Volatile with steam. Yields o-tolyl cranate on distilling with Prop. Isobutyl ether C.H.A'. (275°-280°). Oil (Mylius, B. 5, 974). Parially decomposed on

distillation into tolyl cyanate and isobutyl alcohol.

Bensyl ether CH.PhA'. [84°]. Formed from o-tolyl cyanate and benzyl alcohol (Gattermann a. Cantzler, B. 25, 1097). Needles

Phonyl ether PhA'. [92°]. Formed by boiling di-o-tolyl-ures with di-phenyl carbonate for some hours (Eckenroth a. Rückel, B. 23, 699). Crystals (from ligroin).

m-Phenylene ether C₆H₄A'₂. [154°]. Formed by heating o-tolyl cyanate with resorcin at 120° (G. a. C.). Colourless plates.
p-Phenylene ether C₆H₄A'₂. [206·5°].

Formed by heating o-tolyl cyanate with hydroquinone at 150°.

o-Tolyl ether C,H,A'. [126]. Formed from o-tolyl cyanate and o-cresol (G. a. C.). Needles.

(β)-Naphthyl ether C₁₀H,A'. [149]. Formed by heating o-tolyl cyanate with (β)-naphthol at 160° (G. a. C.). Plates.

Di-phenyl-othylene ether C.H.Ph.A [234°]. Formed by heating o-tolyl cyanate with hydrobenzoïn at 100° (Auwers, B. 24, 1778). Needles. An isomeride [163°] is obtained from isohydrobenzoïn.

m-Tolyl-carbamic acid [1:3]C,H,Me.NH.CO.H.

Ethyl ether C₁₀H₁₃NO₂. Prepared from m-toluidine and chloro-formic ether (Cosack, B. 13, 1090). Oil, v. sol. alcohol and ether.

p-Tolyl-carbamic acid

[1:4]C.H.Me.NH.CO.H. Ethyl ether EtA'. [52]. Formed from p-toluidine and ClCO Et (Hofmann, Pr. 19, 108; B. 3, 656). Monoclinic prisms, v. sol. alcohol (Levin, J. 1882, 381).

Phenyl ether PhA'. [115°]. Formed by distilling di-p-tolyl-urea with di-phenyl carbonate (Eckenroth a. Rückel, B. 23, 698). Needles (from hot ligroin).

Di.p.tolyl-carbamic acid (C,H,),N.CO.H.

Ethyl ether Eth'. [62']. Formed from (C,H,),N.COCl and NaOEt (Hammerich, B. 25,

(C_t)_{1/2}, v. sol. alcohol and ether.

Chloride (C_tH₄Me)₂N.COCl. [103].

Formed from COCl₂, a solution of di-p-tolylamine in benzene, and conc. NaOHAq (Hammerich, B. 25, 1821). Needles (from alcohol), v. e. sol. ether. AgCy forms the compound (C,H,)₂N.CO.CN(AgCy)₂ crystallising in needles which begin to melt at 103°.

o-TOLYL-CARBAMINE [1:2]C,H,Mc.N.C.

(184°). S.G. 24 968. Formed by the action of alcoholic potash on o-toluidine and chloroform (Nef, A. 270, 309). Oil, volatile with steam. When heated at 245° for 3 hours it changes to the isomeric o-toluic nitrile. Heated with S in the isomeric bettile inner. Heater with S in CS, at 130° it yields o toly! thiocarbinide. H.S at 100° forms C. H.Mc.NH.CHS [101°].

Chloride C. H.Mc.N.CCl. (215°). Found

by passing chlorine into a chloroform solution of the carbamine.

p-Tolyl-carbamine CaH, Me.N:C. (99° at 36

p-rolyl-carbannie C₆H₁Mc.N:C. (199° at 36 nm.). Formed in like manner from p-toluiding (Nef). Oil.

Chloride C₆H₁Me.N:CCl₂. (226°). Converted by p-toluidine into tri-p-tolyl-guanidine.

o-TOLYL-SEMI-CARBAZIDE C₆H₁N₁O i.e.

NH₂CO.N₂H₂C,H₁. [160°]. Formed by heating o-tolyl-hydrazine with urea (Pinner, B. 21, 1210). Eight needless meal water.

1219). Flat needles, m. sol. water.

p.Tolyl-semi-carbanide C,H,,NO. [158].

Sl. sol. cold water. Reduces Fehling's solution.

Di-p-tolyl-carbanide CO(NH.NHC,H.), [201°]. Formed from p-tolyl-hydrazine and carbamic ether (Preund, B. 24, 4197). Tables, insol. water, v. sol. hot alcohol.

TOLYL-CARBINIDE Q. TOLYL ISOCYANATE, vol. ii. p. 316, o-TOLYL-CARBINOL C.H.O i.e.

[1:2]C₆H,Me.CH.OH. ω-Oxy-o-xylens. Mol. w. 122. [34°]. (223°i.V.). S.G. 12 1 02. S.1 in the cold; 1.5 at 100°. Formed by boiling w-bromo-oxylene with KOHAq (Colson, Bl. [2] 43, 8; A. Ch. [6] 6,116). Formed also by reducing the aldehyde C. H. Me.CHO (Raymann, Bl. [2] 27, 498), by the action of HNO, on the amine C. H. Me. CH., NH. (Kröber, B. 23, 1028), and by reducing o-toluic

(Hutchinson, B. 21, 174). Needles, v. sol. alcohol and ether, sol. hot water. Oxidised by alkaline KMnO, to o-toluic acid [103°].

m-Tolyl-carbinol [1:3]C.H.Me m-Tolyl-carbinol [1:3]C₀H,Me.CH₂·OH. (217°). S.G. 2 1·036 (C.); ¹² ·016•(R. a. W.). S. 5 in the cold. Formed by boiling the bromide

S. of the could refine a pointing the bronder C_0H Mc.CH.Br with alkalis (C.). Liquid, v. sol. alcohol and ether, sl. sol. cold water. Yields mallic acid [108°] on exidation.

12 hylyt ether C, H. CH. OEt. (202°) at 740 mm. S.G. 11 93. Oil.

Acetyl derivative C.H., CH, OAc. (226°). Formed from C,H,CH,Br and KOAc (Radziszewski a. Wispek, B. 15, 1747). Oil.

p-Tolyl-carbinol [1:4]C,II,Me.CII,OH. [59°] (217°). Formed from p-toluic algebyde and alcoholic potash (Cannizzaro, C. R. 54, 1225; A. 124, 255). Needles, sl. sol. cold water.

Ethyl ether C_nH_w.OEt. (203°) at 740 mm. S.G. 17 93. Formed from w-bromo-p-

Will-carbinol (C₀H₀Me₂OH.OH. (69°) (W.); [62°] (Ador a. Crafts, B. 10, 2175). amalgam (Weller, B. 7, 1184). Needles (from alcohol), insol. water.

Reference .--Oxy-tolyl-carbinol.

TOLYL-CARBINYL-AMINE METHYL BENZYL-AMINE

DI-p-TOLYL-CARBINYL AMINE

(C₇H₁₎₂CH.NH₂. [93°]. Formed by reducing the oxim of di-p-tolyl ketone in alcoholic solution with sodium-amalgam and HOAc at 60° (Goldschmidt a. Stöcker, B. 24, 2798). Tables.

-B'HCl. [235°]. White needles.
Acetyl derivative [159°]. Needles.
• TOLYL-CARBINYL-UREA v. Ms1 BENZYL-UREA.

Di.p. totyl-carbinyl-urea
NH., CU.NH.CH(C,H.),. [152°]. Formed from
the hydrochloride of the amine and KCyO
(Goldschmidt, B. 24, 2799). Needles.

DI-p-TOLYL-CARBONATE (C,H,O),CO. [115], Formed, together with diethyl carbonate, by heating p-tolyl ethyl carbonate at 300 (Bender, B. 19, 2268). V. sl. sol. cold alcohol. DI-TOLYL DICARBOXYLIC ACID

[3:4:1]C,H,Me(CO,H),C,H,Me(CO,H)[1:8:4] [over 300°]. Formed by heating its nitrile with dilute H₂SO₄ (Löwenherz, B. 25, 1036). Plates, insol. water, sl. sol. hot alcohol.

Nitrile C, H₁₂(CN), [190°]. Formed from di-amido-ditolyl by Sandmeyer's disco- reaction. Formed from Needles, m. sol. cold alcohol.

Reference.—OXY-DITOLYL DICARBOXYLIC ACID. TOLYL CHLORIDE v. w-CHLORO-XYLENE,

p-TOLYL CHLORO-BENZYL SULPHONE C.H.Mc.SO.cOHOI.C.H.M. [203°]. Formed by heating sodium toluene p-sulphinate with benzylidene chloride (Otto, J. pr. [2] 40, 519).

Needles (from HOAc). p-TOLYL CHLORO-ETHYL SULPHONE

[1:4]C_uH₄Me.SO₂.CHCl.CH₃. [48°]. Formed by boiling CH₃.CCl₂.CO₂Na (1 mol.) with C,H,.SO,Na (2 mols.) in aqueous, solution.

Formed also by heating ethylidene chloride (2.5 g.) with sodium toluene p-sulphinate (4.5 g.) and alcohol at 150° (Otto, J. pr. [2] 40, 515,534). Trimetric tables, v. sol. hot alcohol. Des not

act upon C,H.,SO,Na even at 200°.
p-Tolyl chloro-ethyl sulphone
C₆H,Me.SO,CH,CH,Cl. [79°]. Formed from
C₄H,Me.SO,CH,CH,CH,DH and PCl, (Otto, J. pr.
[2] 30, 357). Needles or plates, v. sol. hot alcohol.

p. TOLYL CHLORO METHYL SULPHONE C_aH_aMe.SO_x.CH₂Cl. [84°]. Formed by heating an aqueous solution of CHCl_x.CO_xNa (1 mol.) with C,H,SO2Na (2 me.s.) on the water-bath (Otto, J. pr. [2] 40, 528). Tables (front benzene), v. sol. hot alcohol.

p-Tolyl di-chloro methyl sulphone
Collime SO. CHCl. [114°]. Formed by passing chlorine into a warm aqueous solution of Collime So. CH. CO. H. (Otto, J. pr. [2] 40, 544). Crystals, ingol. water, v. sol. hot alcohol.

C₆H₄Me.CH₂.C₆H₄.OH. TOLYL-CRESOL (250°-255° at 10 mm.). Formed by heating wchloro-xylene with phenol and zinc filings (Mazzara, G. 9, 421). Oil, sol. alcohol, ether, and alkalis. Not coloured by FcCl₃.

Acety: derivative (250° at 9 mm.).

Decomposed in moist air into HOAc and tolyl-

p-TOLYL-CUMINYL-AMINE $C_{17}H_{21}N$ i.e. $C_{4}H_{4}Me$, NH, CH_{2} , $C_{4}H_{4}Pr$. [36°]. (above 200°). Formed by the reduction by sodium-amalgam of the product of the action of cuminol on p-toluidine (Uebel, A. 245, 293). Plates or prisms.—B'HCl. Plates or needles, sl. sol. hot

Nitrosamine C_{1.}H_{...}N.NO. [67°]. Prisms. p-TOLYL-CUMINYL-UREA C₁₈H_{...}N₂O i.e. C₁₆H₁₈.NH.CO.NHC₈H_.Me. [150°]. Formed from cuminylamine and p-tolyl cyanate (Goldschmidt a. Gessner, B. 22, 928). Needles, v. sol. alcohol.

p-TOLYL-CUMYLIDENE AMINE

O_sH,Me.N:CH.C_sH,Pr. [51°]. Formed from cuminic aldehyde (cuminol) and p-toluidine in alcoholic solution (Uebel, A. 245, 292). Yellowish plates (from alcohol). Decomposed into the parent substances by heating with acids and alkalis.

alkalis.
p-TOLYL-\$\psi\$-CUMYL-UBEA

C_tH_Me.NH.CO.NH.C_tH_tMe_3. [218°]. Formed from \$\psi\$-cumidine and \$p\$-tolyl cyanate (Goldschmidt a. Bardach, \$B. 25, 1361). Needles.
p-TOLYL-CYANAMIDE C_tH_Me.NH.CN.

[77°]. Formed by heating C,H,NH.CS.NH.OH.

or by the action of hydroxylamine on o-tolyl thiocarbimide (Tiemann, B. 22, 1940; Voltmer, B. 22, 881). Tables, v. sol. alcohol and KOHAq, m. sol. water.

DI-o-TOLYI-CYANAMIDE C₁₅H₁₄N₅ i.e. C(NC,H₁₅)₂. Carboditolylimide. (above 300°). Formed by heating the alkyl derivatives of dio-tolyl-thio-urea (Will a. Bielschowski, B. 15, 1317). Amorphous, v. sol. benzene. Converted by dilute HClAq into di-o-tolyl-urea.

Di.p-tolyl-oyanamide C₁₆H₁N₂SO or C(NC,H₁)₂, [60°]. (above 230°). Formed by the action of HgO on a benzene solution of ditolyl-thio-urea (Will, B. 14, 1488). Thick prisms, sol. benzene and ether. On heating with aniline it gives phenyl-di-tolyl-guanidine. Acids and alkalis convert it into di-p-tolyl-urea. On distillation it yields compounds melting at 49° to 60° and at 149° (Schall a. Paschkowetzky, 25 to 60° and at 143° (Schall a. Paschawezzy, B. 25, 2892). Phenyl-hydrazine at 190° forms C₃₆H₃₆N₆ [163°], which crystallises from alcohol in plates, and yields B'₄4HCl and B'₂2H₂PtCl, On heating with phenyl-hydrazine at 165° there is formed N₂PhH:C(NC, H₁)₂ [138°], crystallising in pale-red needles, yielding B'₂H₂PtCl₄ (Wessel, Ph. 21, 140°). $B.\ 21,\ 2274$). Tolylene-o-diamine at 140° forms $C_{zz}II_{zz}N$, [196°], which yields B'_z3HCl [143°]

(Dahm a. Gasiorowski, B. 19, 3057).
TOLYL CYANATE v. CYANIC ACID.

TOLYL CYANIDE v. Nitrile of TOLUIC ACID. TOLYL-CYANURIC ACID v. CYANIC ACIDS. TOLYLENE ALCOHOL v. DI-OXY-XYLENE TOLYLENE-DI-ALLYL-DI-THIO-DI-UREA

CaHaMe(NH.CS.NHCaHa)... [152°]. Formed from c-tolylene-o-diamine and oil of mustard (Lellmann, A. 228, 246). Needles (from alcohol), decomposed on fusing into tolylene-

thio-urea and di-allyl-thio-urea.
Tolylene-di-allyl-di-thio-di-urea [150°]. [1:3:4] $C_sH_3Mc(NH.CS.NHC_3H_s)_2$. [150°]. Formed from *i*-tolylene-o-diamine and oil of mustard (Lellmann, A. 221, 24). Decomposed by heat like the preceding isomeride; melting a second time at 210°-230°.

Tolylene-di-allyl-di-thio-di-urea [1:2:5] C, H, Me(NH.CS.NHC, H,)2. Formed from tolylene-p-diamine and allyl thiocarbimide (Lellmann a. Würthner, A. 228, 209). Plates or prisms, nearly insol. ether.

Telylene-di-allyl-di-thio-di-urea. Formed from tolylene m?-di-amine and allyl thiocarbimide. Prisms (from alcohol), insol. ether, v. sol. HOAc. Melts without decomposi-

TOLYLENE-DI-AMIDO-DI-ACETIC ETHER [1:2:4] C₀H₃M₆(NH.CH_{..}CO₂Et)₂. [70°]. Formed from tolylene-*m*-diamine and chloro-acetic ether (Zimmermann a. Knyrim, B. 16, 516). Needles

(from water).

c-TOLYLENE-o-DIAMINE C,H10N2 i.e.

Mol. w. 122. [62°]. $C_8H_4Me(NH_2)$, [1:2:3]. Mol. w. 122. [62°]. (255°). Formed from $C_8H_4Me(NH_2)(NO_2)$ [1:2:3] by reducing with Sn and HCl (Lellmann, A. 228, Reddish crystals, smelling of acetamide.

-B"2HCl. Sol. water, ppd. by HCl. c-Tolylene-m-diamine C₂H₃Me(NH₂)₂ [1:2:6]. [104°]. Formed by reduction of nitro-toluidine (0.2°) , or of liquid di-nitro-toluene (Ullmann, B. 17, 1960). Prisms, sol. hot water. Gives a brown colour with nitrous acid. CrO₃ and FeCl₄ give a brown colour .- B'HCl: crystals, v. e. sol.

i-Tolylene-m-diamine C.H.Me(NH2), [1:2:4]. 190°]. (c. 280°). Formed by reducing di-nitro-toluene (Hofmann, Pr. 11, 518) by reducing (44,2)-nitro-toludine (Nölting a. Collin, B. 17, 268), and by the action of SnCl, on amido-toluene-azo-amido-cresol (Graeff, A. 229, 348). Needles (from water), v. sol. alcohol, ether, and

hot water. Chloroformic ether, ClCO_Et, forms [1:2:4] C_H_Me(NH_)(NH_CO_Et) [91°], and chiefly C_dH_Me(NH_CO_Et). [137°] (Schiff, A. 268, 314). Phenyl-thio-carbimide yields CO_Et.NH_C_H_Me.NH_CS.NHPh [155°]. Hep-thio-carbimide with the control of tole aldehyde in the cold forms C, H, N, (C, H,), but when heated it yields an orange mass which forms a highly fluorescent solution (Schiff a. Vanni, A. 253,319). Benzoicaldehydeforms C.H. (N:CHPh). [122°-128°], while cinnamic aldehyde gives C,H,(NC,H,), [162°] (Schiff, A. 140, 98; 239, Cl.CO.CO.Et forms C.H.Me NH.CO [c. 260°] and [1:2:4] C.H.Me(NH.).NH.CO.CO.Et [170°], which yields an acctyl derivative (192° Phenyl-thiocarbimide forms the compound NHPh.CS.NH.C, H, Me.NH.CO.CO, Et [1555] and $C_{\rm e}H_{\rm s}Me < NH.CS > NPh [198°] (Schiff, A. 268,$ 307). Tolylene-m-diamine heated with citric acid at 125° forms C13H12N2O1, crystallising from acid at 125° forms C₁₁H₁₂N₂O₁, crystatusing from boiling alcohol in minute octahedra, decomposing at about 187° (Schneider, B. 21, 665). Acetyl-acetone at 100° forms a syrup, which when heated with H₂SO₄ yields C₁₂H₁₁N₂ [191°] (Combes, C. R. 108, 1252).—B"HCl.—B"2HCl.—B"2HBr.—B"H₂SO₄2aq; prisms. S. 5°6 at 19·5 (Bailstein a. Kuhlberg. A. 158, 351).— 19.5 (Beilstein a. Kuhlberg, A. 158, 351). -B"HPtCl_e.-B"2HCyS. Prisms (Lussy, B. 7, Prisms (Lussy, B. 7,

o.Acetyl derivative CoH₂Me(NHAc)NH₂[1:2:4]. [140]. Formed from CoH₂Me(NH₂)(NO₂) [107°] by acetylation and reduction (Wallach, A. 234, 350). Needles. -B'2H2PtCl6. • p-Acetyl derivative

C₀H₂Me(NH₂)(NHAc) [1:2:4]. [160°]. Formed white needles.

Di-acetyl derivative C.H., Mic(NIIAC),. [224°]. Got by boiling the base with Ac,O or HOAc (Roch, A. 153, 132; Tiemann, B. 3, 8; Ladenburg, B. 8, 1211). Needles.

Benzoyl derivative (24H,MC(NO),(NIIBz) [1224]. [142°]. Got by reducing C.H., Mc(NO),(NIIBz) (Bell, B. 7, 1505).

Di-benzoyl derivative [224°]. Tables, Di-acetyl derivative C, H3Me(NHAe)2.

Di-benzoyl derivative [224]. Tables, sl. sol. alcohol (Ruhemann, B. 14, 2056).

Thiobenzoyl derivative C₄H,Me(NH.)NH.CSPh. [1979] (Bernthsen a. Teophysics B. 14, 1760)

Trompetter, R. 11, 1760).

Phthalyl derivative

C.H.McONLO, C.H. [192°]. Formed from the base and phthalic anhydride (Bicdermann,

B. 10, 1161). Needles, split up by dilute HCl into phthalic acid and a base C₃, H₄, N₆O₄. Di-hthalyl derivative

C,H,Me(NC,H,O2)2. [233°]. Crystals, insol. water and alcohol.

s-Tolylene-m-diamine C.H.Me(NH2), [1:3:5].

33-10. Formed by reducing s-di-nitro toluene (Staedel, A. 217, 202). Syrup.—B"H₂SO₄.—B"H₂SO₄.—B"H₂SO₄.—Cydiamine C₂H₃Me(NH₂)₂ [1:2:5]. [64]. (274°). Formed by reducing (5,1,2). and (2,1,5)-nitro-toluidines (Beilstein a. Kuhlberg, A. 158, 352; Fileti a. Crosa, G. 18, 306), and C.H.Me.N.-C.H.Me.NH. [2:1:5] or [5:1:2]

(Nietzki, B. 10, 832, 1158). Plates (from benz-ene), v. sol. water, alcohol, and ether. Forms toluquinone on oxidation. FeCl, added to a solution of folylene-p-diamine hydrochloride mixed with o-toluidine gives an intense green colour.—B"2MCl. Plates.—B"H₂SO₄. S. 84 at 11.5°.

Di-acctyl derivative C.H.Me(NHAc), [220']. Prisms (from dilute alcohol) (Nietzki, B. 10, 1157; 12, 2237).

Tolylene-o-diamine C.H.Me(NH.), [1:3:4]. [88:5]. (2659). Formed by feducing (3 1,4)-mitro-y-toluidine (Beilstein a. Kuhlberg, A. 158, 351. Graeff, A. 224, 343). Plates, m. sol. cold water. Its aqueous solution quickly blackens when exposed to air. FeCl₃ forms by oxidation C11H15N2O, crystallising from wood spirit in brownish-red plates [247] (O. Fischer a. Sieder,

Reactions .- 1. Benzoic aldehyde at 140° forms $C_{.1}H_{18}N_{2}$ or $C_{.7}H_{6} \underset{N}{\overbrace{\hspace{1cm}N}} \overset{N(C,11,)}{N} \nearrow CPh$ [195-5°]

(Laderburg, B. 11, 591, 1656; Hinsberg, B. 19. 2026; 20, 1585), which yields B'MeI [209°], B'EtI [181°], and B'EtI, [125°], and is oxidised by KMnO, to an acid C21H16N2O2 [254°].-2. Furfuraldehyde, acting on the hydrochloride, forms C, H, N, O, [128:5], which yields B'McI [195:5], B'MeI, [128], and B'MeI, [109], 3. electic aldehyde (2 mols.) added to a cold solution of • the base (1 mol.) in glacial acetic acid forms

€,H_u < NEt >CMo (Hinsberg).-4. Anisic aldehyde, added to a dilute aqueous solution of tolylenc-o-diamine hydrochloride containing a little alcohol, forms C "H "N2O2 [1529-1569], which separates on addition of ammonia (L.). - 5. Salicylic aldehyde at 110° forms C2,11,2,N,O3 [106° 110°], and at 135° it forms azurine C, H, N,O, [250.5°], which exhibits blue fluorescence in alkaline solutions. -6. Glucose (2 mols.) added to an alcoholic solution of tolylene-o-diamine forms on account southern or only all sing in satiny needles, v. sol. water [c. 160], which gives a red colour with FcCl₃. Glucose converts tolylene-o-diwith reci₃. Chicose converts tolyiene-o-anamine accitate into amorphous 'glycodiamidotoluene' C₁₃H₁₈N₂O₃, m. sol. water (Hinsberg, B. 20, 495; Griess a. Harrow, B. 20, 2209). Glucoson C₆H₁₆O₆ acts in aqueous solution on phenylene-o-diamino, forming C₁₄H₁₆N₂O₄ [c. 186*] (E. Fischer, B. 22, 93). -7. Arabinose forms C₁₂H₁₆N₂O₄ [238*] (G. a. II.).—8. Acrolem in boiling agments solution forms tolylene-o-diaminosis of the control of the cont in boiling aqueous solution forms tolylene-o-di-amine acroson [185°] (Fischer a. Tafel, B. 22, 99)...9. Formic aldehyde forms C₁₈II₂₂N₄ [222°] (Fischer a. Wrezinski, B. 25, 2713)...10. Butyric

 C_1H_1 N N CPr [158°], and the compound $C_{15}H_{22}N_2$ or $C_7H_4 < N_2 < N_2 < N_3 > CFr$ (Hinsberg, B. 20, 1590).-11. Nitrous acid or, better, amyl 90, 1590).—11. Nitrous acid or, better, amyl nitrite acting on a salt of tolylese-c-diamine forms azimido-toluene C,H,N, [84°] (323°), which is v. sol. alcohol and hot toluene (Zincke a. Lawson, A. 240, 115; c/s Ladenburg, B. 9, 220; Bössneck, B. 19, 1759; Nölting a. Abt, B. 20, 3001). Azimido-toluene forms the salts B'₂H₂PtCl_s, NaC,H_sN_s, Hg(C,H_sN_s)₂ [235°], and AgC,H_sN_s. AcCl converts azimido-toluene into

aldchyde forms tolylene-butenyl-diamine

the (3)-acetyl derivative $C_rH_0 < N > NAc$ [94°], while the isomeric (a)-acetyl derivative C_rH_s $\stackrel{NA_0}{\sim}$ N [132°] is formed by the action of nitrous acid on the acetyl derivative of tolvlenep-diamine. -12. Boiling chloro-acetic ether forms exytoluquinoxaline dihydride and a compound Daytoluquinoxanne dinydride and a compound $C_{18}H_{18}N_{1}O_{2}$ (?) [147°], whence HNO forms a compound [248°] (Hinsberg, A. 237, 365).—13. Isalin yields $C_{18}H_{11}N_{8}$ [290°], sl. sol. alcohol (Hinsberg, A. 237, 344).—14. Equal mols, of tolylene-o-diamine and acetoacetic ether when gently warmed together eliminate H.O. and form a condonsation product $C_{18}H_{18}N_2O_2$ [82°]; if this is heated at 100°–120° acetic ether is evolved, and a tolyleneethenyl-o-diamine $C_6H_3Me < NH > C.CH_3$ is pro-

duced (Ladenburg a. Rügheimer, B. 12, 953; Witt, B. 19, 2977, 3299).—15. Chloro-aceto-acetic ether forms C,H_a(NH),CMc.CHCl.CO_sCt [110°], crystallising in needles (Autenrieth a. Hinsberg, B. 25, 606).—16. Oxydehydmaetic acid forms C₄H₄O₅(C₄H₃Me(NII₂)₂) [147°] (Feist, B. 25, 325).—17. o-Aldehydo-benzoic acid in hot

water forms C H₃Me \(\bigc \text{N}{NH} \) C.C₆H₄.CO₂H [258°]

(Bistrzycki, B. 23, 1043).—18. Di-oxy-quinons forms di-oxy-methyl-phenazine $C_{12}H_{10}N_{\nu}O_{2}$ [c. 265°], which yields a di-acetyl derivative [160°]. 19. Opianic acid gives, in alcoholic solution at 0°, the acid C₀H₂Me:(N₂H):C.C₀H₂(OMe)₂·CO₂H₃. orystallising in needles, decomposing at 234' (Bistrzycki, B. 24, 627).—20. Di-bromo-pyruvic acid (1 mol.) forms, on boiling, C, H, N:C.CHBr2

Salts.—B"2HCl. Needles (Hübner, A. 209, 364). - B"H₂SO₄1 aq. Scales. S. 9.29 at 19.5°.

-B"2H₂C₂O₄ aq (Hinsberg, B. 16, 1532). Compound with pyrocal pyrocatechin B"C.H.O. [78°]. Needles (from ligroin) (Merz, B. 19, 726).

Compound with cyanogen B"Cy2 aq. [c. 244°]. Formed by passing cyanogen into an alcoholic solution of the base (Bladin, B. 18, 666). Crystals, m. sol. alcohol and ether. Converted by heating with water into NII, and two isomeric compounds C,H,N,O, one melting at 290°, the other beginning to decompose at 230°-240°. B"Cy₂ yields the salts B"Cy₂HCl 1 luq, B"Cy₂2HCl, B"Cy₂H₂PtCl₂ 2aq, minute needles, (B"Cy₂)₂H₂PtCl₂2aq, and B"Cy₂H₂SO₄ aq : minute tables.

p-Acetyl derivative
C.H.Me(NH_{**})(NHAc) [1:3:4]. [131°]. Formed
by reducing C.H.Me(NO_{*})(NHAc) with iron plate dilute HOAc (Bossneck, B. 19, 1757), Plates (from water). Converted by nitrous acid-into acetyl-azimido-toluene. On distillation it yields tolylene-acetamidine $C_0H_3Me < N > CMe [203°]$

(Niementowski, B. 25, 861).

Di-acctyl derivative C_aH_aMe(NAcH), [216]. Formed by boiling the base with Ac₂O (Bistraycki, B. 23, 1878). This prisms (from water). Yields HOAc and tolylene-acctamidine

Yields tolylené-propenyl-amine manner (B.). [166°] on distillation.

Benzoyl derivative by reduction of C_aH₂Me(NO₂)(NHBz) with tin and HClAq (Hübner, A. 208, 314). Crystals, split up by distillation into water and tolylenebenzamidine [240°].

Di-benzoyl derivative C₄H₃Me(NHBz)₂. [264°]. Got by shaking tolylene-o-diamine with BzCl and NaOHAq (Hinsberg, A. 254, 255), by the action of Bz O on the diamine (Bistrzycki, B. 23, 1879; 24, 631), and by the action of Bz Ql on the benzoyl derivative (Hübner, A. 208, 314). Needles (from HOAc).

o-Chloro-benzoyl derivative C₄H₄Me(NH₂).NH.CO.C₅H₄Cl. [153°] (Schreib, B. 13, 467). Converted by benzoyl chloride into C6H3Me(NHBz).NH.CO.C4H4Cl [178°]. Di-cinnamyl derivative

C_eH₃Me(NH.CO.Č_xH₂)₂. [206°]. Formed from tolylene-o-diamine and cinnamic anhydride (B.). Groups of small needles (from dilute alcohol).

Groups of small needles (from dilute alconol).

Oxalyl derivative C.O.(NH.C.H.e.NH.).
[above 300°]. Obtained by the reduction of C.O.(NH.C.H.e.NO.). (Hinsberg, B. 15, 2691).

Small needles (from alcohol-ligroin). On fusion it splits up into Aq and C.H.A. [193°].—

Salts.—B"H.ZO.5aq. Colourlers needles.

Phthalyl derivatives.

The compounds C₈H_MeN₃H₂(C₈H₄O₂) [104°] and C₈H₄Me(NC₈H₄O₂)₂[272°] are known (Biedermann, B. 10, 1165; Ladenburg, B. 10, 1125).

Benzene-sulphonyl derivative C_aH₃Me(NH₂).NH.SO₂Ph. The hydrochloride, B'HCl, is formed by the action of benzene sulphonic chloride on tolylene-o-diamine in benz-ene (Bistrzycki a. Cybulski, B. 24, 633; cf. Lellmann, A. 221, 18).

Phenyl-acetyl derivative C.H.Me(NH.).NH.CO.CH.Ph. [195°]. Formed from tolylene-o-diamine and phenylacetyl chloride (B. a. C.). Needles, v. sol. hot alcohol.

Di-phenylacetyl derivative C₆H₄Me(NH.CO.CH₂Ph)₂. [176°]. Needles, insol. ether, v. sol. hot. alcohol.

References .- Bromo-, Chloro-, and Nitro-TOLY ENE-DIAMINE.

TOLYLENE-DIAMINE SULPHINIC ACID v. DI-AMIDO-TOLUENE SULPHINIC ACID.

TOLYLENE-O-DIAMINE SULPHONIC ACID C₆H₂Me(NH₂)₂.SO₃H [1:2:3:5]. Formed by reducing nitro-toluidine sulphonic acid (Nietzki a. Pollini, B. 23, 139). Needles. Forms azines with o-diketones.

c-Tolylene-m-diamine sulphonic acid C.H., N.SO. i.e. C.H.Mc(NH.), SO. H [1:2:6:4]. S. .07 at 14°. Formed from toluene p-sulphonic acid by nitration and reduction (Schwahert, A. 186, 360; Marckwald, A. 274, 349). Prisms, not melted at 280°.—BaA', 4aq.—HA'HCl 2aq.—HA'HBr 2aq.—HA'HNO, aq: needles, sl. sol. alcohol.—(HA'), H_SO, aq: plates.

Tolylene-m-diamine aulphonic acid (Bistraycki, B. 23, 1878). Thin prisms (from water). Vields HOAc and tolylene-acetamidine on distillation.

Di-propionyl derivative

CH,Me(NH,Jr,SO,H [1:2:4:5]. S. 1054 at 10°. GH,Me(NH,Jr,SO,H [1:2:4:5]. S. 1054 at 10°. GH,Me(NH,Jr,SO,H [1:2:4:5]. With SnCl, (Limpricht a. Foth, B. 18, 2185; A. 230, 309). Small prisms.—KA'aq.—CH,Me(NH,CO,Et). [133°]. Formed in like BA'. 5 aq.—HA'HCl aq.—HA'HBraq: prisms. Tolylene-m diamine sulphonic acid

C.H.Me(NH.),:SO₂H [1:2:4:x]. Formed from tolylene-m-diamine and fuming H₂SO₄ (Wiesinger, B. 7, 464). Small prisms.—NaA'4aq.—KA'aq.—MgA'₂5aq.—CaA'₂6\frac{1}{2}aq.—SrA'₂7aq.—BaA',6\frac{1}{2}aq.—MnA'₂3aq.

TOLYLENE - DIAMINE THIOSULPHONIC

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TOLYLENE-BENZAMIDINE v. BENZENYL-TOLYLENE-DIAMINE

TOLYLENE-BENZENYL-DIAMINE v. BEN-EENYL-TOLYLENE-DIAMINE

• p-TOLYLENE-BENZYL-DI-AMINE
[1:2:5] C₆H₃Me(NH₂).NHCH₂Ph. Got by reducing p-nitroso-benzyl-o-toluidine by alcoholic ammonium sulphide (Boeddinghaus, A. 263, 809).—B"2HCl. Needles, sl. sol. alcohol. TOLYLENE BLUE $C_{\rm h}H_{\rm 18}N_{\rm i}$ HCl. Formed by

mixing solutions of nitroso-dimethyl-aniline hydrochloride and (1,2,4)-tolylene-m-diamine (Witt, C. J. 35, 358; B. 12, 931). Prisms (containing aq) with coppery lustre, forming blue solutions in water and alcohol. Acids turn the solutions reddish-brown. Alkalis pp. the base as a tarry mass. Tin and HClAq reduce it to the leuco-base, which forms a deliquescent hydrochloride and crystalline (C1, H2, N1) HSnCl3. On boiling tolylene-blue with water for some time part is reduced to leuce-tolylene blue and part oxidised to tolylene red C15H16N1. Tolylene blue heated in aqueous solution containing HOAc for 12 hours at 40° forms tolylene violet $C_{11}H_{14}N_4$, characterised by an insoluble sulphate. Hydrated tolylene-violet $C_{11}H_{14}N_4$ aq is a scarlet powder which dissolves in alcohol and in ether, forming solutions with orange fluorescence.

Tolylene red $\begin{bmatrix} \mathbf{1_4^3} \end{bmatrix} C_e H_3 (\mathrm{NMe_2}) < \stackrel{N}{N} > C_e H_2 Me (\mathrm{NH_2}) \begin{bmatrix} \mathbf{3} \\ \mathbf{4} \\ \end{bmatrix} G : \mathbf{1} \end{bmatrix}$

(Bernthsen a. Schweitzer, A. 236, 332; Andresen, B. 19, 2217). Orange-red reedles (containing 4aq). Forms a red fluorescent solution in al-cohol. Its neutral salts are red, its acid salts are blue. By elimination of NH₂ by the diazoreaction it is converted into di-methyl-amidomethyl-phenazine.

Isomeride of tolylene red

 $\begin{bmatrix} \mathbf{1_4^3} \end{bmatrix} \mathbf{C_0 H_3 (\mathrm{NMc_2})} < \overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}\overset{\mathrm{N}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}\overset{\mathrm{N}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}\overset{\mathrm{N}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{N}}}{\overset{\mathrm{N}}}{\overset{N}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}}{\overset{\mathrm{N}}}{\overset{$

Formed from chloro-di-nitro-tolucue and dimethyl-p-phenylene-diamine and reduction of the product (Witt, B. 25, 3008). Coppery needles, sol. warm water. TOLYLENE-BUTENYL-DIAMINE v. Bu-

TENYL-TOLYLENE-DIAMINE.

TOLYLENE-DICARBAMIC ETHER v. i-TOLYLENE-m-DIAMINE.

C.H.N.O. TOLYLENE DICYANATE [1:2:4] C₆H₂Me(N:CO)₂. [94°]. Formed from tolylene m-diamine and COCl₂ (Snape, C. J. 49, Formed from 258). Needles, sol. ether. When heated with phenol at 130° it yields C₄H₃Me(NH.CO₂Ph)₂ [147.5°] crystallising in needles.

TOLYLENE-ETHENYL-DIAMINE C.H., N. i.e. C.H.Me NH CMe. [203°] (Niementowski, B. 25, 861). (3502) (Nölting a. Witt, B. 17, 81). Formed by boiling (1,3,4)-tolylene-o-diamine with HOAc (Ladenburg, B. 8, 67) by reducing the acetyl derivative of nitro-p-toludine (Hobrecker, B. 5, 920), and by adding aldehyde to a solution of tolylene-o-diamine in very dilute HOAc (Hinsberg, B. 20, 1589). Tables (from water). Forms with acctone and SO, the comwater). Forms with acetone and SU, the compound (C,H,0,N,C,II,0)SO, (Boessneck, B. 21, 1909).—B',H,PiCl,.—B'HNO,.

TOLYLENE ETHENYL ETHYL DIAMINE

CMa-CH.C.N.—SCALA [1669].

C₁₁H₁₄N₂ i.e. CMe:CH.C.N CMe. CH:CH.C.NEt Formed from [1:3:4] C_aH₃Me(NH₂).NHEt and Ac₂O (O. Fischer, B. 26, 200).

Tolylene-ethenyl-ethyl diamine

CMe:CH.C.NEt CMe. [93°]. Got by ethylation of tolylene-ethenyl-diamine (Hübner, A. 210, 351). Formed also by the action of aldehyde (2 mols.) on tolyene-o-diamine (1 mol.) (Hinsberg, B. 20, 1585) and by heating C₆H₄Me(NO₂)NEtAc with zinc-dust and HOAc (Niementowski, B. 20, 1884). Needles (containhing Saq). Combines with ethyl iodide, forming B'EtI and B'EtI, [111], which yield B'EtOH and B'Et_PtOl. Salts.—K'HI aq [148].—B'HNO, ng. [99°]. Milts at 95° when anhydrous—B'C,II,N,O,—Crystals, sl. sol. alcohol.

TOLYLENE-ETHYL-DIAMINE

CMe:CH.C.NH., CH :CH.C.NHEt [55°]. Formed by reduction of nitro-ethyl-p-toluidine (Gattermann, B. 18, 1184; Fischer, B. 26, 199). White plates, quickly blackened by light and air. Rotates on

Reactions .- 1. Bisulphide of carbon yields C_sH_sMe N_{Et} C.SH [139].-2. Ac_sO forms tolylene-ethenyl-ethyl-diamine [166°]. •3. Benzoic aldehyde yields $C_0H_3Me < N_{NEt} > CPh$; while o- and p-nitro- and o-oxy- benzoic aldehydes from corresponding bodies [170°], [176°], and [78°].

Salts. B'HCl. [176']. B',H,C,O,. [151']. Tolylene-ethyl-diamine C. H. Me (NHEt). NH, [1:2:5]. (264° cor.). Formed by reducing nitroso-ethyl-o-toluidine (Koch, A. 243, 307). Oil, v. sol. ether. - B"2HCl. [124°]. Crystals, insol. ether.

Tolylene-ethyl-diamine $O_0H_3Me(NH_2)(NHEt)$ [1:2:4]. $(282^{\circ}$ uncor.). Formed by reduction of nitro ethyl p-toluidine (Nölting a. Stricker, B. 19, 549). Oil. Gives

the reactions characteristic of m-diamines. Tolylene-di-ethyl-diamine C_aH₃Me(NHEt)₂[1:3:4]. (265° uncor.). (Hinsberg, A. 265, 191). Turns black in air.

Tolylene di-ethyl-diamine Tolyiene sliethyl-diamine
C₃H₃Me(NEt₂)(NH₂) [1:2:5]. (240° i.V.). Formed
Dyreducing nitro-di-cth yl-o-toluidine (Bernthsen,
B. 25, 3138). Oil. FcCl₃ slowly gives a purple
colour in an aqueous solution of the sulphate.
Na, 92O, and K, Cr₂O, added to its solution in
HOAc slowly ppt. SO₃H.S.C₃H₂Me(NEt₂)(NH₂)
[210°-215°].—B'H₂SO, Large colourless tables.
DI-TOLYLENE-ETHYLENE-TETRA-AMINE

DI-TOLYLENE-ETH I LEGIL-AMENE.

v. ETHYLENE-DI-TOLYLENE-TETHAL-AMENE.

TOLYLENE-DI-ETHYL-DI-THIO-DI-UREA

OHIOGNHEEL. [140°]. Got TOLYLENE-DI-ETHYL-DI-THIO-DI-UREA [1:3:4] McC₃H,(NH.CS.NHEI)₂ [149°]. Got from ethyl mustard oil (5·5 s.) and tolylene-di-amine (3 g.) in alcohol (15 c.c.) (Lellmann, A. 221, 23). V. sol. alcohol, more sol. HOAc, sl. sol. water. Decomposes when melted into tolylene-thio-urea, Me.C₂H₂(NH)₂CS, and CS(NHEt)_p.

(1.2.4)-Isomeride [225°]. Formed from tolyl- | ene-di-thio-di-urea and EtI at 105° (Lussy, B.

8, 668). Crystals.
TOLYLENE-DI-ETHYL-DI-UREA

[1:2:4]C,H₃Me(NH.CO.NHEt)₂, [175°]. Formed by heating tolylene-urea with Etlat 110° (Lussy, B. 8, 292). Crystals, v. sol. alcohol and ether. TOLYLENE HYDRATE v. PHENYL-BENZYL-

DI-TOLYLENE KETONE OXIDE

 $\begin{bmatrix} \mathbf{1_4^3} \end{bmatrix} \mathbf{C_6H_3Me} \overset{\mathbf{O}}{\underset{\mathbf{CQ}}{\mathbf{O}}} \mathbf{C_6H_3Me} \begin{bmatrix} 3 \\ 4 \end{bmatrix}. \quad [166^\circ].$ Formed by heating oxytoluic acid with Ac.O (Weber, B. 25, 1745). White flakes, sol. alcohol

l ether.

TOLYLENE MERCAPTAN C₆H₃Me(SH)₂
Dithiocresorcin. [37°]. (263°) T1:2:4]. Dithiocresorcin. [37°]. (Klason, B. 20, 355).

Di-toly ene mercaptan

HS.C₆H₃Me.C₆H₃Me.SH. [113°]. Formed from the diazo- compound of di-amido-o-ditolyl by combination with potassium xanthate at 75° and saponification of the resulting oil with alcoholic potash (Leuckart, J. pr. [2] 41, 214). Yellowish plates, v. sol. alcohol and ether. Methyl ether [118°]. Needles

TOLYLENE METHENYL-AMIDINE C.H.N.

i.e. $C_0H_0Me < NH > CH$. [114°]. Formed by boiling from (1,3,4)-tolylene-diamine with formic acid (Ladenburg, B. 10, 1123; O. Fischer, B. 22, 644). -B',H,PtCl_e. Yellow prisms.

TOLYLENE-METHENYL-DIAMINE v. METHENYL-TOLYLENE-DIAMINE and the preceding

body.
TOLYR METHENYL - METHYL - DIAMINE

 $C_0H_{10}N_2$ i.e. CMe:CH.C.N CH. (91°). Formed by heating C,H.(NHL).NIIMe with formic acid (O. Fischer, B. 26, 195).

Isomeride CH.C.NMe CH. (279°).

Formed by heating tolylene-methenyl-amidine with McI (O. Fischer, B. 22, 614). Formed also from (1,3,4)-tolylene-diamine and formic aldehyde (Fischer a. Wreszinski, B. 25, 2711). Oil.

—B'HI aq.—B'HCl. Prisms (from HClAq).

TOLYLENE-METHYL-DIAMINE

[1:3:4] C_aH₃Me(NH₂).NHMe. [44°]. Formed by reducing nitro-methyl-p-toluidine (Gattermann, B. 18, 1487; O. Fischer, B. 26, 194). Formed also by heating methyl-p-amido-toluene-agobenzene sulphonic acid with SnCl, and HClAq (Bamberger a. Wulz, B. 21, 2082). Four-sided tables.

Reactions .- 1. Acetic anhydride yields C,H. CNH CMe [1420]:-2. CS, reacts, forming.

C,H, NH CS [194°].-3. Benzvic aldehyde

· forms C,H₆<N_{NMe} CPh [127°], while o-nitroand o-oxy-benzoic aldehyde form corresponding

bodies [153°] and [180°]. Salts. -B'HCl. [175°-180°]. Plates (from [124°].-B'C,H,N,O, alcohol).-B'H2C2O4.

[164°].
Tolylene-di-methyl-diamine C.H.Me(NMe.)(NH.) [1:5:2]. [28°]. (270°). Formed by reducing nitroso-di-methyl-m-toluidine (Wurster a. Riedel, B. 12, 1801; 13,

126). Needles or prisms, v. sol. water, alcohol, 120). Needles of prisms, v. sol. water, alcor and ether. Yields toluquinone on oxidation.

Acetyl derivative [158].—

B'_2H_PtCl_4aq.

Tolylene-di-methyl-diamine

C₀H₃Me(NMe₂)(NH₂) [1:2:5]. [47°]. (240° i.V.). Formed by reducing nitro-di-methyl-o-toluidine (Bernthsen, B. 25, 3134). FeCl, gives an intense bluish-red colour in neutral solutions. Na S.O. and K2Cr2O, added to the acetic acid solution ppt. C₆H₂Me(NMe₂)(NH₂)S.SO₃H [c. 240°]. Salt.--B'2H SO, Needles, v. e. sol. water.

Tolylene-tetra-methyl-diamine C_oH₁Me(NMe₂)₂ [1:2:5]. (c. 2:0°). Formed by heating the preceding body with MeOII and HCl at 180° (W. a. R.). Liquid. Coloured blue in aqueous solution by FeCl₃.

Methylo-iodide B'MeI. [160°]. Needles.

Tolylene-tetra-methyl-diamine C_aH₃Me(NMe)₂[1:3:4]. (226°) at 717 mm. Got by methylation (Niementowski, B. 20, 1888). Liquid, v. sl. sol. water. FcCl₃ at 40° to 50° gives a reddish-brown colour. HNO₃ added to its solution in H.SO, gives a red colouration.-B'.H₂PtCl_g.-B'HHgCl₃.-B'C_gH₃N₃O₇. Yello tables.

Reference .-- NITRO - TOLYLENE - TETRA-METHYL-

TOLYLENE-METHYL-ETHENYL-AMIDINE

CMe:CH.C.N CH :CH.C.NMe SCMe. [142°]. C₁₀H₁₂N₂ i.e. Formed, together with $C_{10}H_{12}N_2O$ [163°], which . crystallises with 2aq, by reducing the compound $C_6H_3Me(NO_2).NMeAc$ (Niementowski, B. 20, C₃H₃Me(NO₂).NMeac (Nicinenowski, B. 25, 1878), and by acting on tolylene-methyldiamine with Ac₂O (O. Fischer, B. 26, 196). Needles (from hot water). B'₂H₂PtCl₃ (dried at 1974). 100°), [234°-244°],—B'HCl \(\frac{1}{2}aq.\)—B'MeI. [221°].
—B'MeOH. [115°-135°].

TOLYLENE TETRA-METHYL DI-PYRROLE $\begin{array}{llll} \textbf{TETRACARBOXYLIC} & \textbf{ACID} & \textbf{C}_{zz}\textbf{H}_{zz}\textbf{N}_z\textbf{O}, & \textit{i.e.} \\ \textbf{[1:2:4]C}_{o}\textbf{H}_{z}\textbf{Me} \big(\textbf{N} < \begin{matrix} \textbf{CMe}: \textbf{C}, \textbf{CO}_{z}\textbf{H} \\ \textbf{CMe}: \textbf{C}, \textbf{CO}_{z}\textbf{H} \end{matrix} \big), & \textbf{[248°]}. & \textbf{SL}. \end{array}$ sol, hot alcohol and ether.

Ethyl other Et, A'v. Formed by heating di-acetyl-succinic ether with tolylene-m-diamine and HOAc at 150° (Knorr, A. 236, 314). Oil. TOLYLENE-METHYL-THIO-UREA

CMe:CH.C.NH >CS. [194°]. Formed from CH:CH.C.NMe C.H. (NH.) (NHMe) and CS₂ (Fischer, B. 26, 196). Needles (from alcohol).

TOLYLENE-DI-OXAMIC ACID C₁₁H₁₀N₂O₃i.c.

C, H, Me(NH.CO.CO, H), [1:2:4]. Formed, together with the amide, by the action of alcoholic NH3 on the ether. Crystalline. Very sweet. Decomposed by warm KOHAq into oxalic acid and tolylenediamine. - Ag A". - PbA". - BaA" 2aq.

Di. amide C, H, Me(NH.CO.CONH.), [1:2:4]. Cormed from the other and alcoholic ammonia (Schiff, A. 268, 3 3). White powder, m. sol. alcohol.

Ethyl ether [1:2:4] C.H.Me(NH.CO.CO.Et). [130°]. Formed by boiling C.H.Me(NH.).NH.CO.CO.Et with alcohol and oxalic ether (Schiff a. dvanni, A. 268, 340). Small needles (from ether).

C.H.Me.CO.CO.NH. [1:2] [210°]. Formed from C.H.Me(NH.).NH.CO.CO.NH. by boiling

with alcohol and oxalic ether (Schiff, A. 268, |

Amide ether

 ${}^{*}C_{\bullet}H_{\bullet}Me < NH.CO.CO.H_{2}[1_{4}^{2}]$ [c. 220°]. by fusing C,H,Me(NH,).NH.CO.CO.Et with ox. amic ether.

TOLYLENE-OXAMIDE C.H.3Mc NH>C.O.

[c. 260°]. Formed from (1,2,4)-tolylene-diamine and chloro-glyoxylic ether, and also by heating tolylone-diamine oxalate to 160° (Schiff a. Vanni, A. 268, 312).

TOLYLENE-PENTENYL-DIAMINE

 $\begin{bmatrix} 1_4^3 \end{bmatrix} C_6 H_3 M_9 < N_{\text{H}} > C.C_4 H_9. \quad [116^\circ]. \quad \text{Formed}$ by reducing the valeryl derivative of nitro-p-toluidine (Friederici, B.~11,~1974; Hübner, A.~209, Prisms (from ligroin), v. c. sol. alcohol.

TOLYLENE - DI - PHENYL - DI - AMIDO-METHYLENE-DIAMINE C2, H20N, i.c.

C_sH_sMe<NH>C(NHPh)₂. [161°]. Formed from C(NPh), and (1,3,4)-tolylene-diamine at 130°. 149° (Dahm a. Gasiorowski, B. 19, 3057). Needles (from benzene), v. sol. alcohol. -B' 3HCl. [171]. B'H.SO. Plates, v. sol. water and alcohol. TOLYLENE-PROPENYL-DIAMINE

 $C_aH_aMe < NH > CEt.$ [166*]. Formed by distilling the dipropionyl derivative of tolylene-odiamine (Bistrzycki, B. 23, 1879). Needles, m. sol. water, almost insol. ligroïn.

TOLYLENE RED v. TOLYLENE BLUE,

DI-TOLYLENE, DISULPHIDE

CMe:CH.C.S.C.CH:CH [116°]. Formed by the action of heat at 200°-250° on tolylene liazosulphide C_eH₃Me
N [43], obtained from cthenyl - amido - tolyl mercaptan and HNO, (Jacobsen a. Ney, B. 22, 911). Conc. H₂SO₄ gives an intense blue colour.

TOLYLENE - DI - THIO - DI - CARBAMIC ETHER [1:3:4] C, H, Me(N:C(SH).OEt), [120]. Formed by boiling toly!ene-di-thiocarbimide with alcohol (Billeter a. Steiner, B. 20, 230). Plates (from benzene). Yields a yellowish-white silver

TOLYLENE - DI - THIOCARBIMIDE [1:2:4] C.H.Mo(N.CS), [56°], (c. 300°). Formed from tolylene-m-diamine and CSCl., and also by heating tolylene-di-thio-di-urea with conc. HClAq (Billeter a. Steiner, B. 18, 3292; 20, 230). Needles. Converted by NH, Aq into tolylene-dithio-di-urea [206], by aniline into disphenyltolylene-di-thio-di-urea [168]. Copper at 250% produces CaH, MeCy2 [141°

Tolylene-di-thiocarbimide [1:3:4]

C_sH₂Me(N.CS)₂. [42°]. Formed from an aqueous solution of tolylene-o-diamine hydrochloride and CSCl, in CHCl, (B. a. S.). Plates. Converted by HCl at 200° into o-tolylene-thio-urea.

TOLYLENE-DI-THIO-DIGIN COLLIC ACID

C.H.Me(S.CH., CO.H.). [152°]. Formed from thio-orein C.H., Me(S.H.). [35°], chloro-acetic acid, and NaOHAq (Gabriel, B. 12, 1640). Needles, m. sol. hot Aq.

TOLYLENE THIO-URBA $C_aH_aMe < NH > CS$. Formed from C.H.Me(NH,HCl), [1:2:3] and excess of NH SCN by boiling with water, evaporating, and heating to 120° (Lellmann, A. 228, 245). Small red crystals (from alcohol). Does not melt below 326°; may be sublimed. Insol. water, sl. sol. alcohol, dissolved by warm NaOH; re-ppd. by HCl. When boiled with lead acetate and excess of NaOH, no PbS is formed.

O.H.Me</br>
NH>OS. Tolylene - thio - urea [281]. Formed by heating (1,3,4)-tolylene-o-diamine sulphocyanide at 130° (Lellmann, A. 221, 10]. Formed also by the action of alcoholic NH, on o-tolylene di-thiocarbin'de (Billeter a. Steiner, B. 20, 231). Silvery plates, sol. alcohol, HOAe, and cold NaOHAq, sl. sol. water and

m-Tolylene thio - urea C.H.Me NH CS.

[119°]. Formed from (1,2,1) tolyfone-diamine and alcoholic CS₂ (Lussy, B. 8, 293). Crystalline powder, v. c. sol. alcohol.

m-Tolylene-di-thio di urea [1:2:4] G.H.Mc(N.H.O.S.N.H.)... [218°] (L.); [200°] (B. a. S.). Formed by heating tolyleno-m-diamine sulphocyanide (Lussy, B. 7, 1265; Rednamine Saphovyamide (lassy, B. 1, 1205; Gebhardt, B. 17, 3016; Baleter a. Steiner, B. 18, 3293; 20, 228). Crystalling powder, insol. water and ether, nearly insol. alcohol, m. sol. hot

TOLYLENE-TOLENYL-AMIDINE C1.H1.N2 i.e. C₀H₃Me NH C.C₀H₄Me. Formed by reducing [1:4] C.H.Me.CO.NH.C.H.(NO.)Me [4:3:1] (Hübber, A. 210, 331). Needles, sl. sol. water. — B'HCl.—B'HNO., -B'HNO., Crystels, sl. sol.

Water.
TOLYLENE - DI - p - TOLYL - DI - AMIDO -METHYLENE DIAMINE Callan, i.e.

 $C_{\nu}H_{\nu}Me < \frac{NH}{NH} > C(NH_{\nu}C_{\nu}H_{\nu}Me)_{2}$

Formed by heating C(NC₈H,Me), with (1,3,4)-tolylene-diamine (Dahm a. Gasiorowski, B. 10, 3059). Needles (from alcohol).—B'₂3HCl. Deliquescent needles, v. sol. water.

TOLYLENE TOLYL-DIAMINE C, H, N, i.e. [1:3:4] C. H. Mc(NH.) NHC, H. Mc [1:4]. Amido-di-p-tolyl-amine. [109]. Formed by reducing nitro-di-p-tolylamine (O. Fischer, B. 23, 8798; 26, 187). Prisms (from ligroin), turning brownishred in air. H.SO, forms a blue solution changing to green. FeCl, forms C.H.,N,O [188°] crystal-sing in red plates, yielding B',H.PtCl, Boiling with acetic anhydride and sodium acetate with acctic anhydride and sodium acctate produces $C,H_c < N(\frac{C,H_s}{N}) > CMe$ [95°], which forms $H_s^2H_sPtCl_c$. Benzoic aldehyde $C,H_c < N(\frac{C,H_s}{NH}) > CHPh$ [156°], which yields $(C_{sH},N_{sH}$

o Satts. -B'H.C.O., Nearly insol. cold Aq.— B'C₆H,N₃O. Brownish-red crystals. Acetyl derivative [126]. Prisms.

Tolylene-p-tolyl-diamine [1:4:3] C_0H_2 Me(NH $_2$).NHO, H_4 Me [1:4]. Formed from toluene-azo-toluene or s-di-p-tolylhydrazine (hydrazo-toluene) in alcohola solution by the action of SnCl. and HCl (Täuber, B. 25, 1022; cf. Melms, B. 8, 554; Goldschmidt, B. 11, 1626). Plates, v. e. sol. alcohol. NaNO, colours its solution in H₂SO, deep blue (?). Benzoic aldehyde reacts, forming

 $C_{1}H_{\bullet} < \stackrel{N(C_{7}H_{7})}{N} \geqslant OPh \ [165^{\circ}] \ (\textit{cf. Lellmann}, \ \textit{B.}$ 15, 832). Benzil in alcohol and HCl forms C₂,H₂,N₂O [173°]. Ethyl nitrite and H₂SO₄ added to its alcoholic solution form the azimide $C_1H_1 < N(C_1H_1) > N$ [93°]. On oxidation together with p-toluidine it forms the ditoluide of amidotoluquinone (Green, C. J. 63, 1408).

toluquinone (Green, C. J. 63, 1408).

Tolylene-di-p-tolyl-diamine
[1:2:5] C₃H₂Mc(NHC,H₁).

[113°]. Formed by heating hydrotoluquinone (40 g.) with p-toluidine (160 g.) and ZnCl₂ (80 g) to 200°-280° for 5 hours (Green, C. J. 63, 1408). Plates, sol. HOAC, insol.

TOLYLENE-p-TOLYL-GUANIDINE

C.H.Me NH C:NC,H, [198°]. Formed from tolylene-o-diamine and C(NC,H,)2 (Keller, B. 24, 2518). Prisms (from alcohol), or tables (from benzene). Phenyl cyanate forms the compound C,H,N,CO,N,H,CO,NPh [233°], crystallising from hot alcohol in needles .- B'HC! .-B'2H2PtCl6 - B'2H2SO, 5aq. Needles, sl. sol. cold

Acetyl derivative C,H, < NAC > C:NC,H,.

[149°]. Needles, v. sol. alcohol.
Di-tenzeyl derivative [201°]. Needles. Nitrosamine C,H,:N,H(NO):C:NC,H, [c.

Nttrosamine C,H_a;N₂H(NO):C:NC,H₁, [c. 140°]. Decomposed on fusion.

TOLYLENE,p.TOLYL-THIO-UREA
CH:CH.C,N(C,H₁) CS. [270°]. Formed from CMe:CH.C,NH diamine and CS₂ in alcohol (Fischer a. Sieder, B. 23, 3799). Prisms, insol. water, sl. sol. ligroin. Conc. H₂SO₁ forms a green solution green solution.

TOLYLENE-UREA C,H,N,O i.e.

[1:\frac{3}{4}]C_0H_3Me<\frac{NH}{NH}>CO. [292°]. Formed by heating tolylene-o-diamine with urea and got also by the action of HClAq at 140° on $C_eH_sMo < NH > C.OEt [163°]$, which is formed by the action of HN:C(OEt)2 on tolylene-o-diamine hydrochloride (Sandmeyer, B. 19, 2051). Formed also by heating C,H, (NH,).NH.CO.NPh, (Lellmann a. Bonhöffer, B. 20, 2124) or the compound C₁H₆(NH₂).NH.CO.NHPh (Leuckart, J. pr. [2] 41, 324, who states that it melts above 300°); and by heating tolylene-o-diamine in benzene with COCl, in toluene in sealed tubes at 100° (Hartmann, B. 23, 1048). Needles, st. sol. hot water.—B'HCl: prisms.
TOLYLENE - DI - URE:

TOLYLENE - DI - UREL C. H. N.O. i.e. [1:8:4] C. H. Me(NH.CO.NH.). [282°]. Got from tolylene-diamine hydrochloride and potassium cyanate in aqueous solution (Lellmann, A. 221, 14). Needles, sl. sol. water and chloroform,

sol. alcohol and hot conc. HCl; v. sol. HOAc.
Tolylene-di-urea C,H,,N,O, i.e.
[1:2:4] C,H,Me(NH-CO,NH₂)₂. [220°]. Formed from tolylene-m-diamine sulphate and KCyO (Strauss, A. 148, 157). Formed also from tolylene cyanate and ammonia (Lussy, B. 8, 291). Scales, sl. sol. alcohol and hot water.—B"2HCl:

TOLYLENE-VIOLET v. Tolylene blue. s-DI-TOLYL-ETHANE

C.H.Me.CH.CH.O.H.Me. (296°). Formed from

O.H.Me.CH.Cl and sodium (Vollrath, Z. 1866, 489). Oil.

u-Di-p-tolyl-ethane CH₃.CH(C₆H₄Me)₂. (295°). S.G. ²⁰ '974. Formed by shaking paraldehyde with toluene and H₂SO₄ at 0° (O. Fischer, B. 7, 1191). Formed also by heating di-a-tolyl-propionic acid with lime (Haiss, B. 15, 1476) and by the action of ethylidene chloride and AlCl, on toluene (Anschütz, B. 18, 664; A. 235, 315). Oil. Yields toluyl-benzoic acid and di-tolyl ketone on oxidation.

s-mp-Di-tolyl-ethane C2H4(C,H,)2. 300°). Formed from ethylene bromide, toluene, and AlCl₃ (Friedel a. Balsonn, Bl. [2] 35, 52; A. Ch. [6] 1, 487). Yields isophthalic and Formed from ethylene bromide, toluene, . terephthalic acids on oxidation.

References .- AMIDO-, CHLORO-, TRI-CHLORO-

DI-NITRO-, and OXY-TOLYL-, ETHANES.

TOLYL ETHER v. DI-TOLYL OXIDE. o-TOLYL-ETHYL ALCOHOL. hydride CH₂ CH₂ CH₂ CH.CHMe.OH. (195°-200°). Formed, together with the tetrahydride CH₂ CH₂.CMe C.CHMe.OH (142° at 50 mm.) by reducing CaH, Me.CO.CH, in moist ethereal solution by sodium (Kipping a. Perkin, jun., C. J. 57, 22). Oil. Yields an acetyl derivative (201°-208°).

p - TOLYL - ETHYL - m : AMIDO - PHENOL. Ethyl derivative C,H,NEt.C₄H₄,OEt. Formed from C,H,NH.C₆H₄,OH, potash, and Etl (Hatschek a. Zegn, J. pr. [2] 33, 217). Oil.

p-Tolyl-ethyl-p-amido-phenol. Ethyl deri-vative C,,H₂,NO i.e. C,H₂,NEt.C,H₄,OEt. (c. 340°). From C,H₂,NH.C₆H₄,OH, potash, and EtI (H. a. Z.). Oil.

TOLYL-ETHYL-AMINE v. ETHYL-TOLUIDINE. Di-tolyl-ethyl-amine (C,H,Me),NEt. (255°-260° at 20 mm.). Formed by heating di-p-tolyl-amine with EtOH and HCl at 250°-280° (Girard, Bl. [2] 21, 120). Oil.

o-TOLYL ETHYL CARBONATE C10H12O3 i.e. [1:2] C_oH₄Me.O.CO.OEt. (236°). Formed from sodium o-cresol and ClCO₂Et (Bender, B.13,700).

m. Tolyl ethyl carbonate. (246°). Formed in like manner from m-crosol. Oil.

p. Tolyl ethyl carbonate. (245°). Oil. By

long heating at 300° it yields di-p-tolyl carbonate and di-ethyl carbonate (Bender, B. 19, 2268).

DI - p - TOLYL - ETHYLENE C₁₆H₁₀ i.e. C₄H_Me.CH:CH.C₆H_Me. Di.methyl-stilbene. [179°]. (above 300°). Formed by distilling (C₆H₄Me)₂CH.CCl₃ with zinc-dust (Goldschmiedt a, Hepp, B. 6, 1504; Elbs a. Förster, J. pr. [2] 30, 30(0), and by besting distably furgers. Co. 39, 300), and by heating dip-tolyl fumarate, Cobeing evolved (Anschütz, B. 18, 1948). Plates, v. sol. CHCl₂. Yields a dibromide [204°]

u-Di-tolyl-ethylene CH₂:C(C₆H₁Me)₂ (305°). Formed by the action of alcoholic potash on CH₂Cl.CH(C,H₁)₂ (Hepp, B. 7, 1413). Oil Yields di-tolyl-ketrne [94°] on oxidation.

Tetra-tolyl-ethylene $C_{10}H_{10}$ i.e. $(C,H_{1})_2C:C(C,H_{2})_2$ [215°]. A product of the action of chloroform and Al(I₃ on toluene (Schwarz, B. 14, 1529). Plates, with greenishyellow fluorescence, sol. benzene.

References .- Bromo- and Di-chloro- Tolti-

ETHYLENE.

A-TOLYL-ETHYLENE-DIAMINE

C,H,NH.C,H,NH, (c. 267°). Formed from c-tolylamido-ethyl-phthalimide and HCl (Newman, B. 24, 2194). Sol. water and alcohol.— B"2HCl. [168°-178°].—B"2C₄H₄N₃O₄. [148°]. Green needles.

Di-benzoyl derivative [164.5°]. Needles.

Di-bensoyl derivative [164:57]. Needles.
p-Tolyl-ethylene-diamine. Formed in like
manner (N.). Liquid.—B"2HCl. [218].—
B"H.PtCl., Yellowish plates.
Di-acetyl derivative [107°]. Needles.
Di-bensoyl derivative [161°]. Cubes.
Di-o-tolyl-ethylene-diamine C_kH₂₃N₂.i.c.
C.H.NH.CH._NHC.H., [71°]. 48. 3 at 100°.
S. (cold alcohol) 9. S. (ether) 14. Formed by
the action of o-toluidine on ethylene bromide in presence of Na₂CO₂ (Bischoff, B. 23, 1982, 2031; 25, 3257; cf. Mauthner a. Suida, M. 7, 230; Colson, Bl. [2] 48, 799). Plates (from ligroin), v. sol. alcohol. Yields indole on leating with zine-dust. CH₂Cl.CO₂H and NaOAe from ditolyl-pyrazine hexahydride [1514]. -B"2HCL.-B"H_PtCl_a.—B"H_SO, (dried at 100)).—B'2HBr. [222°]. S. 3 at 100°.

Acetyl derivative C2H4(NAc.C,H2).

[153°].

Bromo-acetyl derivative C2H4(NC,H,.CO.CH2Br)2. [205]. Sl. sol. cold HOAc and ligroin.

Bromo-propiogyl derivative C₂₂H₂₈N₂Br₂O₂. [181°].
Bromo-n-butyryl derivative

 $(C_{2i}H_{30}N_2Br_2O_2)C_0H_a$ (from benzene). [190°].

Bromo-isobutyryl derivatives C,H,NH.C,H,NC,H,CÖ.CBrMe, [137°]

C₂₁H₃₀N₂Br₂O₂ [173°]. Di-p-tolyl-ethylene-diamine [97.5°]. Formed by heating p-toluidine with ethylene browide at 150° (Gretillat, M. S. [3] 3, 383; Bischoff, B. 25, 3260). Crystals, v. e. sol. alcohol. - Hydrobromide [255°].

Acetyl derivative C,H,(NAc.C,H,),

[139°].

Bromo-acetyl derivative C. H. N. Br. O. [196°].

Bromo-propionyl derivative. [182°]. Bromo-n-butyryl derivative C₂₁H₃₀N₂Br₂O₂. [125°]. Bromo-isobutyryl derivative

C₂₄H₃₀N₂Br₂O₂. [175°]. Di-o-tolyl-di-ethylene-diamine [171°]. Formed, together with die-tolyl-ethylene-diamine, by heating o-toluidine with C₂H₄Br₂ (M. a. S.). Needles, sl. sol. alcohol. Forms indole when distilled with zinc-dust.

rorms indoie when distilled with zinc-dust.

Di-p-tolyl-di-ethylene-diamine [190°].

(360°). Formed by heating C,H,Cl.OH with p-toluidine at 220° (Wurtz, A. Suppl. 7, 94°, Demole, A. 173, 138). Prisms, v. sl. sol. alcohol. B'H,PtCl.

Tri-p-tolyl-tri-ethylene-triamine

N₂(C,H),(C,H), (C,H), (E,H). Formed by heating p-toluidine with C,H,Br₂ (G.). Needles, v. alcohol. Is perhaps identical with the preceding body. Its hydrochloride melts at 189°.

Reference.—NITRO-DI-TOLYL-ETHYLENE-DI-

Reference .- NITRO - DI - TOLYL - ETHYLENE - DI-

p-TOLYL ETHYLENE ETHYL DIONIDE C.H.Me.O.CH.CH.OEt. (244°). Formed from O.H.O.C.H.Br and alcoholic potash (Schreiber, B. 24, 195).

DI-p-TOLYL ETHYLENE DIKETONE

C₁₆H₁₆O₂ i.s. C₄H₄(CO.O₄H₄Me)_p Di-toluyl-ethane. [159°]. Formed by the action of suc-cinyl chloridg and AlCl, on toluene (Hollemann, R. T. C. 6, 70; Claus, B. 20, 1877). Needlos, v. sl. sol. cold alcohol, insql. alkalia. AcCl converts it into di-p-tolyl-furfurane C18H10 [1645]. Ammonium acetate and HOAc on boiling form di-p-toly]-pyrrolo [197°]. P₂S, forms di-p-tolyl-thiophene [171°]. DI-p-TOLYL-ETHYLENE-DI-METHYL-DI-

AMINE C_{1.}H_{1,}N₂ .i.c. C_.H₁(NMe.C_.H₁Me). [80°]. Formed by boiling its di-methylo-di-bromide with NH₃Aq (Hübner, A. 224, 337). Tables or prisms (from filcohol), v. sl. sol. water.— B"H₂HgCl₄. [190°]. - B"H₂PtCl₆. Orange-

yellow powder.

Methylo-iodide B"Mel. Noedles. De-

composed at 100°. M. sol. hot water.

Methylo-bromide B"2MeBr. Formed by heating di-methyl-p-toluidine with C₂H₁Br₂ at 105 tor some days. Yields B"Me₂H₂Cl₆ [159 - 162], B'Me₂Sn**C**|_a, B'Me₂PtCl_a, and B"45, HMe₂N₂O₃, [197], which crystallises from classical. alcohol.

TOLYL ETHYLENE OXIDE v. ETHYLENE

ETHER OF CRESOL.
DI-p-TOLYL ETHYLENE DISULPHONE (C.H. SC₂)₂C.H₁, [201°]. Made by boiling sodium (Otto, J. pr. [2] 30, 351; 40, 534). Got also by boiling the same salt with CH₃CCl₂CO₂Na. Needles or plates. Dilute KOHAq converts it into believe sulphinic acid and C.H., SO, C.H., OH [55°], which yields C.H., SO, C.H. (OI [79], C.H., SO, C.H., [100°], C.H., SO, C.H., [100°], C.H., SO, C.H., [100°], C.H., SO, C.H., [100°], Ammonia forms (C.H., SO, C.H., S.H., chloride (201°

DI-p-TOLYL-ETHYLENE-UREA

CH_N(C,H) CH_N(C,H) CO. [228"]. Formed from dip-tolyl-ethylene-diamine and COCL (Michlet a. Keller, B. 14, 2181). Needles.

Relier, B. 14, 2181). Needles.
p. TOLYL. DI. ETHYL. PHOSPHINE
C.H., PEt. (210°). Formed from C.H., PCl.
and ZnEt. (Czimatis, B. 15, 2016). Liquid.—
B'Mel. [137°].—B'.Me., PtCl., Yellow plates.
p. TOLYL ETHYL SULPHONE
C.H., SO., C., H., [56°]. Formed by oxidation of
C.H., SEt and by the action of EtBr on sodium

column p-sulphinate (Otto, B. 13, 1276; 18, 161). Formed also by warming the acid C.H. SO. CHMC.CO.H with KOHAq. Trimetric plates; qb:c=526:1:721. Sol. alcohol and

p-TOLYL ETHYL SULPHONE a-CARB-OXYLIC ACID C.H., SO., CHMe.CO., H. Tolyl-sulphonogropionic acid. [37°]. Formed by heating G.H., SO., ha with CHI., CHBr.CO., Et and alcohol at 150° and baponifying the product (Otto, J. pr. [2] 40, 555). Grystals (from alco-hol), converted by Cl into CH., CHCl. SO., C.H., TOLYL ETHYL DISULPHOXIDE v. Ethyl

her of Tolurne thiosulphonic acid.

TOLYL ETHYL THIOBIURET C, E, N, S, [134°]. Formed from tolyl-thiobiuret, alcohol, aqueous NH₂, and EtI (Tursini, B. 17, 585). Needles (from alcohol).

o-TOLYL-ETHYL-THIOSEMICARBAZIDE

C.H.NH.NH.CS.NHEt. [180°]. Formed o-tolyl-

hydrazine and an alcoholic solution of ethylthiocarbimide (Dixon, C. J. 57, 262). Needles, v. sl. sol. cold water. CuSO₄ colours its alcoholic solution deep blue.
TOLYL ETHYL DI-THIO-CARBONATES

CS(OEt).S.C.H.Me. The o-, m-, and p- compounds formed by the action of potassium xanthate on cold solutions of o., m., and p-diazotoluene chloride are oils (Leuckart, J. pr. [2] 41, 188). They are converted into tolyl mercaptans by boiling with alcoholic potash.
o-TOLYL-ETHYL-THIO-UREA

CS(NHEt).NHC,H,Me. [84°]. Formed from o-tolyl-thiocarbimide and ethylamine (Staats, B. 13, 136). Prisms, insol. water, sol. alcohol and other.

p-Tolyl-ethyl-thio-urea [96°]. Formed in like manner (Weith, B. 8, 1530). Tables, v. sol. hot water.

o-Tolyl-di-ethyl-thio-urea CS(NEt.).NHC,II,. [102°]. Formed from o-tolyl-thiocarbimide and NHEt, (Gebhardt, B. 17, 3038). Needles or

p-TOLYL-ETHYL-TOLUTRIAZINE DISIY. DRIDE C₁₇H₁₀N₂ i.e. C₆H₃Me $< \stackrel{N.CHEt}{\dot{N}.N.C_6H,Me}$

[168°]. Formed by heating toluene-azo-toluidine with propionic addelyde at 140° (Goldschmidt a. Poltzer, B. 24, 1009). Needles (from hot benzene).— B'HC. [96°]. — Platinochloride [221°]. Sinall yellow needles.

p-TOLYL-ETHYL-UREA

 $C_{10}H_{14}N_2O$ NHC,H,.CO.NHEt. Formed from p-toluidine and ethyl cyanate (Sell, A. 126, 162). Crystals,

insol. water, v. o. sol. alcohol.

DIo-TOLUZ-FORMAMIDINE C_{1.5}H₁₀N_{.2} i.c.,
NHC₂H_{.7}CH:NC₂H_{.7} [151°]. Formed by boiling the formyl derivative of o-toluidine for a long time, or by heating it with o-toluidine and PCl_s (Ladenburg, B. 10, 1260). Formed also by distilling the thioformyl derivative of o-toluidine in vacuo (Senier, C. J. 47, 762). Prisms (from alconol), insol. dilute NaOIHAq. Yields crystal-line C₁₆C₁₆N₂Br₂.—B'₂H₂PtCl_n.

Di-m-tolyl-formamidine NHC,H,.CH:NC,H,.

[123°]. Formed by boiling m-toluidine with for-[123]. Formed by boiling m-tolundine with formic acid (Niementowski, B. 20, 1893). Needles or plates, in.ol. water. Br in CS, yields crystalline NHC, H, CHBr. NBrC, H,...—B'HCl. [214°].

—B'₂H, PtCl_a.—B'C_aH, N₁O_r. Yellow needles.

Di-p,tolyl-formamidine [141°]. Formed by distilling C,H,NH. CHS in vacuo (Senier, C. J. 47, 767; B. 18, 2296). Prisms.—B'_2H, PtCl_a.

Di-p-TOLYL-FURFURANE C₁₈H₁₀O i.e.

CH:CÔC.H.).

CH:C(C,H.)>O. [164°]. Formed by the action of AcOl on C.H. (CO.C.H.), telolleman, R. T. C. 6, 72). Small plates, converted by P.S. into discovering the converted by P.S. into dis tolyl-thiophene, and by ammonium accuste into di-tolyl-pyrrole.

p-TOLYL-GLYOXAL C.H.Me.CO.CHO. [102°]. Formed from the oxim by dissolving in aqueous NaHSO₃, stirring the crystalline mass with alcohol and a little HOAo, filtering, and boiling with dilute H₂SO₄ (Müller a. Pechmann, B. 22, 2556). Needles (from hot water), v. sol. alcohol. Reduces cold ammoniacal AgNO, but not Fehling's solution. When shaken with benzene (containing thiophene) and H₂SO₄ it solours the benzene green. Yields p-tolyl-glyoxylic soid and p-toluic soid on oxidation.

Phenyl hydrazide C,H,C(N,HPh),CH(N,HPh) T145°]. Yellow needles (from dilute alcohol)

Oxim C,H,.CO.CH:NOH. Tolyl nitroso. methyl ketone. [100°]. Formed from tolyl methyl ketone, amyl nitrite and NaOEt. Needles (from benzene).

Acetyl derivative of the syn-oxim C.H., CO.CH:NOAc [68°]. From the oxim and Ac.O (Söderbaum, B. 25, 3461). Tables (from MeOH). Cold NaOHAq splits it up into NaCy and p-toluic acid. Conc. H₂SO₄ acts in like manner. Ac₄O at 100° forms C,H,CO.CN [52°],•

whence boiling NaOIIAq forms p-toluic acid.

Acetyl derivative of the anti-oxim
C.H.,C(OII),CH:NOAC. [148°]. From the oxim and AcCl at 0°, followed by water. Cold NaOHAq forms C,H,CH(OH).CO,H [146°], v. sol. ether. Conc. H₂SO₄ converts this acetyl anti-oxim into the oxim. Converted by KCy dissolved in dilute alcohol into p-toluyl-formoïn C.H..CO.CH(OH).CO.CO.C,H, [161°] baum, B. 25, 3473)

p TOLYL GLYOXALINE C10H10N2 $\mathbf{c}_{r}\mathbf{H}_{r}\mathbf{N} <_{\mathbf{CH:N}}^{\mathbf{CH:CH}}$. (285°). Got by warming

C7H7N C(SH):N with dilute HNO, (Marckwald, B. 25, 2365). Yale-yellow crystals, sl. sol. water. Smells like mushrooms. -B₂H₁PtCl₆. -B'AgNO₂.-Picrate. [179°]. Golden needles. p-TOLYL-GLYOXALYL MERCAPTAN

 ${}^{\circ}C_{7}H,N < \stackrel{CH}{\underset{C(SH):N}{\leftarrow}} \stackrel{CH}{\underset{N}{\leftarrow}} .$ [205°]. Got by action of boiling HClAq on the product of the action of amido-acetal on p-tolyl thiocarbimide (Marckwald, B. 25, 2363). Silvery leaflets, m. sol. hot water. Yields (C_{ip}H_{ip}N₂S),PtCl, MeI in alcohol forms (C_{ip}H_pMeN,S)HI [95°], which yields the base C₂H₁N₂C(SMe):N [90°], which forms a

picrate [140°].

p-TOLYL-GLYOXYLIC ACID C_yH_yO₂ i.e. C_bH₁Me.CO.CO.H. [97°]. Formed by the action of AlCl, on a mixture of toluene and Cl.CO.CO.C.H. (Roser, B. 14, 1750). Formed also by oxidising p tolyl methyl ketone with cold alkaline K₃FeCy₅ (Buchka a. Irish, B. 20, 1762, 2213). Needles (from ligroïn), sl. sol. hot water, v. sol. alcohol and ether. Yields p-toluic and terephthalic acids on oxidation. Benzene (containing thiophene) when shaken with tolyl-glyoxylic acid and H2SO, is turned red, and finally bluish-violet.

(Claus a. Krose-Salts.—KA'.—NaA' ½aq (Claus a. Kroseberg, B.20, 2018).—BaA', —BaA', 8aq.—CaA', aq. -AgA'. Needles, v. sol. hot water. Ethyl ether EtA'. (260°-270°)

Amide C,H,NO,. [160°]. Prisms. Phenyl hydrazide [144°].

Phenyt hydrazine [122].

DI-o-TOLYL-GUANIDINE C₁₃H₁, N₃ i.e.

C(NH)(NHC,H₂).

[179°]. Formed by the action of NH₃, lead acetate, and KOHAq on di-o-tolyl-thio-urea (Berger, B. 12, 1855). Crystals, sol. ether. Cyanogen passed into its alcoholic solution forms the dicyanide C₁,H₁,N₂ [174°] which is converted by HCl into the oxalyl derivative C1,H1,N3O2 [207°], whence boiling with alcoholic HCl forms CO NC,H,.CO. [214°]. The dicyanide is converted by boiling with aniline into C_mH_{nl}N_s, which yields crystalline B'HCl aq.—B'₂H₂PtCl₄: yellow pp.
Di-p-tolyl-guanidine NH.C(NHC₁H₂)_s. [108°].

Formed by passing cyanogen chloride into fused p-toluidine (W. Wilson, C. J. 3, 154; A. C. Perkin, C. J. 37, 696). Formed also by desulphuration of di-tolyl-thio-urea in presence of NH₃ (Hofmann, B. 7, 1739). Needles (from ligroïn). Nitric acid (S.G. 1-5) gives a di-nitro-derivative [197°], which forms crystalline B'HNO. Alcohol and HNO, (S.G. 1.4) produce di-nitrop-tolyl-urea. Cyanogen passed into its ethereal solution forms C₁₃H₁, N₂Cy₂, crystallising from ether in prisms, converted by dilute HClAq into NH.C \(\begin{align*}
N(C,H,).CO \([188.5^\circ]\) (Landgrebe, B. 10,

The cyanide is converted by boiling in alcoholic solution with aniline hydrochloride into

C₂₄H₂₁N₃ aq [110°-115°].—Salt B'.H.PtCl₃.
Tri · o · tolyl · guanidine C₂₄H₂₃N₃ i.c.
C(NC,H,)(NHC,H.)₂. [131°]. Formed by the action of o-toluidine in alcoholic solution in presence of lead oxide on di-o-tolyl-thiourea (Berger, B. 12, 1857; cf. Girard, B. 6, 415). Formed also when di-o-tolyl-thiouren is boiled for a long time (Barr, H. 19, 1769). Minute prisms. Yields a dioyanide C₂H₂₃N₅ [141°], converted by cone. HClAq in alcoholic solution into C₂H₂₁N₃O₂ [179°]. B'₂H₂P(O)₈: yellow prisms.

Tri-p-tolyl guanidine C₂H₂₃N₅. [123]. S. (alcohol) 7.4 at 0°. Formed by heating di-p-

tolyl-thio-urea with copper (Merz a. Weith, Z. 1868, 610), or, in alcoholic solution, with ptoluidine and PbO (Hofmann, B. 2, 459). Got by heating p-toluidine with PCl, and p-tolyl, cyanate (Weith, B. 9, 820). Formed also when di-p-tolyl-urea is boiled for a long time (Barr, B. 19, 1768), and likewise by the action of p-toluidine on the product of the action of p-toludine on the product of the action of chlorine on tolyl cyanate (Nef. A. 270, 322). Needles (from ligroin). Yields a dicyanide C₂H₂N₃ [184°], which forms BTHCl 3aq and B'₂H₂PtCl₄ and is converted by boiling with alcoholic HCl into di-tolyl-parabanic acid.

Salts.—B'HCl aq. S. 6 at 0°.—B'₂H₁PtCl₄.
S. 045 at 0°.—B'HO₃. S. 07 at 0°.—B'₂H₃O₄.
Plates (from hot water). Neutral in reactions.

Neutral in reaction. Plates (from hot water). p-TOLYL HEPTADECYL KETONE

HYDRIDE C.H., N., i.e. C., H., Me N., C., H., Me N.N., C., H., Me [165°]. Formed by heating cenanthol with toluene-o-azo-toluidine at 175° (Goldschmidt a. Poltzer, B. 24, 1010).

Needles, sol. hot benzene.—BilCl. [96°].—
B'_H_PtCl_. [171°]. Yellow crystalline pp.

o-TOLYL.HYDANTOIN C₁₀II₁₀N₂O₂. [17g°].
Formed by heating o-tolyl-amido-acetic acid with urea at 180° (Ehrlich, H. 16, 742). Light-rellow plates, sol. alcohol and hot water. On poiling with baryta-water it gives o tolylnydantoïc acid, which, when set free from its salts, at once splits up into water and o-tolylnydantoin.

p-Tolyl-hydantoin C, H, N,O, i.e. 20 \\(\text{NH}_{\text{N}(C,H_1).CH_2}\). [210°].

Formed, together with p-tolyl-hydantoic acid CO(NH.).N(C,H.).CH.,CO,H, by fusing p-tolylamido-acetic acid with urea (Schwebel, 1128). Needles (from water), v. sol. alcohol. p-Tolyl-hydantoic acid is crystalline, sl. sol. hot alcohol and hot water.

Di-o-tolyl-hydantoin [275°]. Got from o-tolyl-amido-acetic toluide and COCl. (Bischoff, B. 25, 2275).

 $\text{CO} {<_{N(\text{C},\text{H}_s),\text{CH}_s}^{N(\text{C},\text{H}_s),\text{CH}_s}}$ Di-p-tolyl-hydantoïn [175°]. Formed from p tolyl-amido-acetic toluide and COCl₂ (Bischoff, B. 25, 2280). Plates (from alcohol), sl. sol. ligroin.

TOLYL - HYDRAZIDO - METHYL-THIAZOLE

DIHYDRIDE CHIMC.S C.NH.NHC,H, Formed by heating tolyl-allyl-thio-semicar-azide with cone. HClAq at 100' (Avenarius, B. 21, 270). The p- compound melts at 133'. Both the o- and the p- compounds form crystalline hydrochlorides.

a TOLYL HYDRAZIDO - PROPIONIC ACID H.Me.NH.NH.CHMe.CO.H. [143°]. Formed by the action of sodium-amaigam on the o-tolylhydrazide of pyruvic acid (Japp a. Klingemann,

(P.); [56°] (F.); [59°] (Gallinek a Richtor, B. 18, 3175). Prepared from o-toluidine in the same manner as phenyl-hydrazine is obtained from aniline (Fischer a. Bösler, A. 212, 338; Preund, B. 24, 4200). Glittering plates, slowly oxidised by air, forming a brown oil.—BHCl aq: needles. B'HNO₃: plates. Wi^{ch} SOCl₂ and other it forms C₂H,NH.N:SO, a yellow oil smelling like geraniums (Michaelis, A. 270, 119). Glucose yields o-tolyl-glucosazone $C_{20}H_{20}N_1O_4$ [201] (Raschen, A. 239, 229). Di-methyl di-ketone forms CH₂C(N₂HC,H₁).C(N₂HC,H₂).CH₃ [198°] (Japp a. Klingemann, A. 247, 221).

Formyl derivative C. II Me.NH.NHCHO. [121°]. Formed from o-tolyl hydrazine and formamide. Needles (Gattermann, B. 25, 1078).

Acetyl derivative C,H,NH.NHAc. [104°].

Formed from o-tolyl-hydrazine and Ac.O (G.). Propionyl derivative

C.H., NH.NH.C.H.O. [84°]. Formed from otolyl-hydrazine and propionic acid (G.). Colourless tables.

• Benzoyl derivative C,H,.NH.NHBz. [180]. Got from the hydrazine and BzCl in Et.O (G.). Needles. Gives off all its nitrogen

[31,9] (c.). Needles. Gives oil all its nitrogen in the free state on boiling with Fehling's solution (Strache a. Iritzer, H. 14, 38).
m. Tolyl-hydraziss C, II, NII, NH., (242°) (Buchka a. Schachtebek, H. 22, 841; cf. V. Meyer a. J.ecco, B. 16, 2976).
Oil. — BHCl. Negdles, v. sol. water and alcohol.

p - Tolyl - hydrazine C.H.NH.NH₂. [61°]. (242°). Obtained from p-toluidine (Fischer, B. 8, 589; 9, 890). White plates (from ether), al. sol. water.

Reactions.—1. With SOCl, and ether it forms C.H.NH.N:SO [112°], crystallising in yellow needles (Michaelis a Jtuhl, 4.270, 118).—2. C.H.PCl, forms C.H.NH.N:PC.H. [162°], crystallising in prisms.—3. POCl, forms (C.H.NH.NH.).PO [189°].—4. Acetons forms OMe2(N2HO,H1) [52°]. - 5. Acetoacetic ether.

forms C₁₃H₁₈N₂O₃ [98°] (Knorr, B. 17, 550).— 6. Oxalic ether forms NHC,H, NH.CO.CO,Et. 1138°] (Preund, B. 24, 4198).—7. Di - methyl diketone yields CH₂.C(N₂HC,H₁).C(N₂HC,H₂).CH₃ [280°], and CH₃.C(N₂HC,H₃)Ac [161°] (Japp, C.J. 53, 544).

Salt.-B'C, H, PH, O2. [148°] (Michaelis, A.

270, 134).

Toluene-p-phosphinate P'C,H,PH,O2.

Formyl derivative

C.H.Me.NH.NH.CHO. [164°]. Formed by heating the alcoholic solution of p-tolyl-hydrazine with chloroform and potash. Formed also by heating p-tolyl-hydrazine with formamide at 130° (Ruhemann, C. J. 55, 248). Plates (from water), v. sol. alcohol.

Acetyl derivative C.H.Me.NH.NHAc. [121°]. Formed from p-tolyl-hydrazine and AcOH (Gattermann, B. 25, 1080). Plates.

Propionyl derivative [170°]. Dibenzoyl derivative [188°] (Fischer). Di-o-tolyl-hydrazine.

Formyl derivative (C,H,),N.N.H.O.HO. [130°]. Formed from C,H,N.H.N.H.C.HO and CuSO, (Gattermann, B. 25, 1078). Plates.

Acetyl Alerivative (C,H,),2N.N.H.Ac.

Acetyl oderivative (C,II,),N.NHAc. [191°]. Formed in like manner from acetyl-o-Propionyl derivative [167°]. Needles.

Propionyl derivative [167°]. Needles.

Benzoyl derivative [209°]. Needles.

Needles.

u-Di-p-tolyl-hydrazine (C,H,),N.NII, [172°]. Formed by reduction of di-tolyl-nitrosamine with zinc-dust and HOAc (Lehne, B. 13, 1546). Plates, v. sol, alcohol and benzene. - B'HCl.

Formyl derivative (C,H,)2N.NH.CHO. [146]. Formed from formyl.p-tolyl-hydrazine and CuSO, (Gattermann, B. 25, 1079). Plates. Acetyl derivative. [170]. Needles. Propionyl derivative [171:5]. Needles. Benzoyl derivative. [1873]. Needles.

∽ s-Di-o-tolyl-hydrazine C,H,NH.NHC,H,. o-Hydrazo-toluene. [165°] (P.); [146°] (S.). Formed by reduction of o-toluene-azo-toluene by Bodium amalgam (Petrieff, B. 6, 557; Schultz, B. 17, 467). Converted into di-amido-ditolyl B. 17, 467). Converted into di-amido-ditolyl [8:4:1]C_uH_Me(NH_u).C_uH_Me(NH_u)[1:3:4] [128°] by heating with HCl. The diamido-derivative $C_tH_u(NH_u)$.NH.NH.C.H $_u(NH_u)$ [180°] is a product

of the action of sodium-amalgam on nitro-ptoluidine (Buckney, B. 11, 1453). s-Di-m-tolyl-hydrazine C,H,NH.NHC,H,. Formed by reducing m-toluene-m-azo-toluene by

alcoholic ammonium sulphide (Goldschmidt, B. 11, 1626; Barsilowsky, A. 207, 116). Liquid, converted by H.SO, into . di-amido-ditolyl.

s-Di-p-tolyl-hydrazine C,H,NH,NHC,H,. [126°]. Formed in like manner from p-toluenep-azo-toluene (Melms, B. 3, 553) and by the action of zinc-dust and NaOHAq on p-nitrotoluene (Janovsky, M. 9, 829). Tables or needles, v. e. sol. alcohol. In alcoholic solution it is readily oxidised by air to C,H, N₁,C,H,. Dilute H₂SO₂ convorts it into toluidine and toluene-azo-foluene. On treatment in alcoholic solution with hydrochloric soid it changes to tolylenetolyl-diamine. The di-amido-derivative [1:2:4]O,H,Me(NH,).NH.NH.C,H,Me(NH,)[4:1:2] obtained from C,H,Me(NH,).N,-C,H,Me(NH,) by reducing with sodium-amalgam, is crystalline and yields B"H,SO,, B"2HCl, B"2HBr, and B"H,PtCl, (Graeff, A. 229, 852).

Reference.—Oxy-tolyl-hydrazine.

o-TOLYL-HYDRAZINE SULPHONIC ACID CaH, Me(N2H2).SOaH [1:2:4]. Formed by adding o-diazo-toluene p-sulphonic acid to a cold solu-tion of SnCl₂ (Limpricht, B. 18, 2193). Colourless needles, v. sol. hot water, nearly insol. alcohol.—KA' 2aq: orange-red prisms.—BaA': yellow crystalline powder.
o-Tolyl-hydrazine sulphonic acid

 $C_{a}H_{a}Me(N_{2}H_{3}).SO_{a}H$ [1:x:2]. Formed by heating o-tolyl-hydrazine (1 pt.) with conc. H,SO, (5 pts.) at 100° (Gallinck a. Richter, B. 18, 3175). Thin needles (containing faq). By boiling with aqueous CuSO, it is quantitatively decomposed

aqueous CuSO, it is quantitatively decomposed into a toluene sulphonic acid and nitrogen.—
NaA' 3½aq.—BaA', 4aq.— ZnA', 2aq.—PbA', 6aq.—PbA', 6q.—PbA', 6q. sl. sol. cold water. Decomposed by fusion. Not attacked by warm H₂SO₄.

attacked by warm H,SO,.

p-Tolyl-hydrazine m-sulphonic acid

C₈H,Mc(N₂H₃),SO₂H [1:3:4]. Obtained by reducing p-diazotolugne m-sulphonic acid by cooled SnCl₂ (Limpricht, B. 18, 2193). Slender prisms, sol. hot water. FeCl₃ evolves nitrogenin the cold. Conc. H,SO₄ at 80° forms a red amorphous substance (Schneider, Am. 8, 271).

p-Tolyl-hydrazine disulphonic acid

C₈H,Mc(N₂H₃)(SO₂H₁. Formed by adding 2-diazotolugne disulphonic acid to a cold soln.

C₀H₂Me(N₂H₃)(SO₂H)₂. Formed by adding p-diazo-toluene disulphonic acid to a cold solution of SnCl2 (Limpricht, B. 18, 2193). Nodules,

v. sol. water.—BaH.A", 21 aq: tables.
Di-tolyl-hydrazine disulphonic acid

C.H.Me(SO.H).NH.NH.C.H.Me(SO.H). duct of the reduction of the corresponding azocompound by SnCl₂ (Neale, A. 203, 72). Crystalline powder (containing 2 aq), sl. sol. water. — BaA" 5aq.—CaA" 3 aq: monoclinic efflorescent

Reference .- NITRO - TOLYL - HYDRAZINE SUL-

PLONIC ACID.

o-TOLYL-IMIDO-DIACETIC ACID

[1:2]C H, Me.N(CH, CO, H), [c. 160°]. Formed by heating o-tolyl-amido-acetic acid (1 mol.) with chloro acetic acid (1 mol.), Na CO, (1) mols.) and a little water at 140° (Bischoff, B. 1005. And a noise water at 140 (Discholl, B. 23, 1994; 25, 2270). White crystals, insol. ligroin, sl. sol. ether, m. sol. alcohol.—NH,A'. [100]. V. sol. Aq. Amide C,H,N(CH,,CO.NH.), [164]. Plates. Di-o-toluide C,H,N(CH,CO.NHC,H,),

[150°].

Imids C,H,N < CH,CO NH. [146°]. Prisms (from alcohol), sl. sol. water.

o-Tolylamic acid C.H.N(CH, CO, H).CH, CO.NHC, H, f148°7. Crystals (from ; lcohol).

p-Tolylimido-diacetic acid

[1:4]C₄H₁Me.N(CH₂CO₂H₂, Diglycotolylamic acid. [c. 140°]. Formed by the action of Ch₂Cl.CO₂H₂ on p-tolyl-glycocoll (Meyer, B. 14, 1323; Bischoff, B. 23, 2000). Needles (from water). Very unstable.— CuA'₂aq: green needles.—Ag₄A'(NO₄): needles.—p-Toluidine

salt (C,H,NH,)HA'. [119°]. Crystals, sol. | hot water.

Mono-amide. [222°]. A product of the action of Ac₂O on the compound [108°] got from chloro-acetic acid and p-toluidine (Bischoff, B.

Di-amide C,H,N(CH,CO.NH,), [250°], Di-p-toluide C,H,N(CH,CO.NHC,H), Di-p-toluide C.H.N(CH..CO.)
[251°]. Long needles (from alcohol).

Amide p-toluide C,H,N(CH,CO.NH.)CH,CO.NHC,H, [210°]. p-Tolylamic acid

C.H.N(CH., CO., L). CH., CONIIC, H., [222°]. Needles, insol. water, sol. hot alcohol.

p.TOLYL-IMIDO-DIACRYLIC ETHER
C.H.MEN(CH:CH.CO,Et). [73°]. Formed from p-toluidine and formyl-acetic ether (Von Pechmann, B. 25, 1053). Yellow needles (from dilute alcohol).

o - TOLYL - 8 - IMIDO - BENZYL - MALONIC

ETHER C₂₁H₂₃NO₄ i.e. C₈H_.,C(NC,H₂).CH(CO₂Et)₂. [95°]. Formed by the action of w-chloro-benzylidene-o-toluidine upon sodium-malonic ether (Just, B. 19, 985). Crystals, v. sol. ether. Split up by dilute HClAq at 120° into acetophenone and o-toluidine. The p-isomeride is liquid.

o-TOLYL-8-IMIDO-BUTYRIC ACID

C.H.Me.N:CMe.CH., CO.H. . [112]. Formed by heating acctoacetic other with o-toluidine at 150° (Knorr, B. 17, 542; Pawlewski, B. 22, 2203). Needles (from hot water), converted by conc. H₂SO₄ into (Py. 1) oxy-(B. 4, Py. 3)-dimethyl-quinoline.

p-Tolyl-\$\beta\$-imido-butyric acid. Formed inc like manner from p-toluidine. Crystals. Converted by H₂SO₄ into (Py. 1)-oxy-(B. 2, Py. 3). di-methyl-quinoline.

p-TOLYL IODO-ETHYL SULPHONE

C,H,SO,CH,CH,I. [100°]. Formed from tolyl oxy-ethyl sulphone and HIAq at 160° (Otto, J. pr. [2] 30, 357). Crystals, v. sol. hot alcohol.

TOLYL IODO-METHYL SULPHONE

C.H., SO, CH.I. (126'). Formed by heating sodium toluene sulphinate with CH.I. and alcohol (Otto, B. 21, 655). Small needles, v. c. sol, hot alcohol.

DI-p-TOLYL KETONE CO(CaH, Me) .. 1920]. (333°) at 725 mm. Fornfed by oxidation of di-(355) is (25 mm. Former by oxidation of in-tolyl-methane (Weiler, B. 7, 1183), of n-di-tolyl-ethane (O. Fischer, B. 7, 1195), and of n-di-tolyl-ethylene (Hepp, B. 7, 1414) by chromic acid mixture.

Preparation .- 50 g. AlCl3, 65 c.c. toluene, 50 c.c. CS, and 11 c.c. of a solution of COCl, in CS, saturated at 0° are put into a corked halflitre flask and gently warmed. After 20 minutes HCl is allowed to escape and a second 11 c.c. of CS₂ saturated with phosgene is added. The operation is repeated 2 or 3 times; the yield is 50 p.c. of the calculated (Elbs, J. pr. [2] 35, 467; cf. Ador a. Crafts, B. 10, 2174).

Properties.—Crystals (from alcohol). Con-

verted by HNO, at 250° into benzoyl-terephthalic acid. Reduced by HI and P to di-tolyl-methane (Ador a. Rilliet, B. 12, 2303):

Oxim (C,H,),C:NOH. [163°]. Prisms (Goldschmidt, B. 23, 2746). Decomposes on keeping with sudden evolution of nitrous fumes. Conc. H2SO, at 100° forms the p-toluide of p-toluie

Di-p-tolyl diketone Di-p-tolyl discone C,1,, Cloud P, Tolil. [105°]. Formed by boiling toluon (1 pt.) with HNO₂ (2 pts.) (Stierlin, B. 22, 381). C,H,.CO.CO.C,H,. violet colour when boiled with alcoholic potash.

(a)-Oxim C.H.,C(NOH).C(NOH).C.H., [217°]. Plates or needles, sl. sol. alcohol. Yields a diacetyl derivative [134°]. (B)-Oxim [225°]. Formed, together with the (a)-oxim, by the action of hydroxylamine hydrochloride on the ketone. Needles, v. sol. alcohol. Yields a di-acetyl derivative [144°].

Di-n-tolyl tetraketone C.H. CO.C(OII), CO.CO.C.H., [88°], Formed by the action of nitric acid (S.G. 1°3) on C.H., CO.CH(OH).CO.CO.C.H., (Söderbaum, B. 25, 3474). Prisms (containing (Callino,), CS2) (when crystallised from CS.).

C.H..C(NOH).CO.CO.C(NOH).C.H,. [1819]. Plates (containing Emil) (from alcohol).

C.H..CO.C(NOH).C(NOH).CO.C.H., So called '(\theta)-nitro-cymene. [125"]. Mol. w. 324 (by Raoult's method). Formed by the action of nitric acid on cymene and on p-tolyl methyl ketone (Holleman, R. T. C. 6, 60; cf. Landolph, Recome (Hoheman, R. T. C. 6, 60; c). Landolph, B. 6, 937; Fittica, A. 172, 311). Needles, v. sol. warm alcohol. Converted by NaOHAq into p. toluic acid. Zinc-dust and HOAc reduce it to C.H.,CO.CH.,CH.,CO.C,H, [159°]. Alcoholic NH, forms p-toluic amide and C.,H,N,Q,[162°]. Alcoholic Boiling Ac₂O forms C_{In}H_{In}N₂O₄Ac₂O [167°

Reference .-- OXY-DI-TOLYL KETORE TOLYL-MALONAMIC ACID v. MALONIC ACID. TOLYL-MELAMINE v. Cyanuramide in the article on Cyanic acids.

o-TOLYL-MERCAPTAN [1:2]C,H,Me.SH. [15°]. (188) (H.); (193°) (V.). Formed by reducing (4,1,2)-bromo-tolyl mercaptan (Hübner, A. 169, 30; Vallin, B. 19, 2953). Prepared by boiling o-tolyl ethyl dithiocarbonate with alcoholic potash, the yield being 70 p.c. of the theoretical amount (Leuckart, J. pr. [2] 41, 188). Plates. - Pb(SC,H,), Brick-red pp., turning

m-Tolyl mercaptan [1:3]C,H,Me.SH. [c. 200]. Formed by reducing toluene m-sul-phonic chloride with tin and HCl (Hübner, A. 169, 51) and by boiling m-tolyl ethyl xanthate with alcoholic potash (L.). Colourless liquid with intense odour of mercaptan. Volatile with steam. In ammonincal alcoholic solution it is oxidised by air toen-tolyl disulphide.

p-Tolyl mercaptan [1:4]C₆H₁Me.SH. [48°]. (188°) (J.) a (191°) (Crafts, B. 19, 3180; Otto, B. 419, 3129); (194°) (Vallin, B. 19, 2953). Formed by reducing toluene p-sulphonic chloride with tin and HCl (Märcker, A. 136, 79; Javorsky, Z. 1865, 222). Formed also by heating p-tolyl ethyl xanthate with alcoholiopolash (L.). Formed also from di-p-tolyl disulphide, alcohol, and H.S. (Otto a. Rössing, B. 19, 3180). Unctuous Raine (from ether), volatile with steam. Conc. H. 804 forms a blue solution. Readily oxidised to di-patolyl disulphide [46°]. Chloro-acetone forms C,H,S.CH,CO.CH, (151° at 15 mm.); S.G. 114 10986 which yields a phenyl-hydrazide [62°] (Delisle, A. 260, 268).—Hg(SC,H,)₂.—C,H,S,HgCl. Plates.

Ethyl ether C,H,SEt. (221°). 1.0016. Colourless oil (Otto, B. 13, 1277).

References.-AMIDO and BROMO-

o-TOLYL-MESITYL-THIO-UREA

CH.,NH.CS.NHC,H.Me., [167°]. Formed from o-toluidine and mesityl thiocarbimide (Eisenberg, B. 15, 1014). Needles, in Sol. Aq. DI. TOLYL-METHANE CH.2(C,H.)2. [23°].

Formation.—1. From forms aldehyde (or methylal), toluene, and H.SO. (Weiler, B. 7, 1181).—2. By reducing di-tolyl ketone with HI and P (Ador a. Billiet, B. 12, 2302).—3. A product of the action of AlCl, and toluene on CH₂Cl₂, on CH₂Cl, or on CCl₃NO₂ (Friedel a. Crafts, A. Ch. [6] 11, 266; Bl. [2] 43, 50; Elbs a. Wittich, B. 18, 347).

Properties.—Prisms, v. sol. ether. Oxidised by chromic acid mixture to di-tolyl ketone, toluyl-benzoic acid, and C^(C₈H₁.CO₂H)₂. Yields

stiehl a. Gerber, A. Ch. [6] 2, 353). Crystalline. References. DI-BROMO- and DI-CHLORO-, DI-

TOLYL-METHANE.

o-TCLYI METHYL-p-AMIDO-PHENOL

Methyl derivative C,H,NMe.C,H,OMe. (336° cor.). From C,H,NH.C,H,OH, KOH, and MeI (Philip, J. pr. [2] 34, 59). Oil.

TOLYL-METHYL-AMINE v. Метнуь-TOLUIDINE, METHYL-BENZYL-AMINE, and AMIDO-XYLENE.

Di-p-tolyl-methyl-amine (C.H.)2NM2. (235°-240° at 20 mm.). Formed from ditolylamine, MeOH, and HCl at 250°-280° (Girard, Bl. [2] 24, 120). Does not combine with acids.

DI-TOLYL-DI-METHYL-DI-TRIAZYL

NN(C,H,)>0.C \leq N(C,H,).N CMe.N | CMo (259°-260°). Formed by boiling p-tolyl-hydrazine cyanide (C,H,NII,NII,),Cy, with Ac₂O (Bladin, B. 22, 3114). Crystals (from alcohol), m. sol. alcohol.

p-TOLYL-METHYL-BENZYL KETONE C.H.Mc.COCH...C.H.Me. [102°]. Got by re-ducing p-toluoin with zinc and alcoholic HCI (Stierlin, B. 22, 383). Needles, insol. water, v. sol. benzene.

o-TOLYL-METHYLENE-AMINE

C,H,N:CH₂ (?). Formed by adding o-toluidine to a solution of formic aldehyde (Wellington a Tollens, B. 18, 3307). Colourless syrup.

p-Tolyl-methylene-amine C,H,N:CH₂ (?). [o. 122°]. Formed, together with a polymeride sol. sol. benzene and alcohol, by adding p-toluidine to a solution of formic aldehyde (W. a. T.). Crystals, v. sol. benzene.

Di-o-tolyl-methylene-diamine (C,H,NH),CH2. (over 350°). Formed, together with the following solid isomeride, by heating o-toluidine with CH₂Cl₂ at 116°-115° (Grünhagen, A. 256, 305). Liquid, v. sol. ether and alcohol. -B', H.PtCl.:

brown amorphous powder.

Isomeride [c. 185°]. Crystalline powder,
al. sol. cold alcohol. — Salts: B"2HCl. ¬B"2HCl. ¬-B"H,SO₁. — B"3H₂C₂O₂.

—B"3H₂C₂O₄. Radiating aggregates,

Di-p-tolyl-methylene-diamine

(C,H,.NH)2CH2. (above 350°). Formed, together with the solid isomeride, by heating p-toluiding

with CH₂Cl₂ (G.). Oil, v. sol. ether.—B"HCl.—B"₂H₂PtCl₃.—B"HAuCl₄.

Isomeride C₁₃H₁₈N₂. [c. 156°]. (over 350°).

Amorphous, sl. sol. ether. — B"2HCl (?). — B"H,PtCla.-B"2HAuCl.-B"2H,C2O4. Crystal. line crusts.

Di-p-tolyl-di-methylene-diamine

C,H,N CH₂ NC,H, [90°]. A product of the action of CH₂Cl. on p-toluidine at 100° (Grünhagen, A. 256, 296). Granules, sol. hot alcohol. Converted by nitrous acid into a crystalline nitroso- derivative (C,H,N),C,H,(NOH) (?) — B"2HGI.—B"2HAuCl,.—B"2HBr.—B"H,SO. o-Tolyl-trimethylene-diamine

C₃H_o(NH₂).NHC,H, (281°). Formed by reducing o-tolyl-pyrazole dihydride in alcoholic solution by sodium (Balbiano, G. 18, 354). Oil. p-Tolyl-trimethylene-diamine

C₃H_a(NH₂).NHC₂H₂, [c. -15°]. (287°). A product of the action of Na on an alcoholic solution of p-tolyl-pyrazole (Balbiano). Liquid. Oxalate. [208°]. Spherical groups of minute needles.

p-TOLYL METHYLENE METHYL SUL-PHONE KETONE C,H,.SO,CH,.CO.CH,. [51°]. Formed from chloro-acctone and sodium toluene p-sulphinate (Otto, J. pr. [2] 36, 401). Silky needles. Yields a bromo-derivative [130°].
m-TOLYL-METHYLENE-PHTHALIDE

C₄H₄COC(CHC,H₂) O. [153°]. Formed by heating m-tolyl-acetic acid with phthalic anhydride and a little NhOAc (Heilmann, B. 23, 8157). Needles (from ligroin), sl. sol. ether.

p-Tolyl-methylene-phthalide $C_{le}H_{lp}O_{r}$ p-Xylal-plthalide. [151°]. Formed in like manner from p-tolyl-acetic acid (Ruhemann, B. 24, 3965). Yellow needles (from alcohol), sl. sol. ether. Nitrous acid passed into its solution in chloroform forms $C_s\Pi_1 < C(C(NO_2), C_7H_7) > 0$ [140°], which may be reduced to the compound $C_0^*H_4 < \stackrel{CH:C.C,II}{CO.O}$. [116°].

Reference .- NITRO-TOLYL-METHYLENE-PHTHAL-

m-TOLYL-METHYLENE-PHTHALIMIDINE $C_{s}H_{i} < C(CHC, H_{i}) > NH.$ [165°]. Formed by heating m-tolyl-methylene-phthalide with alcoholic ammonia (Heilmann, B. 23, 3161). Yellowish needles.

p-1.3lyl-methylene-phthalimidine C_{1e}H_{1,}NO. [2042]. Formed by heating p-tolyl-methylene-phthalide with alcoholic NH₃, the compound NH₂CO.C₄H₁,CO.CH.C.H, being first formed (Ruhemann, B. 24, 3908). Converted by passing nitrous acid through its solution in chloroform into C_oH_i C(C(NO₂).C,H₂) NH [227°].

Isomeride C,H, CH:C.C,H, [228°]. Formed by heating $C_0H_1 < CO.O.H_2$ with alcoholic ammonia (R.).

Reference .- NITEO-TOLYL-METHYLENE-PHTHAL-IMIDINE.

DI-p-TOLYL TRIMETHYLENE DISUL. PHONE C.H. (80.C.H.), [125°]. Formed from trimethylene bromide and sodium toluene p-sulphinate (Otto, B. 24, 1834). Plates. Converted by alcoholic potash at 120° into the compound O(CH,CH,CH,SO.C,H,), [80°].

TOLYL-METHYL-IMESATIN v. Toluide of

Methyl-IBATIN

m-TOLYL METHYL KETONE C,H,.CO.CH, Methyl-acetophenone. (219°). Formed by discilling calcium m-toluate with calcium formate

(Buchka a. Irish, B. 20, 1766).

Tolyl methyl ketone. (225°). S.G. 22 ·9891. V.D. 4.58. Formed, together with the p-compound, by the action of AcCl on toluene and AlCl, (Essner a. Gossin, Bl. [2] 42, 95). This is

perhaps the o-compound.

perhaps the o-compound.
p-Tolyl methyl ketone. (217°) (M.); (230°
cor.) (W.). Formed by the action of AlCl, on a
mixture of toluene and Ac,O or AcCl (Michaelis,
B. 15, 185; Claus, B. 19, 234). Formed also by
heating toluene with HOAc, ZnCl, and POCl;
(Frey, J. pr. [2] 43, 114) and as a by-product in
the oxidation of (a)-nitro-cymene (Widman, B.
19, 587). Oil. Yields a dibromide C_bH_bBr_cO
[100°]. KMnO_b torms terephthalic acid. Alkaline
K.FeCv. forms p-toluic and p-tolyl-glyoxylic [100°]. KMnO, forms terephthanic acid. Aikanne K,FeOy, forms p-toluic and p-tolyl-glyoxylic acids (B. a. K.). HNO, forms C₁₈H₁₄N₁₀, [125°], which is reduced by zinc-dust and HOAc to C₂H₄(CO,C,H₂), (Hollemann, Z. T. C. 10, 211). Oxim [88°]. Crystals (from ligroin). Phenyl-hydrazide [97°]. Prisms. Peterone.—Awthor. Iono. and Oys. Tolyl.

Reference. - AMIDO., IODO., and OXY., TOLYL METHYL RETONE.

METHYL o-TOLYL KETONE TETRA-**HYDRIDE** $OH_2 < CH_2 \cdot CM_2 > C.CQ.CH_2$. (206°).

Formed from a di-acetyl-pentane by treatment with conc. H₂SO₄ (Kipping a. Perkin, jun., C. J. 57, 18). Oil, smelling like peppermint. Does not combine with NaHSO₂. In moist ether it is reduced by Na to the been by highlight reduced by Na to the hexabydride.

Oxim C, H, NO. Liquid. Phenyl hydraside C.H., N., Tolyl methyl ketone hexahydride v. METHYL-HEXAMETHYLENYL METHYL KETONE

m-TOLYL-METHYL-MALONIC ACID [1:3]C₄H₄Me.CH_{...}CH(CO₂H)₂. [133°]. Formed by saponification of the ether (Poppe, B. 23, 110). Rhombohedra, sl. sol. water. K.A" : needles.

Methyl ether Me₂A". • (c. 300°). Ethyl ether Et,A". (320°). Formed from -bromo-m-xylene and sodium malonic ether. Oil. Converted by alcoholic NH₂ at 150° into C₆H₄M₆.CH₂.CH(CO₂Et).CO.NH₂[186°], which on warming with water forms the ammonium salt C.H.Me.CH, CH(CO,Et).CO,NH, [77°]. Et ... is converted by methylamine into the methylamide C₅H₄Me.CH₂CH(CO₂Et).CONHMe [120°], and by aniline into C₅H₄Me.CH₂CH(CO.NHPh)₂ [188°]. •

Di-m-tolyl-di-methyl-malonic ether (C₆H₄Me.CH₂)₂C(CO₂Et)₂. [122°]. A product of the action of w-bromo-m-xylene on sodium

malonic ether (Poppe, B. 23, 109)?
o-TOLYL-METHYL-QXAZOLINE C₁₁H₁₈NO i.e. CHMe.O C.C.H. (258°). Formed by boiling C,H,,CO.NH.CH, CHMeBr with alcoholic potash (Salomon, B. 26, 1323). Oil.—B'C,H,N,O,, [129°].—B',H,PtOl, Vol. IV.

p-Tolyl-methyl-oxazoline C, H, NO. (265°). Formed from the bromopropyl-amide of p-toluio acid (Salomon, B. 26, 1826). Oil.—Picrate B'C.H.N.O., [183°].—B',H.PtOl., [184°].
p-TOLYL-DI-METHYL-PHOSPHINE

C.H.PMe. (210°). Formed from C.H.PCl, and ZnMe. (Czimatis, B. 15, 2014). Oil, oxidised by HgO to C.H.PMe.O. CS. forms C.H.PMe.OS.

[110] crystallising in red plates.

Methylo-iodide B'Mel. [255]. Needles.

Yields B'Mel, and B'_Me.PtCl.

Benzylo-chloride. Yields

B'2(C,H,).PtCla [226°], a yellow crystalline pp.

p-TOLYL METHYLPHTHALIMIDE [4:2:1]C_aH_aMe:C_aO₂N.C_aH_aMe. [180]. Formed by distilling (4,2,1)-methyl-phthalic acid with p-toluidine (Niementowski, M. 12, 630). Crystalline mass, v. e. sol. chloroform, insol. water.

p-TOLYL-METHYL-PHTHALIMIMINE C₆H₄ CO CH(CH₂·C₆H₄Mo) NH. [149°]. Formed from p-tolyl-methylene-phthalimidine, HI and P (Ruhemann, B. 24, 39(%). Needles.

DI-D-TOLYL-METHYL-PIPERAZINE C₁₉H₂₁N₂. [105°]. Formed from di-p-tolyl-propylene-diamine, ethylene bromide, and C19H21Ñ2. Needles (from alcohol) (Bischoff, B.

o-TOLYL-METHYL-PROPYLENE. .. THIO. UREA CHMe.S C.NMe.C.H., (c. 295°). Formed • from o-tolyl-propylene-ψ-thio-urea and MoI (Prager, B. 22, 2999). Yields (β)-methyl-taurine on oxidation.—B'C₀H₁N₃O₇. [138°].—B'HI. [166°].—B'₂H₂PtCl₃. Decomposes over 200°.

p-TOLYL-DI-METHYL-PYRROLE

(C,H,)N < CMe:CH. [46°]. (255°). Got by heating the di-carboxylic acid (Knorr, B. 18, 808). Crystals, volatile with steam.

Reference .- AMIDO-TOLYL-DI-METHYL PYRROLE. p-TOLYL-DI-METHYL-PYRROLE DICARBO

OXYLIC ACID (C,H,)N CMe;C,CO,H Got by saponifying its ether, which is formed by mixing acetic acid solutions of di-acetyl-succinic ether and p-toluidine (Knorr, B. 18, 304). Needles, decomposes at about 250°, with evolution of CO₂.

—K₂A".—AgHA".

Ethyl ether Et, A". [67°]. Tables. Reference. - AMIDO-TOLYL-DI-METHYL-PYRROLE DICARBOXYLIC ACID.

p-TOLYL-DI-METHYL-SULPHAMIDE SO₂(NMe₂).NHC,H,. [91°]. Formed from N. fe. SO Cl and p-toluidine (Behrend, A. 222,

120). Crystals, v. sol. alcohol and ether.

p. TOLYL METHYL SULPHONE
C.H., SO., C.H., [87°]. Formed by the action of conc. Kelling on p. tolyl-sulphono-acetic acid (Otto, B. 18, 161). Got also from C.H., SO.Na and Mel (Otto). Needles (from very dilute

alcohol), v. sol. hot water o-TOLYL-METHYL-THIAZOLINE

CHMe.S C.C,H,. (284°-295°). Formed by beating o-toluic bromo-propylamide with P.S. at 150° (Salondon, B. 26, 1328). Oil.

at 150° (Salomon, 2. 2007).
B'C,H,N,O., [186°].
p-Tolyl-methyl-thiazoline C,H,,NS. (295°).
Oil.—B'C,H,N,O., [141°].—B',H,PlOl.

o-TOLYL-METHYL-THIOHYDANTOIN

 $HMe < \stackrel{CO.N(C,H,)}{NH.CS}$ [198°]. Formed from o-tolyl-thiocarbimide and alanine (Marckwald, B. 24, 3281). Crystals.
p - Tolyl-methyl - thiohydantoïn.

Formed in like manner from p-tolyl-thiocarb-imide and alanine (Aschan, B. 17, 427). Minute prisms. On heating with alcoholic potash it is converted by hydrolysis into a salt of the oily NHO,H,CS.NH.CHMe.CO,H, which slowly changes, in the free state, back into the hydantoïn.

o-Tolyl-di-methyl-thiohydantoin

CMe₂ CO .N(C,H₁). [175°]. Formed from o-tolylthiocarbimide and a-amido-isobutyric acid (Marckwald, B. 24, 3284). Needles, v. sol. hot

p-Tolyl-di-methyl-thiohydantoin. [85°]. Formed in like manner from p-tolyl-thiocarbimide. Crystals, v. sol. most solvents. o-TOLYL-METHYL-TWIO-UREA

NHMe.CS.NHC,H,. [153°]. Formed, from methyl-thiocarbimide and o-toluidine in alcohol (Dixon, C. J. 55, 622). Pearly crystals, m. sol. hot water, sol. alcohol.

p-Tolyl-me.hyl-thio-urea. [126°]. Formed inlike manner from p-toluidine. Vitreous prisms, v. sol, hot water.

Reference .- TOLYL-THIO-UREA

Reference.—TOLYL-THIO-UREA.

o-TOLYL-(a)-NAPHTHYLAMINE O₁,H₁₅N
i.e. O₁₀H₁,NH.O₄H₁Mo. [95°]. Formed by heating (a)-naphthol (1 mol.) with o-toluidine (2 mols.) and CaCl₂ (1 mol.) in sealed*tubes at 290°, the "rield being 37 p.c. of the theoretical amount (Friedländer, B. 16, 2084). Flat needles, v. sol. alcohol and ether.

o-Tolyl-(8)-naphthylamine C₁₀H,NH.C₆H₄Me. [96°]. Formed by heating a mixture of (3)-naphthol with o-toluidine and CaCl, at 280°. B'laghinou with o-toming the county plates (from ligroin), v. sol. alcohol.—B'2C.H.N.O., [110°]. Reddish-brown needles.

Bensoyl derivative [118°]. Plates.
p-Tolyl-(a)-naphthylamine C.,H.N. [79°].

(360° at 528 mm.). Formed by heating (a)-naphthylamine to the county of the county o

thol with p-toluidine and CaCl, at 280°, the yield being 50 p.c. Short prisms (from alcohol). Its solutions exhibit blue fluorescence.

p-Tolyl-(β)-naphthylamine. [104°]. Formed by heating p-toluidine hydrochloride with (3)-naphthol for 8 hours at 200° (Witt, B, 20, 578; cf. Friedländer, B. 16, 2078). Plates (from alcohol). Its solutions have violet-blue fluor-escence. Dissolved in isoamyl alcohol it is reescence. Dissolved in isoamyl alcohol it is reduced by Na to a hydride [44°] (Lamberger/a. Müller, B. 22, 1809). With nitroso-dimethylaniline hydrochloride and HOAo it yields c. saffranine C₁H₁N₂Cl(C₁H₁):C₆H₁NMe₂ (Witt, B. 21, 724). p-Tolyl-naphthyl-amine (10 6.), heated with nitroso-dimethylaniline hydrochloride (4 g.), ZnCl, (10 g.), and HOAc (100 c.c.), forms $C_{20}H_{12}(NH.C_{u}H_{4}Me)_{2}$ [225°], which yields an acetyl derivative [225°].

Acety bederivative [85°]. Needles. "Benzoyl derivative [139°]. Needles. Reference. — TETRA-BROMO-TOLYL-NAPHTHYE

DI-p-TOLYL-NAPHTHYLENE-DIAMINE $C_{10}H_{c}(NHC_{b}H_{r})_{p}$. [237°]. Formed by heating di-oxy-naphthalene with p-toluidine and p-toluidine hydrochloride (Annaheim, B. 20, 1373 Needles (from xylene). Gives a red colour o heating with solid ZnCl...
o-TOLYL-(a)-NAPHTHYL-THIO-UREA

CS(NHC, H.)(NHC, H.). [168°]. Formed be the action of o-tolyl thiocarbimide on (a)-napl thylamine or of (a)-naphthyl thiocarbimide of the control of the con o-toluidine (Mainzer, B. 15, 1416). Shon needles, sol. alcohol. Split up by cone. HClA ct 150° into o-toluidine, (a)-naphthylamino-tolyl-thiocarbimide, and (a)-naphthyl thic carbimide.

o - Tolyl - (β) - naphthyl - thio - urea [194° Formed from o-tolyl thiocarbimide and (3)-napl thylamine (M.).

 $p - \text{Tolyl} - (\alpha) - \text{naphthyl} - \text{thio} - \text{urea}$ Formed from p-tolyl thiocarbimide and (a)-naph thylamine (M.). Slender white needles.

p-Tolyl-(β) - naphthyl-thio-urea [164°]

Formed from p-tolyl thiocarbimide and (β) naphthylamine (M.). Decomposed by HClAq a 150° into p-toluidine, (β)-naphthylamine, p-toly thiocarbimide, and (B)-naphthyl thiocarbimide. p-TOLYL p-NITRO-BENZYL OXIDE

C.H.M.O.C.H., C.H., NO. [91°]. Formed from p-nitro-benzyl chloride and alcoholic C.H., ON (Frische, A. 224, 144). Yellowish plates, so ether.

TOLYL NITROSO-METHYL KETONE 2 Oxim of TOLYL-GLYOXAL

TOLYL-OXAMIC ACID v. vol. iii. p. 654. TOLYL-OXAMIDE v. OXALIC ACID.

o-TOLYL-OXAZOLINE $CH_2, N > C.C_1H_1$.

(255°). Formed by dissolving o-toluic bromo cthyl-amide in hot water and adding alkal (Salomon, B. 26, 1322). Oil. Evaporating with aqueous HCl (1 mol.) forms the compound C₁H_.,CO.O.CH_.,CH_.,NH_., while excess of HC gives C,H.,CO.NH.CH_.,CH,Cl. — B'C₂H₂N₁O₁, P. Tolyl-oxazoline C₁H₁NO. [66°]. (265°) Formed by decomposing C,H.,CO.NH.CH_.CH_.B with alkali. Needles.—B'C.H.N.O. [188°].

with alkali. Needles.—B'C₈H₁N₃O₇. [188°].—B'₂H₂PtCl₆. [186°].

DI-o-TOLYL OXIDE (C.H.Me)2O. Cresy ether. (272°-278°). S.G. ^{24°8} 1.047. A produc of the distillation of Al(OC₆H₄Me), (Gladstone a Tribe, C. J. 49, 27). Oil, smelling like geraniun

Di-m-tolyl oxide $(C,H_1)_2O$. $(284^\circ-288^\circ)$ μ_a 1-5576 at 16°. V.D. 193-9. A product odistillation of aluminium thymol Al $(OC_{10}H_{12})$ (Gladstone a. Tribe, C. J. 41, 13). Oil. Fi-p-tolyl oxide $(C,H_1)_2O$. (50°) . $(270^\circ-800^\circ)$

Formed by distilling aluminium p-cresol (C. a T.). Prisms (from alcohol).

Isomeride [165°]. Formed by heating p-cresol with ZnCl₂ (Busch, B. 17, 2688). Crys tals, volatile with steam.

DI-TOLYL-OXINDOLE $C_0H_1 < \binom{C(C_1H_1)_2}{NH} > CO$

Toluisatin. [200°]. Formed by adding toluent to a solution of isatin in H₂SO₄ (Baeyer a Lazarus, B. 18, 2638). Needles, v. sol. alcoho. and ether, sol. aqueous alke, iis. Yields an acety derivative O₂H₁₂O(NAc) [143°] and an ethy derivative O₂H₁₂O(NEt) [108°], both being crystalline. talline.

TOLYL-OXY-ACETIC ACID v. Tolyl derivative of GLYCOLLIC ACID and OXY-TOLYL-ACETIC ACID. p-TOLYL OXY-ETHYL SULPHONE

The Solution of the state of the solution of t C, H, S, O, [84°].

Bensoyl derivative C.H., SO₂, C₂H₄, OBz. [176°]. Needles, sl. sol. hot alcohol. DI-o-TOLYL-PARABANIC ACID C₁, H₁₄N₂O₂

6.c. CO (N(C,H₁),CO [203°]. Formed by boiling ar alcoholic solution of oxalyl-di-tolyl-guanidine with conc. HClAq (Berger, B. 12, 1856). Small needles.

Di-p-tolyl-parabanic acid [144°]. Formed by boiling di- (or tri-) p-tolyl-guanidine dicyanide with alcohol and HCl (Landgrebe, B. 11, 978).

Vita atconol and HCI (Landgrees, B. 11, 978). Plates. Oxidised by potassium permanganate to CO\N(C_6H, CO_7H).CO [159°?].

p-TOLYL PENTADECYL KETONE
C_1H_1,CO.C_H,Me. [50°]. (262° at 15 mm.). Formed from palmityl chloride, toluene, and AlCl. (Krafft, B. 21, 2266). Needles (from alcohol). Vields at toluic acid on oxidation. Yields p-toluic acid on oxidation.

o-TOLYL-PENTHIAZOLINE C,III,NS i.e. C,H,C.S,-CH₂. Got by heating trimethylene

chlorobromide with thio toluic amide (Pinkus, B. 26, 1081). Oil, volatile with steam. hydrochloride gives a white compound with HgCl₂

p-Tolyl-penthiazoline [53°]. p-TOLYL-PHENTLIAZINE. Dihydride

C.H. N = N CH₂N.C.H., [151°]. Formed by the action of HNO2 on o-amido-benzyl-p-toluidine hydrochloride (Busch, B. 25, 450). Yellow plates (from alcohol).—B'HCl.—B₂H₂PtCl_e. [190°].—B'C₄H₃N₃O₇. [132°]. Dark-yellow needles.

p-TOLYL-PHENYL-ACETAMIDINE C₁H₁₈N₄

p-10111-FHENTE-ACETAMIDINE C_{1,}H₁₀N₂
de. C_{c,}H_{v,}CH₂C(N.O.,H,Me).NH₂ [119²). Formed
by heating phenyl-acetonitrile with p-toluidine
hydrochloride (Bernthsen, A. 184, 342). Crystals (from alcohol).—B'_{v,}H_pF(C₁; yellow prisms.
DI - p - TOLYL - DIPHENYLACETYLENE DIAMINE C₂₈H_{2,}N₂ i.e. C,H₁N·OPh.CPh:NO.H₁.
Idi²]. Formed together with B₂ C(B.N.O.H.

[161°]. Formed, together with Bz.CPh:NO,H, [116°], by heating benzil (1 mol.) with p-toluidine (2 mols.) at 130° (Bandrowski, M. 9, 690). Triclinic plates.

DI - TOLYL - PHENYLENE -DIAMINE v. PHENYLENE-DI-TOLYL-DIAMINE.

TOLYL PHOSPHATES.

Tri-o-tolyl-phosphate (C,H,O),PO. Formed by heating o-cresol with POCl, the yield being 95 p.c. (Heim, B. 16, 1767; Rapp, A. 224, 173). Oil, sol. alcohol and ether.

p-Tolyl phosphate PO(OC,H,)(OH), [116°]. Formed by the action of water on PO(OC,H,)Cls which is a product of the action of POCl, on p-cresol (Rapp, A. 224, 168). Plates, sol. alcohol, ether, and water.

Tri-ptolyl phosphate PO(OC,H,),. [78°]. Formed by heating p cresol with POCl,, the yield being 95 p.c. eColourless tables, insol. Aq. p - TOLYL - PHOSPHINE C,H,NH. [4°]. (178°). Formed by the action of AlCl, on a mixture of toluene and PCl, the resulting

C,H,PCl₂ [20°] (245°), being converted by water into C,H,P(OH)₂, which splits up on heating into tolyl-phosphine and toluene phosphonic acid C,H,PO,H, (Michaelis, B. 12, 1009; 18, 659; A. 212, 230). Oil with strong odour. Rapidly oxidised by air to C.H.P(OH). HI forms C.H.PH.I, crystallising in colourless needles.

p . TOLYL . PHTHALIDE C ... H ... O. i.c. $C_0H_1 < \frac{CO}{CH(E,H_2^2)} > 0.$ [129°]. Formed by reducing C,H,.CO.C,H,.CO,H in alcoholic solution with Zn and HCl (Gresly, A. 234, 235). Needles, sol. hot alcohol, imsol. NH, Aq.

Di - p - tolyl - phthalide $C_0H_4 < \frac{CO}{C(O_1H_1)_2} > O$. [116°]. Formed by heating phthalyl chloride (100 g.) with tolueno (450 g.) and AlCl. (Berchem, Bl. [2] 42, 168; cf. Friedel a. Crafts, Bl. [2] 35, 505). Prisms, sol. alcohol and ether.

TOLYL - PHTHALIMIDE v. Tolylimide of

PHTHALIC ACID. m-TOLYL-PROPIOLIC ACID C,H, CiC.CO,H. [109.5°]. Formed by boiling di-bromo-tolyl-propionic soid C.H., CHBr.CO.H with alcoholic potash (Müller, B. 20, 1215). AgNO.

gives an explosive white pp.
o-TOLYL-PROPIONIC ACID C,H,C,H,O,Monoclinic prisms (Young, B. 25, 9102).

m-Tolyl-propionic acid C,H,.CH2.CH2.CO.H. [43°]. Formed by reducing m-tolyl-acrylic soid with sodium-amalgam (Müller, B. 20, 1214; von Miller, B. 23, 1899). Needles (from ligroin), sol.

water, alcohol, and ether. Volatile with steam.

m-Tolyl-propionic acid [125°]. Formed by oxidation of m-isobutyl-toluene by HNO, (Effront, B. 17, 2330). Needles, sl. sol. hot water. AgA': crystals, sol. hot water.

p-Tolyl propionic acid. [116°] (Von Miller, B. 23, 1898); [120°] (Kröber, B. 23, 1033). Formed by reducing p-tolyl-acrylic acid. Condensed by hot H2SO, to oxy-methyl-indonaph-

Di-a-tolyl-propionic acid CII₂.C(C,H,)₂.CO₂H. [152°]. Prepared by adding toluene to a solution of pyruvic acid in H2SO, at -10° (Böttinger, B. 14, 1596; 15, 1474). Monoclinic crystals, sol. hot alcohol. Give u-di-tolyl-ethane on distillation with lime. Oxidised by KMnO, to di-phenyl-ethane tri-carboxylic acid .-- AgA'.

Ethyl ether EtA'. [145°]. Prisms. References. -- BROMO-, NITRO-, and OXY-,

TOLYL-PROPIONIC ACIDS.
7-TOLYL-PROPIONIC ALDEHYDE

C.H., CH2, CH2, CHO. (223°). S.G. 11 9941. Formed by the action of water on the corround (223°). S.G. 11 .9941. of CrO₂Cl₂ with the dymene got from camphor and P₂O₃ (Richter a. Schüchner, B. 17, 1931). Got also by distilling calcium p-tolyl-propionate with calcium formate (Miller, B. 23, 1082). Oil, smelling like peppermint. Volatile with steam. Yields p-toluic and terephthalic acids on oxida-

DI-o-TOLYL-PROPYLENE-DIAMINE

OHMe(NHC,H,).CH2.NHC,H, (280° at 120 mm.). Got by heating o-toluidine with propylene bromide (Bischoff, B. 25, 3276).

Acetyl derivative Cz, Hz, N.O. [1207].

Di.p-tolyl-propylene-diamine

C.H. (NHO,H.);. (277° at 48 mm.) (Bischoff, B.
25, 3277). Got from p-toluidine and C.H.Br. Oil.

Acetyl derivative C₂₁H₂₈N₂O₂. [114°], Bensoyl derivative C₂₁H₂₀N₂O₂. [152°]. o-TOLYL-PROPYLENE-y-THIO-URBA

C,H,NH.C N.CH. [126°]. Formed from s-o-tolyl-allyl-thio-urea and HCl (Prager, B. 22, 2999). Tables, sl. sol. hot water.—B'₂H₂PtCl₄. [178°]. Prisms.—B'C₆H₃N₄O₇. [176°]. Cubes. DI-o-TOLYL-PROPYLENE UREA

C.H. NC,H. CO. [93°]; Formed from di-otolyl-propylene-diamine and COCl, (Bischoff, B. 25, 3276). Prisms (from dilute alcohol).

Di-p-tolyl-propylene-urea. [130°]. d-TOLYL ISOPROPYL METONE

C.H.Me.CO.Pr. (236°). Formed from toluene, isobutyryl chloride and AlCl. (Claus, J. pr. [2] 46, 480). Oil, with bitter taste and aromatic odour. Yelds p-toluic and terephthalic acids on oxidation. Yields an oxim [92°]. May be reduced to p-tolyl-isopropyl-carbinol; an oil boiling above 300°.

DI-o-TOLYL-PYRAZINE HEXAHYDRIDE $\textbf{C}_{\bullet}\textbf{H}_{\bullet}\textbf{Me.N} \diagdown \begin{matrix} \textbf{CH}_2 \textbf{\cdot} \textbf{CH}_2 \\ \textbf{CH}_2 \textbf{\cdot} \textbf{CH}_2 \end{matrix} \searrow \textbf{N.C}_{\bullet}\textbf{H}_{\bullet}\textbf{Me.}$ Di-o-tolul-Formed from ethylene piperazine. [171°]. bromide, o toluidine, and Na CO, at 160° (Bischoff, B. 22, 1781; 23, 1982; cf. Mauthner a. Suida, M. 7, 233). Crystals (from ether).

Isemeride. [154°]. Formed by heating dio-tolyl-ethylene-diamine with chloro-acetic acid and NaOAc (Bischoff, B. 23, 2031). Thin needles (from alcohol).

Di-p-tolyl-pyrazine hexahydride

C,H,N,CH,N,CH, [188°]. Formed from p-toluidine and C.H.Br. in presence of NaOAc or Na₂CO₂. Prisms, sl. sol. alcohol. With NaNO₂ and HOAc it yields a di-nitrosoderivative [167°].

 $CH {\gtrless}^{CH.N.C_7H_4Me}_{CH:N}$ o-TOLYL-PYRAZOLE

(246.5° cor.). S.G. § 1.0868; 15 1.0753. Formed by boiling epichlorhydrin (1 mol.) with o-tolyl-hydrazine (2 mols.) and benzene, boiling off the

hydrazine (2 mols.) and benzene, boiling off the benzene, and heating the residue at 150° (Balbiano, G. 18, 368). Not reduced by boiling with alcohol and Na.—B',H,PtCl, [201°].—B'EtI. [100°]. Needles, v. e. sol. water.

Dihydritle O,H,N,,C,H,. (271°). S.G. a 1.084. Formed from acroloin tolyl-hydrazide and dilute (2 pc.) H,SO, Oil. Sol. fuming HClAq, but reppd. by water. K,Cr,O, and H,SO, give an indigo-blue colour.

-T-Tulyl-pyraxole. [33°]. (259° cor).

p-Tolyl-pyrazole. [33°]. (259° cor.). Formed, in like manner, from epichlorhydrin and p-tolyl-hydrazine. Yell-wish plates, sl. sol. hot water.—B'H.PlCl, 2aq: needles. [184°].—B'Etf. [105°]. Prisms, v. sol. water.

Dihydrids. [60:5°]. (282° i.V.). Formed from acrolein p-tolyl-flydrazide and dilute H.SO.. Got also hy verbaling actally negraph in the label of the state of the s

Got also by reducing p-tolyl-pyrazole in alcoholic solution by Na. Iridescent plates, sl. sol. hot water. Its acidified solution is coloured violetred by K,Cr,O,

CHMe.N.C.H. (262°). Formed by heating piperidine with p-promotoluene at 270° (Lellmann a. Just, B. 24, 2099). V. sol. alcohol and benzene.

p-TOLYL-PYRROLE C₁₁H₁₁N i.e. CH:CH>NC₆H₆Me. Got by dry distillation of

p-toluidine mucate (Lichtenstein, B. 14, 933). Converted by AcCl into crystalline C,H,NC,Ac. -B',HgCl,.

Di-p-tolyl-pyrrole CH:C(C,H,)

[197°]. Formed by treating di-p-tolyl-furfurane or (O,H,CO)₂C₂H₄ with NH₄OAo (Hollemann, R. T. C. 6, 73). Small plates with bluish lustre. Does not form a K derivative. Boiling HClAq gives a red resin. With isatin, after several days, it gives an intense red colour.
o-TOLYL-QUINAZOLINE DIHYDRIDE

 $C_{13}H_{14}N_2$ i.e. $C_6H_4 < \stackrel{N}{\underset{CH_2,N.C_6}{\text{CH}_2,N.C_6}}H_4Me$. Formed by reducing the formyl derivative of o-nitro-benzylo-toluidine with tin and HClAq (Paal a Busch, B. 22, 2701). Oil.—B'HSnCl,—B'HCl: amorphous.—B',H,PtCl, [210°]. Needles (from alcohol containing HCl).

Formed in like manner. Plates, v. sol. alcohol.

-B'HSnCl. (1859) Pure 2 -B'HSnCl₃. [165°].-B'HCl 2aq. [85°].-B'HCl. [251°].-B'₂H₂PtCl₆. [216°]. Yellow needles.

Methylo-iodide B'MeI. [186°]. Needles. p-Tolyl-quinazoline tetrahydride

C₆H₄ NH.ÇH₂ [127°]. Formed by reducing the dihydride in alcoholic solution by sodium. Needles, m. sol. alcohol. nitrosamine [100°]. Yields a crystalline hydrochloride.

 $\begin{array}{c} \textit{Reference.}{-} \text{Oxy-tolyl-guinazoline.} \\ \textit{(Py. 3)-o-Tolyl-Quinoline } \text{C}_{16}\text{H}_{13}\text{N} \quad \textit{i.e.} \\ \text{C}_{6}\text{H}_{1} {<} \text{CH:CH} \\ \text{N=C.C}_{6}\text{H}_{1}\text{Me}. \quad [77^{\circ}]. \quad \text{Formed by dis-} \end{array}$

tilling oxy-tolyl-quinoline (pseudoflavenol) with zinc-dust (Weidel a. Bamberger, M. 9, 108). Silky needles (from benzene).—B'₂H₂PtCl₆ (dried at 105°). Orange tables. m-Tolyl-isoquinoline $C_cH_i < CH:C.O_rH_r$

[52°]. Formed by heating (1)-chloro- (3)-m-tolyl-isoquinoline with HI and P for three hours at 170° (Heilmann, B. 23, 3168). Needles (from

pcTolyl-isoquinoline C.H. CH; C.C.H.

[78°]. Formed in like manner (Ruhemann, B. 3975). 24, 3975). Needles.—B'HI.—B'H,OrO,—B'₂H₂PtOl₈.—B'C₈H₃N₃O₇. Yellow needles.

Reference.—OXY-TOLYL-QUINOLINE. TETRA-m-TOLYL-SILICANE Si(C,H.),. [1512]. (above 550°). S.G. 22 1-1188. Formed from m-bromo-toluene, SiCl., and sodium (Polis, B. 19, 1021). Prisms (from ether), v. sol. benz-

Tetra-p-tolyl-silicane Si(C,H,), [228°]. (above 450°). S.G. 20 1.0793. Formed from SiCl,, p-bromo-toluene, ether, Na, and a little EtOAc (Polio, B. 18, 1542; 19, 1019). Monoclinic crystals (from chloroform). Decomposed by conc. HNO, forming silica and di-p-nitrotoluene [72°].

TETRA-O-TOLYL SILICATE Si(OC,H,) (c. 437°). Formed by heating o-cresol with Sicl, the yield being 90 p.c. of the theoretical quantity (Hertkorn, B. 18, 1686). Oil, v. sol. alcohol. Decomposed by hot water into silica and o-cresol.

Tetra-m-tolyl silicate Si(OC,H,),. (445°)

at 720 mm. Syrup (H.).

Tetra-p-tolyl silicate Si(OC,H.),. [70°]
(444°). Tables or prisms, v. sol. benzene (H.). [70°].

p-TOLYL SILICO CHLORIDE C,H,SiCl, 219°). Formed from Hg(C,H,), and SiCl, at 310° (Ladenburg, A. 173, 165). Liquid, converged by dilute aqueous ammonia into C,H,,SiO.OH c. 150°], which is converted at 200° into solid C,H,SiO),O.

TOLYL SULPHATES. o-Tolyl sulphuric acid

[1:2] C.H.Me.O.SO.OH. Occurs in small quanrity in the urine of horses (Preusse, H. 2, 355). Prepared from C₆H₄Me.OK and K₂S₂O₇ (Baumann, B. 11, 1911). The K salt crystallises in plates, m. sol. water.

m-Tolyl sulphuric acid C.H.Me.O.SO.OH. Occurs in very small quantity in horses' urine (P.).

p-Tolyl sulphuric acid C.H.Me.O.SO...OH. Occurs in the urine of horses and cows (Baumann, B. 9, 1389, 1716; Städeler, A. 77, 18). Formed by boiling potassium p-cresol with K₄S₂O₂. The K salt is sl. sol. cold alcohol.

DI-o-TOLYL-SULPHAZIDE C14H18N2SO2 i.e. [2:1] C.H.Me.NH.NH.SO..C.T. Me [1:2]. Tolyl-toluene-sulphazide. [142]. Obtained by the action of SO, upon o-diazo-toluene in alcoholic solution. White glistening needles (Limpricht, B. 20, 1241). When boiled with baryta-water it decomposes into o-toluene-sulphinic acid,

toluene, and nitrogen.
Di-p-tolyl-sulphazide C₁₄H₁₆N₂SO₂ i.e. Tolyl-[4:1] C.H.Me.NH.NH.SO., C.H.Me [1:4]. Tolyltoluene-sulphazide. [140°]. Formed in like manner from p-diazo-toluene (L.). Small needles. By boiling with baryta-water it is decomposed into p-toluene-sulphinic acid, toluene, and nitrogen.

Reference. - NITRO-DI-TOLYL-SULPHAZIDE.

DI-p-TOLYL SULPHIDE S(C₄H₄Me)_r [57°]. (above 300°). Formed by distillation of lead p-tolyl-mercaptide (Otto, B. 12, 1175). Small needles, insol. water, sol. alcohol. Yields di-p-tolyl-mercaptide (District March 1988). tolyl sulphone on oxidation by KMnO.

Di-m-tolyl disulphide C.H.

C₁₁H₁₁S₂ (C₄H₄Me)₂S₂. Formed from m-tolyl morcaptan by treatment with dilute HNO₄ (Hübner a. Post, A. 169, 51). Liquid at -22°. Decomposed on boiling or by atmospheric oxidation of its ammoniacal alcoholic solution (Leuckart, J. pr. [2]

Di-p-tolyl disulphide (C.H.Me)2S2. Formed from p-tolyl mercaptan by atmospheric oxidation (Märcker, A. 136, 88) or by the acor by treatment with ICy (Thurnauer, B. 23, 769). Formed also by the action of H₂S on a warm dilute solution of toluene p-sulphinic acid in alcohol (Otto, J. pr. [2] 37, 211). Crystals, v. e. sol. ether. Begins to boil at 307° i.V. but decomposes on dissillation. Alcoholic K.S. forms p-tolyl mercaptan (Otto a. Rössing, B. 19, 8129).

Di p-telyl tetrasulphide (C.H.Me), SO...
°]. Formed by the action of H.S on a cong. solution of toluene p-sulphinic acid (Otto, J. pr. [2] 87, 211). Small plates, insol. water, v. sol. ether.

References .- DI-AMIDO-, DI-BROMO-, and OXX-DI-TOLYL-SULPHIDE.

o-TOLYL SULPHOCYANIDE C.H.Me.S.CN. (c. 245°). Formed by adding cuprous sulphocyanide in KSCy to a solution of o-diazo-toluene (Thurnauer, B. 23, 770). Yellowish-red oil with

(Intrinator, B. 25, 170). Itellowish-red on with unpleasant odour.

p-Tolyl sulphocyanide. (c. 248°). Formed in like manner, and also by passing CyCl through alcohol containing lead p-talyl mercaptide. Liquid, solidifying below 0°.

DI-p-TOLYL SULPHONE (C.H.Me), SO., [158°]. (405°) at 714 mm. Prepared by the action of AlCl, on a mixture of toluene and telepane assulphonic chloride (Bockurta, a. Otto.) toluene p-sulphonic chloride (Beckurts a. Otto. B. 11, 2068; 12, 1177; cf. Michael, B. 10, 584). Formed by the action of fuming H₂90, or SO₂ on tolucne (Deville, A. 44, 306; Otto a. Grüber, A. 154, 193) and by the action of KMnO, and HOAc on di-p-tolyl sulphide. Prisms (from benzene), gl. sol. cold acohol and ether. Potashfusior yields p-cresol and diphenyl (Otto, B. 19, 2426).

DITOLYL DISULPHONIC ACID

[1:4:5] C₀H₃Me(SO₃H).C₀H₃Me(SO₄H) [5:1:4]. Formed from di-amido-ditolyl disulphonia acid by diazotisation followed by boiling with alcoby diazonstation followed by boiling with acco-hol (Halle, A. 270, 363). Crystalm v. e. sol. water, m. sol. alcohol, insol. ether.—K.A". Hexa-gonal plates.—KHA": prisms.—BAA" 5aq.

Chloride C₁₄H₁₂S₂O₂(Cl., [229°].

Amide C₁₄H₁₂S₂O₃(NH₂)₂.

Needles.

p-TOLYL-SULPHONO-ACETIC ACID.

C.II.Me.SO.,CH.,CO.H. [118°]. Permed from sodium benzene sulphinate and chloro-acetic sodium renzene supninate and chloro-accuc acid (Gabriel, B. 14, 834). Crystals (from benz-ene), sl. sol. hot water. Cl passed into its aqueous solution forms C,H_850_CHCl_ [114°]. Br forms C,H_850_CHBr, and C,H_850_CH_Br (Otto, J. pr. [2] 40, 542).—AgA': trimetric tables. Ethyl ether EtA'. Converted by bromine (2 mols.) at 90° into C,H_850_CBr_CO_Et which on sanonification by cold NaOHAc yields

on saponification by cold NaOHAq yields C,H, SO, CHBr, [1179

p.TOLYL-SULPHONO-ACETONE CH, CO.CH, SO, C, H, Me. [51°]. Formed by heating sodium toluene p-sulphinate with chloroneeding southm tolucing-supplinate with chloro-acctone in alcohol (Oito, J. pr. [2] 36, 425). Needles, v. sol. alcohol. Bromine forms Cha.Br.CO.CH.,SO.C.H., [130°], m. sol. alcohol. Di.p-tolyl-di-sulphono-acctone CO(CH.,SO.C.H.,Me). Formed by heating CH.,Br.CO.CH.,SO.C.H., with sodium tolucine p-

sulphinate in alcoholic solution. Plates, v. sol. hot HOAc and chloroform

DI-TOLYL DI - SULPHONO - DI - ETHYL . AMINE NH(C₂H₁,SO₂C₂H₁)₂. Formed by heating di-tolyl ethylene disulphone with NH₂Aq (Otto, J. pr. [2] 30, 859).—B'HCl. [201°].—B'HAuCl; dark-yellow needles.

DI - TOLYL - DI - SULPHONU - DI - ELINE OXIDE O(C.H., SO., C.H.), [84°]. Formed by the action of conc. KOHAq on C.H. (SO.C.H.), and as a by-product in the preparation of C.H., SO., C.H., Q.H. (55°) by the action of dilute KOHAq on the same body (Utto a. Tröger, B. 26, 944; cf. J. pr. (2) 80, 171, 321).

TOLYL DISULPHOXIDE v. Tolyl ether of DI - TOLYL - DI - SULPHONO - DI - ETHYL

TOLUENE THIOSULPHONIC ACID.

Di-p-tolyl sulphoxide SO(O,H,Me), [92°]. Formed from toluene, SOCl,, and AlCl, (Parker, B. 28, 1844). Flat needles (from ligroin), v. e. sol. benzene. Reduced by sodi.m and alcohol to di-telyl sulphide [56°]. KMnO, in HOAo to di-tolyl sulphide [56°]. KMnO, in HOAc forms di-tolyl sulphone [158°].

DI-o-TOLYL-TETRAZINE C₁₈H₁₈N₄ i.e.

C,H,N < N:CH NC,H,. [141°]. Formed from o-tolyl-hydrazine, chloroform, and alcoholic potash (Ruhemann, C. J. 57, 52). Crystals. Yields crystrlline C₁₄H₁(SO₂H)N₄ and O₁₈H₁₆(NO₂)N₄ (207°).—B'HCl: needles.

Methylo-iodide B'Mol. [198°). Nodules. Di-p-tolyl-tetrazine C₁₄H₁₆N₄. Formed in

like manner. B'HCl: very unstable white needles. Methylo-iodide B'MeI. [242°]. Needles. o-TOLYL-THIAZOLE DIHYDRIDE

C.H.Me.C.N.CH. (282°). Formed from thioo-toluic amide and ethylene bromide (Gabriel a. Heymann, B.24, 786). Got also by heating o-toluic bromo-ethyl-amide with P2S3 (Salomon, B. 26, 1329). Converted by bromine-water into taurine and o - toluic acid. - B'2H,PtCla. [199°].brd.H.N.O., [132°].
p-Tolyl-thiazole dihydride. [81°]. Prepared in like manner. Tables.

in like manner. Tables.
p.TOLYL-THIOBIURET C.H., IN., S... [158].
Formed by fusing p-toluidine (2 pts.) with persulphocyanic acid (1 pt.) (Tursini, B. 17, 584).
Minute needles, sol. NaOIIAq. Yields C.H., NAS, Et [134], crystallising from alcohol in needles, and C.H., aAoN, S. [166], orystallising in needles.
p.TOLYL-S-THIOGARBAMIC ACID

[1:2]O.H.Mt.NH.CS.OH.

Ethyl ether C.H.N:C(SH).OEt. Tolyl-thiourethane. Formed by heating o-tolyl-thiocarbinide with alcohol at 130° (Liebermann a. Natanson, B. 13, 1576; A. 207, 161). Oil, sol. alkalis.—Q₀H_{1,2}AgNSO: white pp. insol. NH₁Aq. Converted by Mel into C₂H₁N(OEt).SMe, and by Let into C₂H₂N(OEt).SEt, both being oils boiling above 250°

m-Tolyl-\$-thiocarbamic acid

(1:81C.H.Me.NH.CS.OH.

Ethyl ether C,H,N:C(SH).OEt. [68°].

Formed in like manner (L. a. N.). Yields

C₁₆H_{1.}AgNSO and oily C₁₆H₁₂EtNSO.

p-Tolyl.3-thiocarbamic acid. Ethyl ether Yields

p-Tolyl-\$\text{0.th}\t

ether.

O-Tolyl-a-thiocarbamic acid C.H.NH.CO.SH.

Methyl ether MeA'. [70°]. Formed by
heating C.H.NH.C(NC.H.).SMe with dilute
H.SO. at 140° (Will a. Bielschowski, B. 15

1817). Plates.

Ethyl ether Eth'. [60°]. Tables.

**Tolyl-a-thiocarbamic acid NHC.H.,CO.SH.

Methyl ether MeA'. [107°]. Formed by
heating C.H.NH.C(NC.H.).SMe with dilute
H.SO. at 170°. Needles. v. sol. alcohol and

H.SO, at 170°. Needles, v. sol. alcohol and

Ethyl ether EtA'. [79°]. Formed from

p-toluidine and Cl.CO.SEt. Needles. EtSH and tolyl cyanate on distillation. Yields.

Ethylene derivative
CO \(\frac{N(C,H,)}{S} \rightarrow C_8 H_4. \quad [88°] [88°]. Long slender needles.

o-Tolyl-di-thio-carbamic acid

C.H.NH.CS.SH.—NiA'₂. Brown needles, insol. water.—BaA'₂. Plates (Losanitsch, B. 24, 3027). Forms di-o-tolyl-thio-urea on heating.

Methyl ether Med. [132°]. Formed from the Ba salt and Mel. White needles.

Ethyl ether Eth. [72°]. Formed by heating C,H,NH.C(NC,H,).SEt with CS₂ at 160° (Will a. Bielschowski, B. 15, 1817). Prisms. Ethylene derivative CieHuNS, i.e.

 $CS < N(C,H_1) > C_2H_4$. [129°]. Formed by heating

C,H,N.C S C2H, with CS2 at 200°. Yields

C10H11NS2MeI, crystallising in prisms [151°]. m-Tolyl-di-thio-carbamic acid

C,H,NH.CS.SH.

 $Salts.-BaA'_2$. Formed from m-toluidine, CS_2 , and $Ba(OH)_2$ in alcohol (Losanitsch, B.24, 3027). Needles, sol. water, insol. cold alcohol.-

A'. Yellowish-brown plates.

Methyl ether McA'. [89°]. Needles.
p-Tolyl-di-thic-carbanic acid C,H,NH.CS.H. CS₂, alcohol, and NH₃Aq (Losanitsch, B. 24, 3026). Yellowish prisms, sol. water, insol. alcohol.—BaA'₂. Needles.—NiA'₂. Formed from p-toluidine, CS₂, ammoniaçal NiSO₄, and alcohol. Brown needles, sol. alcohol, insol. water.

Methyl ether MeA'. [84°]. Prisms. Ethyl ether EtA'. [74°]. Formed by heating NHC,H,.C(NC,H,).SEt with CS₂ at 160° (W. a. B.). Needles, split up by heat into p-tolyl thiocarbimide and EtSH.

Ethylene other CS < S C,H, [126°]. Crystals. Yields a methylo-iodide [107°]. which is converted by aniline into C₁₆H₁₈N₂S [128°], and by o-toluidine into C₁₇H₁₈N₂S [82°]. Reference. - NITRO - TOLYL - THIOCARBAMIC ETHER.

q. TOLYL - THIOCARBAZIC ACID o - Tolyl hydrazide C,H,NH.NH.CS.SNH,NHC,H,. Formed from o-tolyt-hydrazine, ether, and CS. (Preund, B. 24, 4200). Prismatic tables, insol. ether, decomposed by water and alcohol. The p-isomeride melts at 109°.

DI-o-TOLYL-THIOCARBAZIDE C15H18N4S i.e. CS(NH.NHC₆H,Me)₂. [130°]. Formed from o-tolyl-thiocarbazic acid and o-tolyl-hydrazine at 90° (Preund, B. 24, 4201). Needles, sol. alco-

hol, insol. Aq.
DI-p-tolyl-thiocarbazide. [121°]. Formed in like manner at 110° (Preund, B. 24, 4194).

Plates, v. sol. hot alcohol.

Di-o-tolyl-thiosemicarbazide C15H17N2S i.e. itisol. Aq.

Di-p-tolyl-thiosemicarbaside. [154°]. Formed in like manner (D.). Prisms, v. e. sol. hot alcoop-Di-telyl-thiosemicarbaside [4:1]C_H_Me.NH.CS.NH.NHC_H_Me [1:2]. [142°].

Formed from p-tolyl-thiocarbimide and o-tolylhydrazine (D.). Prisms, sl. sol. hot alcohol. Isomeride

[2:1]C.H.Me.NH.CS.NH.NHC.H.Me[1:4]. [163°]. Formed from o-tolyl-thiocarbimide and p-tolylhydrazine (Dixon, C. J. 61, 1015). Prisms, m. sol. hot alcohol.

DI-0-TOLYL-THIOCARBAZONE C15H16N.Si.s. C.H.N.N.CS.NH.NHC,H,. [168°]. Formed from di-o-tolyl-thiocarbazide and alcoholic potash (Preund, B. 24, 4201). Blue-black needles, v. sol. chloroform, sl. sol. alcohol. Conc. H.SO. forms a bluish green solution.

Di-p-tolyl-thiocarbazone. [105°]. Formed in like manner. Dark-blue amorphous flakes.

o-TOLYL-THIOCARBIMIDE C.H.NS [1:2]C.H.Me.N.CS. (239°). Formed from dio-tolyl-thio-urea by distilling with P₂O₃ (Staats, B. 13, 136), by heating with aqueous H₂PO₄ (Hofmann, B. 15, 986; Mainzer, B. 16, 2017), or by boiling with fuming HClAq (Girard, B. 6,

Reactions .- 1. Chlorine forms C.H., NCLCSCI (218°), which is converted by alcohol into a mixture of di-o-tolyl-urea and o-tolyl-carbamic ether (Lachmann, B. 12, 1349) .- 2. Chloro-acetic acid and alcohol at 150° form C,H, N:C<S,CH₂ crystallising in needles [120°], decomposed by boiling baryta-water into o-toluidine, CO2, and 3. PhOMe and AlCl₂ on warming form C,H,NH.CS.C₆H,OMe [95°] (Tust a. Gattermann, B. 25, 3528). PhOEt and AlCl₂ give C₁₆H₁₇NSC [116°].

m-Tolyl-thiocarbimide C.H.N.CS. at 732 mm. Formed by boiling di-m-tolyl urea with conc. HClAq (Weith a. Landolt, B. 8, 719). Heavy oil. Converted by copper-powder at 220°

into m-toluic nitrile.

n-town intrie.

p-Tolyl-thiocarbimide [1:4] C_sH₁Mc.N:CS.

[26⁵]. (237°). Formed by heating di-p-tolyl
thio-urea with P₂O_s or aqueous H₁PO_s of S.G.

17 (Hofmann, B. 1, 173; 15, 986; Staats, B.

13, 135). Formed also, together with phenyl
thiocarbimide, by heating PhN:C:NC.H, with

CS₂ at 190° (Huhn, B. 19, 2409). Needles (from

other) v sol elsebol.

ether), v. sol. alcohol.

Reactions .- 1. Ammonia forms tolyl-thiourea, and other bases act in like manner.— 2. Bromine forms C.H.NBr.CSBr, which readily gives off Br, leaving (C,H,NCS)2Br2 crystallising in plates decomposing at 210° (Helmers, B. 20, 790).—2. Chlorins forms (O,H,NCS),Cl., whence dilute alcohol gives (C,H,NCS),O [139°] crystallising in needles.—3. CH,Cl.CO,H and alcohol at 150° form C,H,N:C < S.CH₂ [162°] (Völtzkoff. B. 13, 1579).—4. Warmed with toluene and AlCl, it gives O.H.NH.CS.C.H., [106].—5. Heated with AlCl, it yields (C.H.N.CS).S [176°] (Friedmann a. Gattermann, B. 25, 3525).6. C.H.OMe and AlCl, react, with formation of O.H.NH.CS.C.H.,OMe [157°].—7. C.H.OEt and AlCl, give O.H.N.CS [151°], which may be oxidised to C., H., NOS [170°].

DI.-TOLYL DI-THIO-CARBONATE

CO(S.C.H.Me)... [91°]. Formed from p-tolyl

CO(SC,H,Me), [91°]. Formed from p-tolyl mercaptan and COCl₂. It is also a by-product

in the action of p-diazo-toluene chloride on potassium xanthate (Leuckart, J. pr. [2] 41, 190). Needles (from alcohol).

TRI-TOLYL TRI-THIOGYANURATE
(O₄H₄Me.SCy), [114°]. Formed from sodium
p-tolyl mercaptan and cyanuric shloride
(Klason, J. pr. [2] 33, 120). Crystals (from HOAc).

o-TOLYL-THIOHYDANTOIN C,H, NSO i.e CS<NH. CH₂>CO. [136°]. Formed from o-tolyl-thiocarbimide and amido-acetic acid (Marckwald, B. 24, 3281). Plates, v. sol. alcohol, sl. sol. ligroin.

p-Tolyl-thiohy lantoin [210°] (M.). Formed as above (M.; cf. Aschan, B. 17, 426). Flat prisms, sol. alkalis.

Isomeride [183°]. Formed by fusing CH_Cl.CO.NHC,H, with thio-urea (P. Meyer, B.

DI-p-TOLYL-THIOPHENE C18H18 $CH: C(C_{\bullet}H_{\bullet}Me) > S.$ [171°]. Formed bу heating di.p-tolyl-furfurane with P.S. (Hollemann, R. T. C. 6, 74). Small plates (from alcohol). Gives an intense dark-green colour with isatin and H2SO,.

o-TOLYL-THIO-UREA NH ... CS.NHC, H, Me. [155°]. Formed from o-tolyl thiocarbimide and NII, Aq (Staats, B. 13, 136). V. sol. hot water and alcohol, sl. sol. ether.

Acetyl derivative NHAc.CS.NHC, H.Me.

[184°]. Formed from acetyl thiocarbimide and otoluidine in alcohol (Dixon, C. J. 55, 804). Pale lemon-yellow prisms, insol. water, sol. alcohol. Benzoyl derivative

NHliz.CS.NHC,H.Me. [119°]. Formed in Wke manner (Dixon, C. J. 55, 623). Pale-yellow Formed in Wke

prisms, blackened by AgNO₃.

Di-o-tolyl-thio-urea CS(NH.C₄H₄Me)₂. [158°]. Formed from o-toluidine and CS₂ (Girard, B. 4, 985; Berger, B. 12, 1854; Ador a. Rilliet, B. 12, 2301). Long needles, v. sol. hot alcohol. Converted by heating with MeI into the hydroidide of di-tolyl-methyl-thiourea C. H., N.S. which may be represented as 'methyl di-oblylwhich may be represented as 'methyl di-o-tolyl-imido- thiocarbamate' C.H.N.C(SMe).NHC,H., This body melts at 60°, while the corresponding ethyl derivative melts at 51°. The ethylene de-rivative [91°] may be represented by the formula C,H,N:C \(\frac{N(C,H_1)}{S} \) C2H4 (Will a. Bielschowski, The isomeric compound B. 15, • 1316). got by boiling the methylo-iodide of the ethylene derivative of p-tolyl-di-thio-carbamic acid with o-toluidine.

m-Tolyl-thio-urea NHC,H,. S.NH2. [103°]. Formed from m-tolyl thiocarbimide and ammonia (Weith a. Landolt, B. 8, 719). Prisms, monia (Weith a. Landolt, B. 8, 719). Prisms, m. sol. hot water, v. sol. shochol and ether. Di-m-tolyl-thio-urea CS(MHC,H.), [1229]. Formed from m-toluidine, CS, and alcohol (W.

a. L.). Needles, v. sol. alcohol, nearly insol. hot water.

p-Tolyl-thio-ures NHC,H, CS,NH₂. [188°]. (O. s. W.); [182°] (S.). Formed by heating p-toluidine hydrochloride with ammonium sulphocyapide (De Clermont a. Wehrlin, C. R. 83, 347). Formed also from p-tolyl-thiocarbimide ammonia (Staats, B. 18, 136). Plates (from alcohol) with bitter taste, sl. sol. cold water, m. sol, alcohol.

Acetyl derivative NHC,H,CS.NHAc. [176°]. Formed from acetyl sulphocyanide and p-toluidine (Miguel, Bl. [2] 28, 103). Needles, v. e. sol. hot alcohol, v. sol. ether.

Di.p-tolyl-thio-urea CS(NHC,H,Me), [176°]. Formed by boiling p-toluidine with CS₂ and alcohol (Sell, A. 126, 160). It is also a product of the action of allyl-thiocarbimide on an alcoholic solution of p-toluidine (Maly, Z. [2] 5, alcoholo solution of p-toluidine (Maiy, Z. [2] 5, 258). Trimetric prisms (Levin, J. 1882, 384), insol. water, nearly insol. cold alcohol. In alcoholic solution it is converted by HgO into di-p-tolyl-urea. In benzene solution COCl, forms C₁₈H_{1,1}N₂S₂ [116°] (Will, B. 14, 1487). CSCl, forms C₁₈H_{1,1}N₂S₂ [109°] (Freund a. Wolf, B. 25, 1465). MeI forms C,H,N:C(NHC,H,).SMe 1465). MeI forms C,H,N:C(NHC,H,).SMe [128°], orystallising in needles, split up by heat into C(NC,H,), [60°] and HSMe, converted by heating with acids or alkalis into di-o-tolylurea and MeSH, and forming the salts B'HCl [173°] and E'H,SO, [156°]. Et I forms the corresponding O,H₂₀N, [8 [87°], while ethylene bromide gives C,H,N:C(NC,H) [112°], which yields B'H.SO, [194°] and a hydrochloride [219°] (Will a. Bielschowski, B. 14, 1492; 15, 1309).

Reference.—Nitro- and Оху- толул-тню-

p-TOLYL - TOLUTRIAZINE C₁₂H₁₂N₂ i.e. CH:CH.C.N.CH₂ CMe:CH.C.N.NC₂H₄Me Formed by heating o-amido-azo-toluene with formic paraldehyde and alcohol at 140° (Goldschmidt a. Poltzer, B. 24, 1008). Prisms, v. sol. hot alcohol.—B'HCl. [220°].—B'₂H₂PtCl₂. [216°]. Yellow crystalline pp. o-TOLYL-URAZOLE C₂H₂N₃O₂ i.e.

C,H,N<NH.CO. [170°]. Got by heating otolyl-hydrazine hydrochloride with urea (Pinner,

B. 21, 1219). White leaflets, v. sol. hot water. p-Tolyl-urazole. [274°]. Yellowish needles, v. sl. sol. hot water. o-TOLYL-UREA C.H. N.O i.e.

NH, CO.NH.C, H; Me [1:2]. [185°]. Formed from o-toluidine hydrochloride and potassium cyanate/ (Cosack, B. 18, 1089). Plates, sol. alcohol, ether, and hot water.

Bensoyl derivative CO(NHBz).NHC,H,. [210°]. Formed from o-tolyl cyanate and benzamide at 125° (Gattermann a. Cantzler, B. 25. Needles. 1088).

m-Tolyl-urea NH,.CO.NHC,H,Me [1:8]: [142°]. Formed from m-toluidine hydrochloride and potassium cyanate (Cosack, B. 12, 1450; 13, 1089). Needles or tables (from alcohol) or plates (from water).

p-Tolyl-urea NH_xCO.NHC_xH₄Me [1:4]. [172°] (C.); [180°] (St.; P.). Formed in like manner (C.; cf. Sell, C. J. 16, 190). Formed also by the action of p-toluidine on mercuric

fulminate (Steiner, B. 8, 519), and also from p-toluamidoxim, benzene sulphonic acid, NaOH, and CHCl₂ (Pinnow, B. 24, 4167). Needles, sol. hot water, v. sl. sol. ligroin.

Di-o-tolyl-urea CO(NHC,H.), [248°] (B.); [254°] (W.); [256°] (Barr, B. 19, 1769).

Formation.—1. By the action of 'alcohol or water at 100° on the dichloride of o-toluic nitrile (Lachmann, B. 12, 1849).—2. From otolvidine hydrochloride and cyanamide (Berger, B. 12, 1859.—8. From tolyl cyanate and water (Nevile a. Winther, B. 12, 2325).—4. From o-toluidine and COCl₂ (Girard, B. 6, 444).—5. By heating o-toluidine with urea (G.).—6. A product of the distillation of o-tolyl-amido-acetic (W.).—6. A product of the control of the cont acid (Widman, J. pr. [2] 38, 303).—7. By the action of Ac₂O and benzene on the o-toluide of o-tolyl-imido-diacetic acid (Bischoff, B. 23, 1995).

Properties.—Needles (from HOAc), insol. ether, sl. sol. alcohol. Not volatile with steam. bi-m-tolyl-urea CO(NH.C.+H,Me), [203°] (G. a. C.); [217°] (C). Formed from m-tolyl cyanate and m-toluidine (Gattermann a. Cantz-leaft and m-toluidine) ler, 25, 1089), by the action of ClCO₂Et on m-toluidine, by heating m-tolyl-carbamic ether with water, and by heating m-tolyl-urea with m-toluidine at 160° (Cosack, B. 12, 1450; 13,

1090). Needlos (from alcohol), insol. water.

Di-p-tolyl-urea CO(NH.O₂H.Me)₂. [255°].

Formation.—1. By boiling an alcoholic solution of di-p-tolyl-thio-urea with HgO as long as HgS is formed (Sell, C. J. 16, 190; A. 126, 161).—2. By passing COCl, into p-toluidine dissolved in chloroform (Michler, B. 9, 710; Kühn, a. Henschel, B. 21, 505).—3. By heating tolylurea with p-toluidine at 160° (Weith, B. 9, 821).
4. From p-tolyl-cyanate and p-toluidine (Gattermann a. Cantzler, B. 25, 1089).

Properties.-Needles, insol. water, sl. sol. cold

alcohol.

Tri-p-tolyl-urea C₂₂H₂₂N₂O. [189°]. Got from (C,H,)₂N.COCl and p-toluidine (Hammerich, B. 25, 1822). Needles, sol. warm benzene, insol. ether. Gives a benzoyl derivative [137°].

Tetra-p-tolyl-urea C.,H.,N2O. [80°]. Got from $(C_7H_7)_2N.COC!$ and di-p-tolyl-amine. Needles, v. e. sol. alcohol.

References .- AMIDO. NITRO-, and Oxy-

TOLYL.XYLIDINE C.H., N i.e.

C.H., Me.NH.C., H., Mey. [70°]. (c. 800° at 487 mm.). Silky needles (from alcohol) (Girard a.

mm.). Sury necessive Vogt, Bl. [2] 18, 69).

o-TOLYL m-XYLYL KETONE 'C₁₆H₁₁O i.e. (330°) at and [1:2] C_tH₄Me,CO.C_tH₄Me, [1:2:3]. (830°) at 728 mm, Formed from o-teluic chloride and m-xylene (Smith, B. 24, 4050). Oil. Converted by hydroxylamine at 120° into a mixture of anilides

TONKA BEANS, the fruit of Dipterize oderata, contains coumarin (q. v.) (Boullay s. Boutron-Charlard, J. Ph. 11, 426; [3] 7, 160).

TRAGACANTH GUM. Exudes from Astra-

galus verus, a treb growing in Armenia and the north of Persia. It swells up in water, about one-half of it dissolving. It contains arabin,

TRANSPIRATION. Graham, in 1846 and 1849, applied the term 'transpiration' to the passage of gases through capillary tubes into a

vacuum (c. T. 1846, 578; 1849, 849). The rates of transpiration of different gases bear constant relations to each other; but these rates have not been connected in any definite ways with the compositions of the gases. M. M. P. M.

TREE GUM v. XYLAN. TREHALOSE v. SUGAR.

TREHALUM $C_{2,H_{\rm p}O_{\rm pl}}$. S. 06 at 17°; 1·8 at 100°. [a]_D = +179°. Occurs in Trehala manna (Scheibler a. Mittelmeier, B. 26, 1336). Tasteless, minute prisms. Very hygroscopic. Does not reduce Fehling's solution. Does not react with phenyl-hydrazine. Boiling dilute H2SO, forms glucose. At 180° it slowly forms Boiling dilute trehalin, which is v. sol. water and ppd. by alcohol. Trehalin dissolves in phenyl-hydrazine. Iodine colours trehalum and trehalin violet. Diastase, yeast, and invertin have no action. Ac₂O and NaOAc yield an acetyl derivative

[above 210°]. TRI-. In the alphabetical arrangement of this dictionary the prefix 'tri,' when indicating the presence of three radicles, is treated as if it did not form part of a name, except where the entire name is numerical, as in 'tridecane.'

TRIANOSPERMIN. A crystalline substance occurring in Trianosperma ficifolia, a climbing plant of Brazil (Peckholt, Ar. Ph. [2] 113, 104; Parodi, Ph. [3] 10, 667). It has a pungent taste, is alkaline in reaction, sol. water, alcohol, and ether, and is ppd. by Pb(OAc), and PtCl.

TRIAZOLE NSCH.NH. [120.5°]. (260°). V.D. 2.39 (calc. 2.49). Formed by heating its carboxylic acid alone or with boiling water (Andreocci, B. 25, 229; Bladin, B. 25, 745). Needles (from ether), v. sol. water and alcohol, may be sublimed. The di-oxy-derivatives of alkyl-triazoles $N \leqslant_{C(OH),NR}^{C(OH);N}$ named by

Pinner 'urazoles,' are obtained by heating hydrazines with urea (Pinner, B. 20, 2358).

TRIAZOLE CARBOXYLIC ACID

N C(CO₂H).NH. [137°]. Obtained by oxidising methyl-triazole (Andreocci, B, 25, 229) or amido-phenyl-triazole carboxylic acid and alkaline KMnO₄ (Bladin, B. 25, 744). Amorphous powder.—CuA'₂aq. Green crystalline powder.—TRICARBALLYLIC ACID 2. vol. i. p. 679.

TRICOSANE v. TRI-ICOSANE.

TRIDECANE C₁H₂₈. [-6°]. (234°). S.G. 9. 771; 4° 761. Formed by reduction of methyl dodecyl ketone or of tridecoic acid by HI and P (Krafft, B. 15, 1699). Formed also by distilling barium myristate with NaOMe (Mai, B. 22,

TRIDECOIC ACID C₁₂H₁₃.CO₂H. [41°]. (236° at 100 mm.). Formed by oxidation of methyl tridecyl ketone (Krafft, B. 12, 1669). Crystals.

-AgĂ′.●

Amide C₁₂H₂₂.CO.NH₂. [98·5°]. Formed by digesting the nitrile with conc. H₂SO₄ and pouring into water (Lutz, B. 19, 1439). Plates (from alcohol).

Nitrile C,H,CN. (275°). Formed from tridecylamine, Br. and NaOH. Oil, vs sol. alcohol and ether.

TRIDECYL ALCOHOL (C.H.,), CH.OH. [42°]. Formed by reducing di-hexyl ketone (Kipping, C. J. 57, 536). Plates (from dilute alcohol),

insol. water. May be distilled. HBr forms $(O_aH_{11})_a$ CHBr [89°].

TRIDECYLABINE $O_{11}H_{21}NH_{21}$. [87°]. (266°).

FOrmed by boiling myristyl-tridecyl-urea with KOHAq (Luts, B. 19, 1437). Unctuous mass, v. sol. alcohol and ether. Absorbs water and CO. from the ar. REHCl: readles decomposing CO2 from the air. -B'HCl: needles, decomposing at 100°.—B',H,PtCl,.—B',H,SO,: needles, insol. cold water.

TRIDESYLENE Q₁₁H₂₈. (238° cor.). S.G. 2 8445. Occurs in petroleum from Burmah (Warren a. Storer, Z. 1868, 232).

TRIDECYL-UZEA. Myristyl derivative C., H., N.O. i.e. C., H., N.O. i.e. C., H., N.H. CO. NHO, H., O. [108°]. Formed by the action of Br and KOHAq on the amide of myristic acid (Reimer a. Will, B. 18, 18). 2016). Crystals (from alcohol), almost insol. cold water, sol, ether.

TRIGENIC ACID v. ETHYLIDENE BURET.

TRIGONELLIN C,H,NO, i.c.

CH CH CH CO Occurs in the seeds of CH:NMe O CHINNe O Trigonella Fienum-gracum (Jahns, B. 18, 2518;

20, 2840). It is also produced by saponification of the product of the reaction of MeI on potassium pyridine (β)-carboxylate (Hantzsch, B. 19, 31). Colourless prisms (containing 1q), converted by HOlAq at 265° into pyridine (B)-carboxylic acid (q. v., Reaction 4).—B'HOl.—B', L.P.Ol.—B'HAuCl. [186°]. Slender needles.

n-TRI-IOOSANE C₂₂H_{4s}, [48]. (234° at 15 mm.). E.G. 4⁵·7785; ⁸¹·7570. Formed from laurone (C₁₁H₂₂)₂90 by treatment with PCl, and reduction of the resulting (C₁₁H₂₃) CCl₂ with HI and P at 240° (Krafft, B. 15, 1712). Obtained also by fractional distillation of paraflin oil from brown coal (Krafft, B. 21, 2203). Glittering plates (from ether-alcohol), sl. sol. alcohol.
TRI-ICOSANE DICARBOXYLIC ACID

C₂₇H₄₆(CO₂H)₂. [102·5°]. Formed by heating di-oxy-penta-icosylene with soda-lime (Stärckee A. 223, 300). Flocculent pp. (from ligroin-ether).

TRI-ICOSYL ALCOHOL (C,H,,),CH.OH. [76°]. Formed by reducing laurone with Na and the property of the state of th

an acetyl derivative [65°].

TRIMELLITIC ACID v. vol. iii. p. 2014 TRIMESITE ACID v. vol. iii. p. 230.
TRIMESITIC ACID, v. Pyriding TRICARD-

OXYLIC ACID.

TRIMETHYLENE v. vol. iii. p. 304.

TRIMETHYLENE v. vol. iii. p. 304.

TRITCIN C₁₃H₂₂O₁₁. [a]_b = -43·6° (Reidemeister, J. Th. 1881, 69). Extracted by dilute alcohol from the root of couch-grass (Triticum repens) (H. Müller, Ar. Ph. [3] 2, 500; 3, 1).

Tasteless hygroscopic powder, v. sol. water, insol. alcohol and ether. Laworotatory. On boiling with water capacilly in researce of saids it. with water, especially in presence of scide, it changes into lavulose. Its solutions are not ppd. by metallic salts, nor coloured by iodine.

TROPEUNES v. Azo- compounds.
TROPEUNES. A name given by Ladenburg to alkoyl derivatives of tropine (q. v.).

TROPIC ACID &. Oxy-PHENYL-PROPIONIC

TROPIDINE v. METHYL-ETHYLENE PYRIDINE TETRAHYDRIDE.

(a) Methyl-tropidine C,H, N i.e. CH, CH.CH.CH.CH.CH.CH, NMe, (Ladenburg) or CH CH:CH OH.CH, NMe, (Merling). Formed by distilling tropidine methylo-hydroxide with water (Roth, B. 17, 157; 'Meiling, B. 24, 3118). Oil. HClAq forms 'hydrochloro-(a)-methyl-tropidine' which gradually changes into the isomeric tropidine mathylo-chloride. -

Methylo-iodide B'Met. [162°]. Needles. (8)-Methylo-iodide B'Met. [162°]. Needles. (8)-Methyl-tropidine C.H.,N. (205°). S.G. 14 922. Formed by heating (a)-methyl-tropidine at 150°-200°. Oil. Converted by HCl into

TROPIGENIN C, II₁₃NO. [161°]. Got by oxidation of tropine by alkaline KMnO, (Merling, B. 15, 287). Got also by boiling 'homohydroapotropine' with baryta water (Pesci, G. 12, 329). Needles, sol. water and alcohol. Reconverted by MrV into transp. Oxidized by chronic acid MeI into tropine. Oxidised by chromic acidmixture to ecgonic acid and a small quantity of tropic acid (Liebermann, B. 24, 615).-B'HI.-B',CO₂: crystalline pp. — B',H₂PtCl_e aq. -B'HAuCl₁: golden-yellow plates, sol. alcohol.

TROPILENE C,H,O i.e. 2403; 15, 1028; A. 217, 138). Formed also from (B)-methyl-tropidine and cold HClAq (Merling, B. 24, 3123). Oil, smelling like oil of bitter almonds and acetone, sol. dilute HClAq, v. sol. alcohol and ether. Reduces warm ammoniacal AgNO, forming a mirror. Reduces Fehling's solution and KMnO, in the cold. Not attacked by Accl. Combines with NaHSO₃ (M.). Nitric acid forms an adipic acid $C_0H_{10}O_4$. Slowly combines with methylamine, forming (β)-methyl-

TROPILIDENE C,H, i.e.

CH < CH.CH. > C:CH₂. (114°). S.G. 2 ·9129.

Formed by distilling methyl-tropine methylo-iodide with KOH (Ladenburg, A. 217, 133; B. 14, 2403; 26, 1067). Formed also, together with methylamine, by distilling tropine with soda-lime. Oil, smelling somewhat like toluene, but combining readily with bromine, forming

CH-CH-CH-VIII) MMc (Merning). Metnyl-cery-cylindric tetrahydride. [62°] (229°d). Totals: harether with tropic acid, by hydrosthy). Need: ne or hyoscyamine by baryta or Formed, water). A. 128, 281; 133, 87; Lader-lysis, of atrophil (; 217, 115; "B. 18, 608; 20, HCIAq (Kraut, II, 66, 1067). Hygroscopic tables burg, A. 206, 2. sol. water and alcohol. Does 1653; 23, 1763 chrom the air. Its aqueous solution of the control of th (from ether), v. not absorb CO.

tion ppts. metallic oxides from their salts. Not attacked by nitrous acid. Not volatile with steam. According to Eykman (B. 26, 1400) the refractive index agrees best with Merling's formula.

Reactions .- 1. Decomposed by distilling with Reactions.—1. Decomposed by distilling with soda-lime into tropilidene, methylamine, and H₂O.—2. Loses H₂O, being converted into tropidine by heating with fuming HCl and HOAc at 180° or by heating with H₂SO₄ (1 pt.) and water (14 pts.) at 230°.—3. Conc. HIAq and red P at 150° form tropidine and tropidine periodide, but at 140° they form 'tropine iodide' C₂H₁,NI₂, which extendings from water in prignal [1148]. which crystallises from water in prisms [116°], whence silver chloride followed by PtCl, give (C₈H₁₇NICl)₂PtCl₄ crystallising in red octahedra. By treatment with Ag.O followed by HCl and PtCl₄ very soluble (C₈H₁₇NCl₂)PtCl₄ is got.—4. PtCl₄ very soluble (C_bH₁,NCl₂)PtCl₄ is got.—4. Alkaline KMnO₄ forms tropigenin and, finally, oxalio acid and NH₂ (Merling, A. 216, 341).—5. CrO₃ forms tropinic acid C_bH₁₁N(CO₂H)₂.—6. Aqueous HOCl yields prisms [111°], whence alcohol produces C_aH₃NCl₄,CH.OH [108°], which forms a hydrochloride [162°] crystallising in plates (Einhorn a. Fischer, B. 25, 1391).

Salts.—B'HCl.—B'₂H₁PtCl₄. Orange-red proposition crystals [200°] (Schmidt A. 208

Salts. — B'HCl. —B'.H., P. U., Orange-rea monoclinic crystals. [200°] (Schmidt, A. 208, 214).—B'HAuCl., [212°].—B'HCl6HgCl., [246°] (Ladenburg, B. 24, 1631).—B'C., H., ONO., N. Nitroxyl Ucrivative C., H., (ONO., N.

Nitroxyl Ucrivative C,H, (ONO,)N.
Nitro-tropein. Formed by warming tropine (2 g.)
with HNO, (12 g. of S.G. 1.25) at 100° (Ladenburg, B. 15, 1025).
Alkaline liquid, sol. water, alcohol, and ether.
KOH.—B',H,PtCl. Needles.—B'HI. Prisms.
Benzoyl derivative C,H, (OB2)N.

Benzoyl-tropeine. Formed by heating tropine hydrochloride with benzoic acid and dilute HCl (Ladenburg, B. 13, 1983; d. 217, 96). Crystallises as C₁₃H₁₉NO, 2aq [58°], C₁₅H₁₉NO, 2aq [58°], C₁₅H₁₉NO, 2aq ed there. B'₁H₁₉NO, B'₂H₁₉NO, B'₂H₁₉NO, B'₂H₁₉NO, B'₂H₁₉NO, B'₂H₁₉NO, B'₂H₁₉NO, B'₂H₁₉NO, B'₂H₂NO, B'₂H₂

С_кH₁₁(O.ČO.**C**₈H₄.ÕП)N. Salicyl-tropeine. Formed in like manner, using salicylic acid (Gaebe a. Caro, B. 13, 106; L.). Silky plates. Feeble poison, 025 g. killing a frog in a few hours. Has no apparent effect on the pupil.—B'HCl.—B'H.PtCl.—B'HAuCl.; yellow plates.

(n-Oxy-bentoyl derivative C₁₃H₁₉NO.

('n-Oxy-bentoyl derivative C₁₃H₁₈NO₂. [226°]. Small plates, v. sl. sol. water. Acts slightly on the pupil of the eye.—B'HCl.—B₁₂H₂SO₄4aq.—B'₂H₂PtCl₃: orange plates.
p-Oxy-bensoyl derivative C₁₄H₁₈NO₂. [227°]. Trimetric plates (containing 2aq).—B'HNO₃.—B'₂H₂PtCl₃ 2aq. Orange plates.
Fhenyl-acetyl derivative C₁₄H₁₈NO₃. is. C₄H₁₈N(O.CO.CH₂h). Phenylacettroperae. Aromatic oil.—B'HBr.—B'₂H₄PtCl₃.—B'HAuCl₄.—B'₂H₃SO₄. Soluble tables.
Mandelyl derivative C₁₄H₁₈UO₃. is. C₄H₁₁N(O.CO.CHPh.OH). Homatropine. Formed by heating tropine with mandelic acid, HCl (1pt.), and water (40 pts.), the yield being 50 p.c. of the theorefical amount (Ladenburg, C. R. 90, of the theoretical amount (Ladenburg, C. R. 90, 921; A. 217, 82). Deliquescent prisms (from ether), sl. sol. water. A solution of its hydrochloride is ppd. by potassio increaric iodide, but not by tannin. It enlarges the pupil of the eye almost as energetically as atropine, but the en-largement passes off much more rapidly (Völkers,

TRUXENE.

4.217.86; Bertheau, Berl. Klin. Wochenschrift, 4.217, 85; Bertheau, Bert. Aun. mocnessumy, 1680, No. 41; Tweedy a. Ringer, Lancet, 1880, No. 21).—B'HBr. Trimetric crystals; a:b:c='414:1:'472.—B'C₆H₃N₃O₇. Yellow plates.—B'HAuCl₄.—B'₂H₂SO₇. Needles.
Cinzamoyl derivative C₁, H₂₁NO₂. [70°].

Small plates (from dilute alcohol). Gives pps. with tannin, pieric acid, potassio-mercuric iodide, and I in KI. Strong poison, '03 g. killing a frog in three minutes. Has little action on the Physil,

B'HCl.—B'HLPtCl₅.—B'HAuCl, Needles.

Atropyl derivative C₁H₁NO₂. Atroptropeine. Oil.—B'HAuCl₄. Small needles.

Atrolactyl derivative C,H2NO [120°]. Formed from atro-Pseudo-atropine. lactic acid, tropine, and dilute HCl (1:400) by repeated evaporation (Ladenburg, A. 217, 87). Needles (from water). Resembles atropine in physiological action, two drops of a 1 p.c. solumodation for a week.—B'HAuCl., [114°].

Phthalyl derivative C₂,H₂,N₂O₄. [70°].

Formed, in very small quantity, by evaporating phthalic acid with tropine and dilute HCl.

Mass of silky needles. - B'H. PtCl. Methylo-iodide C. H. NOMeI. crystals, nearly insol. alcohol. Yields B'McOH and B'₂Me₂PtCl_e (Merling, B. 14, 1829; Ladenburg, A. 217, 131).

Ethylo-iodide B'EII. Crystalline. Yields B'Et.PtCl, a yellow crystalline powder.
(a)-Methyl-tropine C.H.,MeNO. (243°).
Formed by distilling tropine methylo-iodide. Liquid, v. sol. water and alcohol. Strongly-alkaline. Its hydrochloride, distilled with solid KOH, yields dimethylamine. -B'HAuCl,. Very unstable.

Methylo-iodide (C,H,MeNO)MeI. Deliquescent needles, decomposed by distilling with solid KOH into tropilidene and trimethylamine.

-(C,H₁,MeNO)₂Me₂PtCl₃. Orange crystals.
(B) Methyl-tropine C,H₁,NO. (198-205°).
Formed by shaking tropliene with an aqueous solution of dimethylamine (Ladenburg, B. 14,

solution of dimethylamine (Ladenburg, B. 14, 2404). Liquid, split up by gaseous HCl into tropilene and NMe,H. B'HAuCl. Prisms.

(γ)-Methyl-tropine C_pH₁,NO. Formed in small quantity by distilling the methylo-hydroxide of (a)-methyl-tropine (Merling, B. 15, 288). V. sl. sol. Aq. B',H. PtCl., V. sl. sol. Aq. Metatropine C_pH₁,NO. (238°). Formed by shaking tropine iodide with water and Ag₂O. Not colid et 30° - RTICl. tables.

shaking tropine iodide with water and Ag₂O.

Not solid at -30°.—B'HCl: tables.

Hydrotropidine C₂H_{1,N}N. (168°). S.G. 2°.937;

15°.926. Formed by reducing tropine iodide

C₂H_{1,N}I₂ with zinc-dust and HClAq (Ladenburg,

B. 16, 1408). Liquid, m. sol. water. B'HCl:

deliquescent crystals.—B'₂H₂PtCl₈. Tables.

Norhydrotropidine C₂H_{1,N}N. (60°). (161°).

Formed by distilling hydrotropidine by distilling hydrotropidine by distilling hydrotropidine.

nornydrotropidine C.H.N. [60°]. (161°). Formed by distilling hydrotropidine hydrochloride in a current of HCl (Ladenburg, B. 20, 1649). Crystalline.—B'HCl. [281°].—B'HPCl.—B'HHgCl.—B'C.H.N.O. [281°].

chloride in a current of HCI (Ladenburg, 5. 20, 1649). Crystalline.—B'HCl. [287°).—
B'H.PtCl.—B'HHgCl.—B'C.H.N.O., Needles,
Nitrosamine C.H.,N.O. (117°). Cubes.
Paratropine C.H.,N.O. (202°). Formed from hydrotropine and K.FeCy, (Ladenburg, B. 24, 1626).—B',H.PtCl. [197°].—B'HAUCL. [182°].—B'HClBHgCl. [225°]. V. sol. water.

4. Tropine C.H.,NO. [108°]. (242°). Formed, together with tropic acid, by warning hyoscine with haveta water (Ladenburg, B. 13, 1551: 17.

with baryta-water (Ladenburg, B. 13, 1551; 17,

151; Liebermann, 24, 2587). Formed also by dissolving its benzoyl derivative in hot conc. HClAq (Hesse, A. 271, 210). Hygroscopic prisms (from chloroform), v. e. sol. water. Yields tro-(from chloroform), v. e. sol. water. Inside tro-pinic and ecgonic acids on oxidation.—B'sH_SO,. Hygroscopiq crystals.—B'HAuCl., [198] (Ladenburg); [202"] (H.); [225"] (Lieber-mann).—B'sH_2PtCl₀ 4ad. [206", anhydrous]. Trimetric prisms; abice -7021; *379. Methylo-iodide B'McI. [270"]. Rhom-bohedra. Yields B'McI. and B'sMe,PtCl₀.

[216°] crystallising from water.

Benzoyl derivative C13H19NO2. [48°]. Occurs in the leaves of Java coca (Liebermann, B. 24, 2336; Lesse, A. 271, 208). Colourless plates (from ether). - B'HCl. [270°]. -B'₂H₂PtCl_a. Pale-yellow needles. - B'MeI. -B'McCl. - B'MeAuCl₁. - B'Me₂PtCl_a 2aq.

Mandelyl derivative C,H,,NO(CO.CH(OH),C,H,). ψ-Homatropine. Formed by heating 4-tropino with mandelic an-hydride at 200' (Liebermann a. Limpach, B. 25,

hydride at 200' (Liebermann a. Limpan, — 931).—B'HCl.—B'.H.J.PtCl., —B'HAuCl., — B'HAuCl., — "rop'y derivative C.H.,NO(C.H.O.). Isomeride of hyoscine. [88]. [a]_p = -4'9'. water. sol. alcohol.—B'HCl. Nodules, insol. water, sol. alcohol. — [183°].—B'₂H₂PtCl₆.—B'HAuCl₄. [135°].

Atropyl derivative. [129]. Formed from tropide and \(\psi\)-tropine at 200°. Crystals, Formed sol. water. Split up by HClAq into atropic acid and \-tropine.

Oxy-tropine carboxylic acid CH.CH.CH.CH(OH).CH(OH).CO.H. Dioxyan-CH.CH..NMe hydroccgonine. Formed by oxidising hydroegonine with KMnO, and aqueous Na₂CO₂ at 1° (Einhorn a Rassoff, B. 25, 1395). Decomposes

eegonine with KMnO, and aqueous Na,CO, at 1-(Emhorn a. Rassoff, B. 25, 1395). Decomposes at 280°. V. e. sol. water and MeOH, insol. EtOH.—B'HICl. [251°].—B'C H_N,O,.—KA'. Methyl ether MeA'. [139°]. Tables, v. e. sol. CHCl., Vields B',H,PtCl., [210°]. Benzoyl derivative of the methyl ether C,H,MeN.CH(OH).CH(OB2).CQ.H. 1100°1. Nacdlee B'HNO. [216°].—B'HCl. $\begin{array}{llll} [108^\circ]. & \text{Needles.--}B'\text{HNO}_{\text{\tiny 3}}. & [216^\circ].--B'\text{HCl}. \\ [203^\circ].--B'\text{HAuCl}_{\text{\tiny 4}}. & [173^\circ].--B'_2\text{H}_2\text{PtCl}_{\text{\tiny 6}}. & [208^\circ]. \end{array}$

Di-benzoyl derivative of the methyl ether C,H,MeN.CH(OBz).CH(OBz).CO,H.
Needles.—B'HNO₂. [190³].—B'HCl. [280°].—
B'₂H,PtCl₂. [205°].—B'HAuCl₁. [203°].

Reference.—OXYTROPINE.
TROPINE DIHYDRIDE C.H., NO i.e.

CH_CH_CH_CH_CH_OH CH_CH_NMe Hudrotropina. Methyloxyethylpyridine hexahydride. (238). Formed from oxy-ethyl-piperidine and KMeSO, (Ladenburg, B. 24, 1622). V. sol. water and alcohol. — B'HCl5HgCl₂. [214²]. — B'HAuCl₄. [170²]. Crystals.

TROPINIC ACID C.H.; NO. [253] (L.); [220] (M.). A product of oxidation of tropine and of ecgonine by chromic acid mixture (Merling, M. 216, 348; Liebermann, B. 23, 2519). Meedles, v. sol. water, sl. sol. alcohol, insol. benzene. Gives off CO, when heated. Forms salts with acids and bases.—BaA'₂. Very hygroscopic.—CaA'₂.—AgA'. Readily reduced.—(HA),PtCl.,—HA'HAuCl., Golden prisms.—

HA'HCl aq.

TROPYLENE v. TROPILENE,
TRUXENE (C.H.). Formed by heating
truxone with red P and HIAq (S.G. 1.7) at 180°

(Liebermann a. Bergami, B. 22, 786; 23, 817). Formed also by heating hydrindone with conc. Hollaq, and by heating phenyl-propionic acid with P₂O₂ (Hausmann; Kipping, C. J. 65, 269). Needles or plates, melting above 860°, insol. CHCl₂. Uxidised by boiling HOAc and CrO, to crystalline 'tri-benzoylene-benzene,' which is not melted at 860°. HNO₂ forms (4,2,1)-nitrophthalic acid.

(a)-TRUXILLIC ACID Cit HisO, i.e.

CO₂H.CH—CHPh. (?) (γ)-Isatropic acid

[274°]. Formed, together with (\$)-truxillic acid, by the action of boiling HClAt on isatropylcocaine, which is a by-product in the preparation of cocaine (Liebermann, B. 21, 2342; 22, 124, 783, 2242). Small needles (from alcohol), sol. hot HOAc. Yields cinnamic acid on distillation. Nitric acid (8.6, 1.52) forms two di-nitro-deri-Nitric acid (S.G. 1-52) forms two di-nitro-derivatives, [229°] and [290°]. Yields two isomeric sulphonic acids.—Na,A" 10aq (Drory, B. 22, 2256),—BaA"8,aq. Crystalline, v. sol. water.—CaA"aq.—Ag,A". Flocculent pp., sol. NH,Aq. Methyl ether Me,A". [174°]. (c. 300°). Ethyl ether Et,A". [146°]. H.C.p. 2,720,900 (Liebermann, B. 25, 92). Yields C₁₈H₁₂(NO₃),Et,O₈ [138°] (Homans, B. 24, 2500). Isoamyl ether (C,H₁),A". [83°]. Prisms. Ac,O at [50° forms (a)-truxillic anhydride, while at 170° the product is (x)-truxillic anhydride.

at 170° the product is (γ)-truxillic anhydride.

Di-amide C₁₈H₁₄O₂(NH₂)₂. [265°]. Needles,
v. sl. sol. hot water, sl. sol. alcohol (Drory, B. 22, 2261).

22, 2201).

Di-piperidide C₁₄H_{1.1}(CO.NC, H₁₀)... [259°].

Got from the chloride and piperidine (Herstein, B. 22, 2264). Orystalline powder, sol. alcohol.

Mono-piperidide
C₁₄H₁₄(CO,H).CO.NC, H₁₀. [250°]. Yields MeA'

[151°] crystallising from ether in needles.

Anhydride (C₃₀H₃₀O₇)₃. [191°]. Mol. w. 1712 (1703 obs. by Raoult's method). Formed Ly beating the acid with Ac,O and NaOAc at 100°. Needles (from benzenc-ligroïn). Gives no fluorescein. When heated for an hour at 200° it changes to (γ)-truxillic anhydride.
(β)-Truxillic acid C_{1s}H_{1e}O₄ i.e.
CHPh.CH.C O.H
(?)

(8)-Isatropic acid. [206°]. Formed at the same time as the (a)- acid (Liebermann, B. 21, same time as the (a)- acid (inevermann, B. a., 2342; 22, 783, 2243; 25, 90; 26, 837). More sol, water than the (a)- isomeride. Yields benzil on oxidation. Nitrio acid (S.G. 1-52) forms a di-nitro- derivative [216°] (Homans, B. 24, 2590). Forms cinnamic acid on distillation.—Na, A° 2aq.

—BaA" 2aq. Sl. sol. water.—CaA" 3 aq. —Ag,A".

**Methylether Me,A". [76]. Mol. w. 309
(by Racult's method); calc. 324. H.C.p.
2,422,900. Monoclinic prisms; a:b:e=

2,423,900. monoconno prisms; a:o:o= 626:1:2·019; β=89° 22'.

Ethylether Et.A.". [47°].

Chloride C., H., O.Cl.. [96°].

prisms, v. sol. ether (Drovy, B. 22, 2260). Tabular

Monopipentdide C₁₆H₁₄(CO₂H), CONC₃H₁₆(224°]. Formed from (β)-truxillic anhydride and piperidine (Herstein, B. 22, 2264). Needles, sl. sol. cold alcohol.

Dipiperidine C₁₆H₁₄(CO.NC₅H₁₀)₂. [180°]. Formed from the chloride and piperidine. Prisms, v. sol. alcohol.

Phonylimids C18H14 CONPh. [180°]. Mol. w. 351 (obs.). Got by heating the anhydride with aniline. Colourless needles (from alcohol). Cold alcoholic potash forms the compound CO₂H.C₁₄H₁₄.CO.NHPh [197°].

Phenyl hydrazide CieH. CO.NH

[218°]. Formed from the acid, phenyl-hydrazine, and MOAc on warming. Crystals (from HOAc).

Fluorescein $C_{1e}H_{1e} < \frac{C(C_{e}H_{2}(OH)_{1})}{CO} > 0$.

Formed by heating the acid or its anhydride, with resorcin'at 240°. Amorphous brownish-red powder, sol. alkalis forming fluorescent solutions.

Anhydride C₁₈H₁₄O₃. [116°]. M 278 calc., 289 obs. by Raoult's method. Mol. w. Does not change to an isomeride when heated.

(γ)-Truxillic acid C_{1ν}H₁₆O₄, ε-Isatropic acid. [228°]. Formed by heating the anhydride of the (a)-isomeride with HCl at 160°. Needles (from dilute alcohol), v. sl. sol. hot water, v. sol. ether. Yields cinnamic acid on distillation. Gives the same anhydride as the (a)-isomeride (Ladenburg, B. 22, 124). Heated with HClAq at 260° it is changed to (α)-truxillic acid. HNO, (S.G. 1.52)

enangeu to (a)-truxinio acid. HNO₃ (S.G. 1-52) forms a di-nitro- derivative [293°].

Salts.—BaA" 11gq.—CaA" 3½aq.—
CaA" 6½aq.—Ag₂A": crystelline pp.

Methyl ether Me₂A". [126°]. Needles.

Mol. w. 332 (cala 324) Mol. w. ·332 (calc. 324).

Mono-cthyl ether C₁₆H₁₁(CO₂H).CO₂Et. (172°). Formed, together with the di-ethyl ether. by saturating an alcoholic solution of the acid with HCl (Liebermann, B. 22, 2240). Needles, yielding AgA'. At 320° it is converted into a mixture of (a)-truxillic acid and (a)-truxillic

Di-cthylether Et.A". [98°]. Needles, v. sol. alcohol (Drory, B. 22, 2260).

Mono-piperidide

C_{1s}H₁₁(CO.NC₃H₁₀).CO₂H. [261°]. Plates (from water or dilute alcohol). Yields MeA' [201°] and a piperidine salt (C₃H₁₁N)HA' Saq [218°], which crystallics (with Saq) from alcohol (Herical Parallel Sage). stein, B. 22, 2262).

Di-piperidide CieH .. (CO.NC. Hie). [248°].

Needles, insol. water, sol. alcohol.

Mono-anilide "CloH, (CO.NHPh).CO.H. [220]. Formed by heating the acid with aniline Liebermann, B. 26, 838). Needles (from dilute

Antline $C_{1c}H_{1c}(CO.NHPh)_2$. [255°]. Anhydride $C_{1c}H_{1c}O_2$. Mol. w. 282 (calc. 3). Gives no fluorescein.

(5)-Tiuxillic acid $C_{18}H_{16}O_4$. [174°]. Formed by fusing (3)-truxillic acid with potash. Needles (from water), v. sol. alcohol (Liebermann, B. 23, 2250; Hesse, A. 271, 205). Yields a di-nitroderivative [226°]. Yields cinnamic acid on disfillation: CaA": rosettes of needles. BaA" 4aq:

tion:—Caā": rosettes of needles.—BaA" 4aq: prisms, sl. sol. Aq.—CuA" 2aq.—Ag,A".

Methyl ether Me,A". [77]. Needles.

Reference.—OXY-TRUXILLIO ACID.

TRUXONE (C,H₄O)₂, x = 2vr 8. [289°]. Formed from (a)-truxillio acid and fuming H,SO, (S.G. 1-96)- at 15° (Liebermann a. Hergami, B. 22, 784; 23, 320). Plates (by sublimation), insol. water, acids, and bases. Not attacked by HNO₂. Yields (C,H₂Ol₂), [178°]. Aniline and HOAs on

boiling form the anilide (C, H,: NPh), crystallising

boiling form the anilide (C,H₄:NPh)_z crystallising in needles, [270°], decomposed by fusion.

Phenyi-hydrasids (C₂H₄:N₂HPh)_z. [c. 270°]. Needles, v. sl. sol. alcohol.

Oxim (C,H₂:NOH)_z. Very unstable, easily changing to an anhydride. Boiling Ao₂O yields (B,H₂:NOAc)_z [261°], m. sol. HOAc.

TULUCUNIN C₂₂H₄O₄. Occurs in the bark of Tarapa Tulucuna (Caventou, J. Ph. [3] 35, 1201 Light-vallow amperphase resin with very 189). Light-yellow amorphous resin, with very bitter taste, sl. sol. water, v. sol. alcohol, finsol. ether. Turned blue by cold H.SO.

TUNGSTATES, and derivatives of; v. Tung-STEN OXYACIDS, SALTS, AND DERIVATIVES OF, p. 802;

Also TUNGSTEN. W. (Wolfram.) At. w. 183-6.

TUNGSTEN. W. (Wolfram.) At. w. 183-6.

Mol. w. is unknown. S.G. 18-77 (Waddell, Am. 8, 280); 18-77 (Moissan, C. R. 116, 1225); 19-13 at 4° (Roscoe, C. J. [2] 10, 286); for other determinations v. Bernoulli (P. 111, 576), Zettnow (P. 111, 16). S.H. (6° to 15°) 035 (De la Rive a. Marcet, A. Ch. [2] 75, 113). S.V.S. c. 9·7. Historical.—In 1785 a new acid was prepared

by J. and F. d'Elhujar from the mineral wolframite, and shown to be identical with an acid obtained three years before from tungstein by Scheele (Opusc. 2, 119). The metal of the new acid was isolated by J. and F. d'E. For many years the new metal was known as wolfram or tungsten (from Swedish = heavy stone); the latter name has gradually driven out the former in England and France, but the metal is generally called wolfram in Germany; the symbol W is universally employed.

Occurrence .- Never uncombined. Wolframite (tungstate of Fe and Mn) is found in considerable quantities in Cornwall, Saxony, Bohemia, &c.; tungstenite, or scheelite (tungstate of Ca), scheeletine (tungstate of Pb), and come other tungstates occur in various localities; wolframine or wolfram-ochre, WO., is also found. Some tin ores contain compounds of W. and W. is therefore not infrequently found in specimens

Formation.-1. By reducing WO, by heating to redness in H (Berzelius, P. 4, 147; Wöhler, A. 77, 262; Zettnow, P 111, 16; Roscoe, C. N. 25, 61, 78).—2. By heating WO, with Na and NaCl (Z., lo.).—3. By reducing WO, by mixing with 10 p.c. charcoal and 2 p.c. resin, and heating in a closed crucible for some hours to a white heat (Filsinger, S. C. I. 1878, 229).—4. By passing vapour of oxychloride of W and H passing vapour of expendence of W and H through a red-hot tube (von Uslar, A. 94, 255).

5. By heating WCl, in H, in a zinc bath (Roscoe, Lc.).—6. By strongly heating the salt (NH₄), WO₄ in a carbon crucible (Bucholz, P. 111, 576).—7. By strongly heating the nitride (q. v., p. 800) in H (Wöhler, A. 73, 190).

**Preparation.—1. Pure WO₄ is heated to bright redness in a Pt tube in a stream of property.

redness, in a Pt tube, in a stream of pure dry di (v. Hormation, No. 1).—2. A mixture of pure WO, and dry lampblack is heated in an electric

Wo, and dry lampoison is neated in an electric furnace (Moissan, C. R. 116, 1225).

WO, is prepared from wolframits by heating the very finely powdered mineral with conc. HClAq, pouring off the solution from time to time and adding more HClAq, and after some time adding a little HNO, Aq until most of the brown solid is changed to yellow WO, xH,O, washing the residue thoroughly by decantation,

adding a considerable quantity of NH, Aq and warming, filtering from quartz, unchanged wolframite, &c., evaporating the solution until small lustrous crystals of an acid ammonium tungstate separate, boiling these crystals for a long time with HNO, Aq, washing, and heating the residue (Scheibler, J. pr. 83, 239; cf. Bernoulli, P. 111, 590).

Properties.—A steel-grey, hard, brittle, crystalline powder (Riche, A. Ch. [3] 50, 5). By reducing the nitride in H, Wöhler (A. 78, 190) obtained W as a black powder. By reducing WO. by C in an electric furnace, Moissan (C. R. 116, 1228) obtained a lustrous, very hard, greyish white solid. As produced by passing the vapour of WO,Cl, mixed with H through a red-hot tube, W forms a shining, dark steel-grey, mirror-like deposit, which can be detached from the tube in hard, brittle crusts (von Uslar, A. 94, 255). W can be melted in the O-H flame, part of it burning to WO₄ (Riche, l.c.); or by using a current from 600 Bansen cells, in an atmosphere of N (Desprez, C. R. 29, 549). Considerable masses may be malted by employing the current from a dynamo (v. Huntington, C. N. 46, 163). W was regarded by Faraday as diamagnetic (T. 1846. 49). The emission spectrum is described by Thalen (A. Ch. [4] 18, 202). Wis unchanged in air, but when the pulverulent metal is heated it burns to WO,; compact W burns in air only at very high temperatures; as obtained by reducing WCla by H, W is said to be pyrophoric. Water is decomposed by W at a red heat. The metal is scarcely acted on by HClAq or H_SO, Aq; it is oxidised by HNO, Aq to WO, xH,O; the pulverulent metal dissolves slowly in caustic alkali solutions. Finely divided W reduces and ppts. many metals from solutions of their salts. combines directly with Br, Cl, I, or S. acted on by heating in NII, nor in CO (v. Rideal, C. J. 55, 45; Smith a. Oberholtzer, Zeit. f. anorg. Chemie, 5, 63).

The at. w. of W has been determined (1) by reducing WO, in H, and again oxidising W to

WO3 (Berzelius, P. 4, 151 [1825]; Schneider, J. pr. 50, 158, 161 [1850]; Marchand, A. 77, 263 [1850]; von Borch, J. pr. 54, 254 [1851]; Riche, A. Ch. [3] 50, 10 [1856]; Dumas, A. Ch. [3] 55, 143 [1859]; Bernoulli, P. 111, 597 [1860]; Persoz, 130 [1609]; Periodini, 2-111, 597 [1600]; Persoz, A. Ch. [4], 1, 93 [1864]; Roscoe, C. N. 25, 61, 73 [1872]; Waddell, Am. 8, 280 [1887]); (2) by determining H₂O in BaW₂O₁, 9H₂O' [Scheibler, pr. 83, 324 [1861]); (3) by reducing WO₂ in H and determining H₂O produced (Bernoulli, P. Hand actermining H₂O produced (Bernoulli, P. 111, 597 (1860)); (4) by analysing Ag, WO,, and FeWO, (Zettnow, P. 130, 16, 240 [1867]); (5) by enalysing WCl₂ (Roscoe, C. N. 25, 61, 78 [1872]); (6) by determining & H. of W (De la Rive a. Marcet, A. Ch. (2) 75, 113 [1840]); (7) by determining V₂D. of WCl₂, WCl₃ and WOCl₄ (v. these compounds). The older determinations gave values for at. w. varying from 186 to 189; the most fecent determination (by Waddell) gave 184.04; Roscoe's determinations, made by reducing WO, to W and oxidising W again to WO, by finding the ratio of WCl, to AgCl and to Ag, and by reducing WCl, in H, gave value—sarying from 183-25, to 183-77. The number 183-6 is probably correct to half a finit. The atom of W ds pentavalent in the gaseous molecule WCl, and hexavalent in the gaseous molecule WCL.

W is the fourth member (the third is as yet unknown) of the even series, or chromium, family of Group VI. in the periodic arrangement of the elements. Wis followed in its family by U, and it succeeds Mo and Cr. W very closely resembles Mo; like that element W is both metallic and non-metallic; the balance of these properties being, however, not quite so evenly maintained in W as in Mo. It is doubtful whether any definite salt has been isolated derived from an oxyacid by replacing H by W. The oxide WO, acts as a fairly acidic oxide; like MoO, it is remarkable for the large number of compounds it forms, simultaneously, with oxides that are more basic and oxides that are less basic than itself. The chemical relations of Ware discussed in the article Chromium group of elements, vol. ii. p. 168.

Reactions.—1. Heated in air burns to WO₃; finely divided W burns easily; compact W only at a very high temperature (v. Roscoe, C. N. 25. 61, 73).-2. Heated to redness in steam gives H and oxide (? WO3).-3. Reacts with hot nitric acid, or aqua regia, to form WO, xH₂O; the same product is obtained by heating W with conc. sulproduct is obtained by heating W with conc. sul-phuric or hydrochloric acid, but oxides inter-mediate between WO, and WO, are formed at first (Riche, A. Ch. [3] 50, 15).—4. Pulverulent W dissolves in boiling conc. potash solution, giving H and a tungstate of K (Riche, Lc.). 5. Heated ir carbonyl chloride to 150°-200° "WOCL is produced, mixed with C (Smith a. Ober-bellton, West of george Chemic E 63) 6. Per holtzer, Zeit. f. anorg. Chemic, 5, 63).-6. By heating to redness with sulphur chloride a red, crystalline thiochloride, probably W2S.Cls, is formed as, a sublimate, unstable in air (S. a. O., l.c.) .- 7. Finely divided W reduces solutions of several metallic salts; AgNO, and AuCl, solutions are reduced to Ag and Au, HgCl, to HgCl, Cu, Pd, Pt and Rh are partially ppd. from solutions; Bi, Cd, and Pb are not ppd. (Smith, Zeit. f. anorg. Chemie, 1, 360).

Combinations .- 1. Heated in oxygen, WO, is formed .- 2. Combines with chlorine, to form WCl, at c. 800°; with bromine, to form WBr, at a higher temperature; and with iodine, to form WI, when strongly heated.—3. Heated with sulphur, forms WS,—4. The compound W,P, is said to be formed by strongly heating Win phosphorus vapour (Wöhler a. Wright, A.

79, 244).

Detection and Estimation.—Compounds of W form colourless beads with borax or micro cosmic salt in the outer blowpipe flame. The borax bead is yellow in the inner flame if a considerable quantity of a compound of Wis present. The microcosmic salt bead is blue in the inner flame in the absence of compounds that themselves form coloured beads; in presence of iron compounds the bend is blood-red, but addition of tin causes it to become blue. Soluble alkali tungstates are formed by fusion with alkali carbonate or nitrate; addition of excess of H.SO.Aq, HClAq, H.PO.Aq, H.C.O.Aq, or HC.H. Aq to an aqueous solution of a tung-state, followed by immersion of a piece of zinc in the liquid, produces a blue colour; addition of H.S to an acidulated solution c! a tungstate gives no pp., but a blue colour. According to Mallet (O. J. 28, 1229), the successive addition of small pieces of zinc to the solution obtained by adding excess of sone. HClAq to an alkaline tungstate produces various colours, the most marked of which is a brilliant magenta-red. By adding KCNSAq and then small pieces of zinc to a solution of an alkaline tungstate in excess of conc. HClAq, a deep green colour is produced; and an amethyst colour is noticed when KCNSAq is added to the solution of an alkaline tungstate, the solution is then diluted, HClAq is then added, and lastly zinc in placed in the liquid. Very minute quantities of W can be detected by adding SO₂Aq and Zn to solution of an alkaline tungstate, whereby a light-blue colour is obtained (M., l.c., p. 1233). W is estimated as WO₂, obtained by evaporation and strongly heating; for separation from other elements a Manual of Analysis must be consulted.

Tungsten, alloys of. By reducing mixtures of WO₃ with oxides of Sb, Bi, Co, Cu, Pb, Ni, or Zn, Bernoulli (P. 111, 573) obtained alloys of W with these metals, provided there was not more than 10 p.c. of the foreign metal present. An alloy with aluminium, approximately WAI, was obtained by Wöhler a. Michel (A. 115, 102) by heating a mixture of WO3, Al, cryolite, and NaCl and KCl. W alloys with iron; v. Poleck a. Grützer (B. 26, 35) for an alloy approximately W₂Fe. An alloy of 9 or 10 p.c. W with steel is extremely hard (v. Bornoulli, l.c.; Philipp, Hofmann's Ber. àber chem. Industrien, 745; Le Guen, C. R. 56, 593; 59, 786; 63, 967; 64, 619; 68, 592; Caron, A. Ch. [3] 68, 143; Osmond, C. R. 104, 985; Gruner, C. R. 96, 197). Tungsten, amidonitrides of, v. Tungsten

LITRIDES, AND ALLIED COMPOUNDS, p. 799.

Tungsten, bromides of. The elements com-bine when heated together to form WBr,, and by partial reduction in H this gives WBr.

WBr3. TUNGSTEN PENTABROMIDE formula is probably molecular, from the analogy of WCl. Prepared by heating W in excess of Br vapour, taking care that every trace of water and O are excluded. Dark, violet-brown needles. resembling I; melts at 276° and boils at 333°, giving off a dark-brown vapour; decomposed on distillation, with separation of Br; moist air or water forms HBrAq and blue oxide of W; heated to 350° in a stream of H, WBr, is formed (Roscor, C. N. 25, 73; cf. Borck, J. pr. 54, 254; Blomstrand, J. pr. 82, 408).

TUNGSTEN DIBROMIDE WBr. Obtained, as a bluish-black, velvety solid, when WBr, is heated dat c. 350° (in a bath of ZnCl₂) in a stream of dry H; WBr₃, WOBr₄, and Br distil over, and WBr₂ remains. Heated above c. 400° in H gives W and HBr; with HNO, Aq gives WO, HBrAq,

and NH, NO, Aq (Roscoe, l.c.).
Tungsten, chlorides of. When W is heated in Cl the compound WCl, is formed, and by reduction in H or CO, this gives WCl, WCl, and WCl. Great confusion existed about the compositions of the chlorides of W until Roscoe's esearches in 1872 established the formulæ.

TUNGSTER HI KACHLORDE WCl. Mol. w. 395-82. Prepared by heating W in Cl (Roscoe, C. N. 25, 61). The materials must be perfectly dry, and every trace of air myst be excluded, else WOCl, is formed; the WCl, sublimes on the cooler part of the tube, and is then distilled several times in a stream of dry Cl, and then in

a current of dry H (a small quantity of WCl, is formed, and distils off with the H). Teolu (A. 187, 255) obtained WCl, by heating WO, and PCl, in a sealed tube at 170°. WCl, forms dark-POI, in a scaled tube at 170°. WCl. forms dark-violet crystals; crystallises from CS, in brown, six-sided tablets, from POCl. in steel-blue, metal-like, regular crystals (T., l.o.). Melts, out of contact with air, at 275°, and boils at 346°7° at 760 mm. pressure (R., l.o.). V.D. 190 at 350° (Debray, C. R. 60, 820; Roscoe, l.c.); V.D. 168.8 at 440° (D., l.o.; R., l.o.; Rieht, B. 3, 666). Dissolves readily in CS, or POCl, (T., l.o.). Distilled in CO, gives WCl, and Cl; this fact taken in connection with V.D. at 440° shows that at somewhat above b.p. WCl, probably dissolved. at somewhat above b.p. WCl, probably disso-ciates to WCl, and Cl. WCl, is unchanged in ciates to WCl, and Cl. WCl, is unchanged in air; but if a trace of WOCl, is present, HClAq and WO, are formed. Hot water produces WO, and HClAq. Heated in air, or in O, forms WOCl, (Roscoe, l.c.; Blomstrand, J. pr. 82, 417). WOCI, is also formed by heating WO, with WCl. WCl, interacts with NH, at the ordinary temperature, to form NH4Cl and WaN, (Rideal,

C. J. 55, 44).
TUNGBTEN PENTACHLORIDE WCl., Mol. 360.45. Prepared by repeatedly heating WCl, somewhat above its b.p. (346.7°) in a stream of dry H, and when a solid residue has been formed removing the WCl, from less volatile lower chlorides by heating in CO. (Roscoe, C. N. 25, 61). Black, lustrous, heedle-shaped crystals; 61). Black, Instrous, needle-snaped crystals; very deliquescent; melts at 248°, and boils at 275-6° (R., l.c.). V.D. 175-6 to 179-9 at 350°; 185-7 to 186-4 at 440° (R., l.c.). Slightly soluble in CS₂ forming a blue liquid; forms an olivegreen solution in water, but is mostly decomposed to HClAq and blue oxide of W. Heated

posed to HCLR4 and blue battle of W. Heated in O forms WOCl, and Cl (R., l.c.; cf. Blomstrand, J. pr. 82, 425; 89, 230).

TUNGSTEN TETRACHLORIDE WCl. This compound is present in the solid residue obtained by heating WCl, in H in the preparation of WCl, (v. supra); it is prepared by distilling this residue, in a bath of H2SO, in a stream of dry CO2, returning the distillate to the distilling vessel and heating again, and repeating these processes heating again, and repeating these processes several times (Roscoe, l.c.). A soft, crystalline, greyish-brown powder; very hygroscopic; has not been fused or volatilised; heated strongly, it gives WCl, and WCl. Heated in H to ca440° pyrophorio W is produced. Decomposed by water to WO, and a greenish-brown solution

Tungsten Dichloride WCl., Prepared by heating WCl., in a bath of zinc, in a stream of dry CO.; WCl, distils off and WCl, remains. A loose, grey, amorphous powder; water-forms loose, grey, amorphous powder; water_torms WO, and HClAq, with evolution of H; interacts with H which has been passed through HNO, Aq to form WO, HCl. and NH, NO, (R., l.c.).

Tuagsten, cyanides of. No cyanides of W

have been isolated; according to Wyrouloff (A. Ch. [5] 8, 444; cf. Atterberg, Bl. [2] 24, 355), compounds containing W. K. and FcCy, are ob-

compounds containing w, h, and recy, are ortained by adding HClAq to mixture of K tungstates and K ferrogyanide.

Tungsten, fluorides of. No fluoride of W has been isolated According to Berzelius (P. 4, 147), when a solution of WO, H o in HFAG is evaporated and the residue is treated with water, a solid remains which is free from F after being

heated in NH₂. According to Riche (A. Ch. [8] 50, 41), a solution of tungstic hydroxide in HFAq gives crystals of WO₂.H₂O on evapora-

Tungstoxyfluorides. (Fluotungstates.) By dissolving tungstates of the form M.WO. in HFAq, Mavignac obtained a series of compounds of the forms 2MF.WO,F,xH,O and M"F,WO,F,xH,O, and also a few compounds of the form MF.WO,F, H,O (A. Ch. [3] 69, 67). These compounds may be regarded as salts of the hypothetical acids H,WO,F, and HWO,F,; they are similar to some classes of the com-pounds described as fluomolybdates (this vol. p.

The tungstoxyfluorides etch glass even when dry; they react slowly with acids, giving WO, H₂O. The salts of the forms M¹₂WO₂F₄ and MiWO,F, were prepared by dissolving Mi₂WO, and MiWO, in HFAq and evaporating; in some cases also by dissolving WO, H2O in HFAq, adding MOH, and evaporating. salts of the form M'WO,F, were formed by dis-solving acid tungstates in HFAq and evapora-BOIVING Not a compounds were isolated: (1) $M^1_{\nu} \text{VO}_2 \text{F}_{\nu} \text{xH}_2 \text{O}$; $M = \text{NH}_4$, x = 0; M = K, x = 1; M = Na, x = 0; (2) $M^{11} \text{VO}_2 \text{F}_{\nu} \text{xH}_2 \text{O}$; $M = \text{ZH}_1$, x = 10; (3) $M^{11} \text{VO}_2 \text{F}_{\nu} \text{xH}_2 \text{O}$; $M = \text{NH}_4$, x = 1. The salts $(NH_4)_{\nu} \text{VO}_2 \text{F}_{\nu} \text{(NH}_4)_2 \text{VO}_4$ and $\text{CuVO}_2 \text{F}_4 \text{NH}_4$

By dissolving K, WO, F, H,O in 4 p.c. H,O,Aq, . and crystallising from dilute H2O.Aq containing 21) obtained K₂WO₂F₄,H₂O. P. calls this compound fluoroxypertungstate; it might also be

named pertungstoxyfluoride.

Tungsten, haloid compounds of. When Wis heated in a stream of Cl the compound WCl, is nented in a stream of Ci the compound WCl, is formed, and this by reduction in H gives WCl, WCl, and WCl. The compound WBr, is formed by heating W in Br vapour, and WBr, is obtained by partially reducing WCl, in H. Small quantities of WI, are obtained by heating W in vapour of I. No fluoride of W has been isolated. Oxychlorides and oxybromides of the forms WCV and WCV are obtained by heating Forms WOX, and WO₂X₂ are obtained by heating W oxides in Cl or Br, and in other ways. The following compounds have been vaporised, and Word, and Worls, and Words, and W of Mo of the form MozX2z is to be followed (v. vol. iii. pp. 427, 428) it is probable that the molegular formulæ of the dichloride and dibfomide of Ware not less than WaX.

Tungsten, hydroxides of, v. Tungsten oxides AND HYDRATED OXIDES (p. 800), also TUNGSTEN

OXYACIDS (P. 802).
Tungsten, iodide of, WI2. This, the only iodide of W that has been isolated, is obtained, in very small quantities, by passing I vapour, mixed with CO₂, over red-hot W. It forms a metal-like, greenish crust; heated in air it gives

metal-like, greenish crust; heated main a greenish crust; heated with a large word of I and leaves WO, jt it is not decomposed by water (Roscoe, C. N. 25, 78).

Tungsten, nitrides of and allied pounds. Compounds of with N, and greenish also with N and H, are formed by heating words. WCl or WOCl in NH, ; the interaction of NH, and WO, probably produces a compound, or com-pounds, of W, N, H, and O; and a compound of W, N, and O is perhaps formed by heating WO. with NH.Cl.

Tungsten nitrides. By passing dry NH, TUNOSCEN MITRIDES. By passing dry NH₂ over WOl₂, and washing away the NH₂Ol produced, by water, Rideal (O. J. 55, 44) obtained a black lustrous powder, agreeing fairly with the composition W₂N₂. This substance is insoluble in HNO₂Aq, dilute H₂SO₂Aq, or NaOHAq; hot conc. H₂SO₂ produces NH₂ and WO₂; fusion with NaOH forms Na tungstate; heating in air, with accurage region vidiage it to WO₂ (R. Le.).

or with aqua regia, oxidises it to WO, (R., Lc.).

By continued heating WUI, in NH, to a temperature difficult to regulate, as slightly too high a temperature produces W, Uhrlaub obtained a black substance to which he gave the

ormula W₁N₂ (Die Verbindungen einiger Metalle mit Stickstoff, Göttingen, 1859).

Tungsten amidontraides. By the action of NH₂ on WO₁₈, Wöhler (A. 73, 198) obtained a black substance ordining from 86.78 a 90.8 black substance containing from 86.76 to 90.8 p.c. W, and 8.24 p.c. N; W. supposed this substance to be a mixture of two amidonitrides, 2WN₂W(NH₂)₂ and 2WN.W(NH₂)₂. W. oktained similar black substances, which he did not analyse by heating ablerides of W mith NH C. analyse, by heating chlorides of W with NH,Cl (A. 105, 258).

Compounds of tungsten with N, H, and O. Wöhler (4.78, 198) obtained a black substance by heating WO, to dull redness in dry NH,; the percentage of W in this substance varied from 87.65 to 88.47, and it contained 7.15 p.c. N, and c. 2 p.c. To be substance W. gave the formula W.N.H.Q. (= 4WN...W.(NH.)...2WO.). Riden (C. J. 55, 44) passed dry NII, over WO.; heated to a dull gedness until the yellow WO. was changed to a black, amorphous powder; he allowed to cool, and removed excess of NH, by passing a current of dry air through that the tube. The black substance thus obtained contained 85-26 p.c. W, and 7-4 p.c. N; assuming c. 3 p.c. H, the numbers agreed fairly with the formula O.H.N.Y

Compound of tungsten with N and O. Rideal (l.c.) obtained a black powder, agreeing in composition approximately with the formula WN, WO, by heating WO, with NH,Cl until the weight became constant. According to Rideal (Lc.) finely divided W does not change when heated in a stream of dry NH, after having been heated to redness in dry H; nor does NH, react with the blue oxide of W when

heated therewith.

Tungsten, oxides and hydrated oxides of. When pawdered W is heated in O it combines to form WO, by heating this oxide in H a blue oxide is formed, to which various formulæ intermediate between WO, and WO, have been assigned; by further heating in H, or, with C, the dioxide WO, in produced. There are indications of an oxide with more O than WO. WO, dissolves in acids, but corresponding salts have not hean isolated; the blue oxide apparent for solves in acids, but corresponding salts have not been isolated; the blue oxide separates from these solutions; WO₂ is also soluble in alkali solutions. WO₂ is insoluble in acids; it dissolves in alkali and alkaline carbonate solutions, forming tungstates (v. under Tungstan oxxaodes, p. 802). WO₂ coabines with many acidic exides to form compounds which react as acidic exides to form the compound of (v. p. 801). WO, is the anhydride of more than

one tungstic soid (v. p. 801). None of the oxides has been vaporised; the mol. w. of none is known.

TUNGSTEN DIOXIDE WO. (Brown oxide of

tungsten.)

Formation .- 1. By heating a mixture of **Mormation.—1. By neating a mixture of WO, and C to redness (Buchholz, S. 8, 1).—2. By heating WO, to incipient redness in H (Wöhler, A. 73, 198; 77, 262).—3. By decomposing WOl,, or WOl., or y H.O (Roscoe, C. N. 25, -61, 73).—4. By the reaction of Zn and HClAq on WO, (Wöhler, P. 2, 345), or on solution of a way to weather (Pick I. 1).

metatungstate (Riche, Lc.).

Preparation.—WO, is placed in a porcelain tube closed at one end and provided with a long opening in the middle; this tube is placed inside another porcelain tube which is kept at red heat, while H is passed through as long as water continues to be formed (Wöhler, A. 77, 262 note); the product is allowed to cool in H, and is kept

in H for 24 hours (Riche, A. Ch. [3] 50, 29).

Properties.—A brown powder with a slight violet sheen; prepared by reducing WO₂ by Zn and HClAq, the oxide is obtained in metal-like

ustrous crystals, pseudomorphs of WO₂. S.G. 12·11 (Karsten, S. 65, 394).

Reactions.—1. Moist WO₂ oxidises rapidly in air to WO₃; as prepared by reducing WO₃ in H it is pyrophoric, but if allowed to cool slowly in H the product is not pyrorhoric (Berzelius, P. 4, 147; 8, 267; Wöhler, l.c.; Riche, l.c.).-2. Heated strongly in hydrogen gives W.—
3. Chlorine forms WO.Cl. when heated with WO. (Roscoe, L.c., p. 63).—4. Heated to dull redness in a stream of ammonia, a compound, or compounds, of W with N. H., and O is formed (v. Compounds of W with N, H, and O, under Tungsten nitrides, supra). — 5. By heating with sal ammoniac, Rideal (C. J. 55, 44) obtained a black powder approximately Wn. WO, (v. Compound of W with N and O, supra).—6. Moist WO, dissolves easily in warm hydrochloric or sulphuric acid, forming reddish-brown solutions from which blue oxide of W separates. WO, prepared in the dry way is scarcely acted on by acids, except aqua regia, which oxidises it to WO₃.—7. WO₂ dissolves in conc. potash solution, giving off H, and forming K tungstate. 8. Reduces mercuric chloride to HgCl, and ppts Cu.O from solutions of copper salts (Riche, A. Ch. [3] 50, 5).—9. Heated in nitric oxide to below 500° gives the blue oxide; oxidised to WO, by heating in nitrogen dioxide to c. 800° (Sabatier a. Senderens, C. R. 114, 1429; 115, 236).

BLUE OXIDE OF TUNGSTEN. Blue compounds of W and O are obtained by heating WO, with of W and O are obtained by heating WO, with reducing agents; analyses lead to formule such as W₂O₃, W₂O₄, or W₂O₁₁, intermediate between WO₂ and WO₂. Malaguti (A. Ch. [2] 60, 273) gave the formula W₂O₄ to the blue product of heating WO₂ in H to c. 250°; von. Uslar (Beiträge sur Kenntniss des W und Mo [Göttingen, 1835]) gave the formula W₂O₄. Gmelin said that a blue oxide of the composition W₂O₁₁ is formed by strongly heating WO₂ in CO.

Blue compounds are also obtained by strongly heating. WH tungstates of the context with air

heating NH, tungstates out of contact with air (Malaguti, I.c.; von Uslar, I.c.). Aqueous solutions of WO, or tungstates are coloured blue by the action of very weak reducers, e.g. by exposing moist WO, on paper to sunlight (Liesegang,

C. C. 1865. 948), or by the action of SnCl, Aq on Scheibler, J. pr. 83, 313). Conc. H.SO, or HClAq gives a blue colour when heated with W (Riche, A. Ch. [3] 50, 15). Tungstates boiled with acetic acid and then electrolysed give blue coloured sabstances (Smith, B. 13, 753).

PEROXIDES OF TUNGSTEN. Fairley (C. J. 31, 141) obtained indications of an oxide with more O than WO,, by dissolving WO, 2HO in H,O,Aq, and evaporating over H,SO, in vacuo; the green, transparent, yellow scales thus obtained dissolved in water, forming a solution which could be titrated with KMnO, Aq, with separation of WO, xH,O. Cammerer (Chem. Zeitung, 15, 957) found that WO, dissolved in boiling H2O2Aq, with evolution of O; on evaporation he obtained yellow powder, to which he gave the formula WO₃.H₂O₂.H₁O (cf. reaction of H₂O.Aq with CrO₃Aq, vol. ii. p. 166). According to Péchard (C. R. 112, 1060), a salt Na₂O.W₂O₂.2H₂O is formed by boiling Na paratungstate solution with H2O2Aq and evaporating in vacuo.

TUNGSTEN TRIOXIDE WOs. (Tungstic anhydride. Sometimes erroneously called tungstic

acid.)

Occurrence.—As tungstic ochre or wolframine in Cumberland, Connecticut, North Carolina, &c. Formation.—1. By strongly heating in air tungstate of NH₄ or of Hg⁴.—2. By strongly heating WO₄:xH₂O.—3. By burning W in air

Preparation. -An aqueous solution of commercial Na, WO, is poured into boiling HClAq (1:1); the ppd. WO, is washed with HClAq until NaCl is completely removed; it is then washed with water to remove all HCl, and dissolved in NH, Aq; the solution is evaporated to dryness, and the NH, salt thus obtained is heated in an open crucible until every trace of NH₄ is driven off (Roscoe, C.N. 25, 73). Bernoulli (P. 111, 590) recommends to boil the NH₄ salt for a long time with successive quantities of HNO, Aq (to remove traces of Na salts), and to wash the residual WO, quite free from acids (cf. Zettnow, P. 130, 16, 240). WO, is obtained in crystals by very strongly heating the amorphous oxide (Bernoulli, P. 111, 595; Schafarik, W. A. B. 47, 246); by dissolving WO, in molten borax (Nordenshiold, P. 114, 612); by strongly heating the oxide in a current of HCl (Debray, C. R. 55, 287); or by heating to whiteness a mixture of Na2WO, and Na₂CO₂ imbedded in NaCl, when crystals of WO, sublime (D., l.c.).

Na, WO, may be prepared from wolframite by heating a mixture of 150 pts. of the finely powdered mineral with 100 pts. calcined Na₂CO₃ and 15 pts. NaNO, for four or five hours, in an iron vessel, lixiviating with water and crystal-lising (g. Franze, J. pr. [2] 4, 238; cf. Huntington, B. 17, 203; Scheibler, J. pr. 83, 239).

Waddell (Am. 8, 380) prepares pure WO, from tungstenite, by treating the powdered mineral with aqua regia, washing the residue, fusing it with KHSO, dissolving in water, and fractionally ppg. by HgNO₂Aq; the first pps. are then decomposed by aquaggia, the WO₂ thus obtained is dried and fused with Na₂CO₂, the fused mass is dissolved in water, tartaric acid is added, and H.S is passed into the solution; the filtrate Vol. IV. from ppd. MnS, &c., is boiled till H₂S is expelled, and is then fractionally ppd. by HgNO₂Aq; the later pps. are collected, washed, and decomposed by heating in an open vessel. For a method of preparing WO₂ from wolframite v. Preparation of Tunusten, p. 197.

Properties .- A heavy, canary-yellow powder; becoming orange-coloured when heated (Roscoe, C. N. 25, 73). Crystalline WO, is described as C. N. 25, 73). Crystalline WO, is described as wine-yellow, very lustrous, rhombic tablets (Nordenskjold, P. 114, 612). A trace of Na tungstate gives a green colour to WO, (R., Lo.). S.G.: amorphous, 7-13, to 7-16 (Zetmow, P. 130, 16, 240; Karsten, S. 65, 394); crystalline, 7-23 at 17° (Z., Lo.); 6-38·(N., Lo.). S.H. (8° to 98°) 07983 (Regnault, A. Ch. [3] 1, 129); (22° to 52°) 0894 (Kopp, T. 1865, 74). Melts readily in the blowpipe (Riche, A. Ch. [3] 50, 29); can be sublimed by mixing with Na CO, and heating be sublimed by mixing with Na CO, and heating to whiteness (Debray, C. R. 55, 287); also by strongly heating in HCl (Schafarik, W. A. B. 47. 246). Not decomposed at m.p. of Pt (c. 1750° (Read, C. J. 65, 313 [1894]). On exposure to light WO₃ turns, greenish, dwing to partial reduction (Roscoe, *l.c.*; cf. Liesogang, C. C. 1865, 943) WO, is insoluble in water or acids, even in boiling conc. H2SO4; it dissolves in hot KOHA4. NH3Aq, or K.CO3Aq, also in molten K2CO3, KHSO3, or K2WO1; also in molten alkali chlorides. in air, with evolution of Cl (Schultze, J. pr. [2] 21, 437, 441). WO₃ acts as an acidio oxide, forming tungstates (v. Tungsten oxyacids, p. 802).

Reactions .- 1. Heated in hydrogen, WO, is reduced to the blue exide, then to WO2, and finally to W (v. Blue exide of Tungstenep. 800; TUNGETEN DIOXIDE, p. 800; and TUNGETEN, p. 797).—2. Reduction to WO, or W is effected by heating with carbon.—3. Heated with potassium or sodium, WO, gives W .- 4. Reduction to the blue oxide, and then to WO, brought about by zine and hydrochloris acid, by stannous chloride, and also by heating with water and different organic compounds .- 5. Heating with carbon in chlorine produces WO,Cl., and WOCl, -6. WOCl, is formed by passing vapour of tungsten hexachloride over heated (Roscoe, C. N. 25, 63) ...- 7. A mixture of WO, and (Moscoe, C. N. 23, 03).—7. A mixture of WO₂ and calcium chloride heated to reduess in carbon dioxide gives WO₂Cl₂ (Schultze, J. pr. [2] 21, 441).—8. Mixed with carbon and heated in bromine, WO₂ gives WOBr₄; and WO₂Br₁ is formed by passing vapour of tungsten pentabromids over hot WO₂ (Roscoe, Lc. p. 73).— WO, is said to dissolve in molten alkali chlorides, in air, giving off Cl; heated in absence of air (in a stream of CO₂) with chloride of calcium, cobalt, iron, magnesium, or nickel, it is said to give WO₂Cl₂ and MWO₄ (Schultze, L.c.).—10. Heating with phosphorus pentachoride produces WCl, and POCl, (Teclu, 2. 187, 255) but WO,Cl, and WOCl, are also formed, accordbut WO, 13, and WOG1, are also formed, according to the relative masses of WO, and PCI, and the temperature (Schiff, A. 197, 185).—
11. WO,CI, WOCI, and CO, are formed by heating WO, in vapour of carbon tetrachloride (Watts a. Bell, C. J. 33, 442).—12. Compounds of W with N, H, and O (v. p. 800) are formed by heating WO, in ammonia; and a compound of Wwith N and O is probably produced by heat. Wwith N and O is probably produced by heating WO, with sal ammoniac (v. p. 800).-13. WS.

is formed by passing sulphur vapour, or hydrogen sulphide, over WO, heated to whiteness (Berzelius); also by heating to redness a mixture of WO, with 6 pts. of mercuric sulphide (B.; Brock, J. pr. 54, 254).

Hydrates of Tungsten Trioxide. Various compounds of the form WO. xH,O have been Various isolated; as these compounds act as acids, they are described under Tungsten oxyacids.

Tungsten oxyacids, salts, and derigatives of. Several hydrates of WO, that react as acids are known. WO, also combines with many acidic oxides—such as $\mathcal{P}_2\mathcal{O}_3$, $\mathcal{B}_2\mathcal{O}_3$, $\mathcal{S}i\mathcal{O}_2$, &c.—and the compounds so formed combine with basic oxides to form salt-like bodies.

TUNGSTIC ACIDS. The hydrates of WO. fall into two classes: tungstic acids, which are insoluble, or nearly insoluble; in water; and

metatungstic acids, which dissolve in water. Tungstic acids. The monohydrate WO, H.O, or orthotungstic acid WO₂(OH), is obtained by dissolving WO₂ in liot alkali or alkaline carbonate solutions, and boiling these solutions with excess of a mineral acid. It is also said to be obtained by decomposing an ammoniacal solution of WO, by Cl (Dumas, A. Ch. [3] 55, 144); and also by boiling powdered wolframite with aqua regia. This acid is a yellow solid; it reddens litmus; is insoluble, or almost insoluble, in water. According to Braun (J. pr. 91, 39), it is changed to $2WO_3$. H_2O at 100° ; according to Zettnow (P. 130, 16, 240), this change is effected at 50°. The acid is slowly reduced by Zn and HClAq, the final product being WO. (O. v. d. Pfordten, B.

The dinydrate WO₃.2H₂O is said to be formed by adding a mineral acid to a dilute solution of by adding a mineral acid to a dilute solution of an alkali tungstate M₂WO₄, and drying in the air; also by decomposing WCl₂, WOCl₄, or WO₅Cl₂ by water (Forcher, W. A. B. 44 [2], 173; of. Riche, A. Ch. [3] 50, 36; Anthon, J. pr. 9, 6). Forms WO₅H₂O by drying over H₂SO₄ (Braun, J. pr. 91, 89). This hydrate is described Ostaun, J. pr. 91, 33). This hydrate is described as an amorphous, white solid; reddens litmus; somewhat soluble in water, but insoluble if a little acid is present. By boiling with dilute acids is said to give WO.H.O.

The heminydrate 2WO.H.O. or distinguish

acid H₂W₂O₃, is said by Braun (l.c.) to be formed by heating the monohydrate to 100°; the change is complete at 50° according to Zettnow (P. 130,

METATUNGSTIC ACIDS. Acids of the composition 4WO₃.xH₂O are obtained by decomposing hot could. BaW₄O₁₃Aq by the equivalent position 4WO_{3.}ER.O are obtained by mosapposing hot coile. BaW,O_{1.}Aq by the equivalent quantity of H.SO₄, filtering from BaSO₄, and evaporating (Scheibler, *J. pr.* 83, 310); also by decomposing PbW,O_{1.}Aq by H.S. filtering, and evaporating (Forcher, W. A. B. 44 [2], 173). The composition of the acid formed by evaporating in vacuo over H.SO₄ is probably H.W,O_{1.}, ?H_O (Scheibler, *l.o.*; cf. Persoz, C. R. 34, 185; Lotz, A. 91, 52). BaW,O_{1.} is dotained by ppg. a hot cone. solution of (NH,)₂W,O_{1.} shop balling (NH₂)₂Aq; (NH₂)₂Ny,O_{1.} by ppg. (NH₂)₂Aq by Pb(O₂H₂O₃)₂Aq; (NH₂)₂Ny,O_{1.} is formed by boiling (NH₂)₂W₄O₄ and evaporating. According to Zettnow (P. 100, 16, 240), the pp. obtained by decomposing Na, WO₄Aq by a mineral acid has the composition 4WO₂H₂O(=H₂W₄O₁₂) after drying at 200°.

4WO₃.H₂O(=H₂W₄O₁₂) after drying at 200°.

Metatungstic acid crystallises in sulphur. yellow octahedra; the acid is readily soluble in water, forming a very sour, intensely bitter liquid. A cone solution gives a pp. of WO₂.BL_O on standing; when a dilute solution is boiled it congulates and gives a pp. of white WO, 2H₂O, and then of yellow WO, H₂O. The heats of neutralisation of H₂W₁O₁Aq by Na₂OAq, K₂OAq, BaOAq, and SrOAq are given by Péchard (C. R. 108, 1167); the values are nearly the same as those for HNO, Aq and H, SO, Aq. When four equivalents of base are added to H2W4O13Aq,

orthotungstates M, WO, are formed (P., Lc.).

By long-continued boiling 2 pts. Na, WO, with 1 pt. As₂O₃, evaporating, treating with alkali solution, and repeatedly crystallising, Lefort (A. Ch. [5] 25, 205) obtained fine, very lustrous crystals, which were very soluble in water and in alcohol; to this acid L. gave the composition H2W1O13.6H2O, and the name luteometatunastic acid.

Colloidal (meta?) tungstic acid. By adding to 5 p.c. Na₂WO₄Aq rather more HClAq than sufficed to neutralise the Na, and dialysing, with addition from time to time of a little HClAq, Graham (C. J. 17, 318) obtained a solution in water of tungstic acid. The solution was not gelatinised by acids, salts, or alcohol at the ordinary temperature; it remained clear at 200°. According to Sabanéeff, (J. R. 21, 515; Abstract in C. J. 58, 1215), determinations of the freezing-point of an aqueous solution of Graham's soluble acid point to the formula $3WO_3.H_2O(=H_2W_3O_{16})$. As the values for mol. w. obtained by S. varied from 679 to 995, there

seems little reason for acopting the formula H₂W₁O₁₀ (713) rather than H₂W₁O₁₁ (944).

TUNGSTATES. A great many tungstates have been prepared. The proportion of basic to acidic radicle varies much in these compounds. The better studied tungstates have been divided into three classes-orthotungstates MO.WO, 8MO.7WO, paratungstates paratungstates 8MO.7WO₂, or perhaps 5MO.12WO₃, and metatungstates MO.4WO₂ but as many tungstates are known which do not fit into any of these classes it seems better to adopt a nomenclature and arrangement similar to those employed for the molybdates (cf. vol. iii. p. 423), based on the number of WO, radicles in the salts. Arranging the tungstates on this plan we get the following table. R = divalent metal, or two atoms of a monovalent metal.

(Ortho) Monotungstates RO.WO, or RWO,

derived from the acid H₂WO₄.

Ditungstates RO.2WO₂ or RW₂O₇; derived from the acid H2W2O7.

m the acid 12 w 20,.

(3:7 tungstates 3RO.7WO, or R, W, O₂₄.

(Para) { 5:12 tungstates 5RO.12WO, or R, W, O₁₁.

2:5 tungstates 2RO.5WO, or R, W, O₁₂.

3:8 tungstates 8RO.8WO₃ or R₃W₃O₂₅₀ Tritungstates RO.3WO₃ or RW₃O₁₀; ?derived from Graham's colloidal acid.

(Meta) Tetratungstates RO.4WO, or RW,O101 derived from the soid H2W4O11

Pentatungstates RO.5WO, or RW, O100 Hexatungstates BO.6WO, or RW.O. Octotungstates RO.8WO, or RW.O.

The tungstates which have been most thoroughly examined are the monotungstates or orthotungstates; the paratungstates, which

are either 3:7 or 5:12 salts; and the tetra- or metatungstates.

For thiotungstates v. Tungsten, Thio-Acids

AND SALTS OF, p. 810.

ORTHOTUNGSTATES OT MONOTUNGSTATES. BO.WO, or RWO. Salts of H₂WO, which is the monohydrate of WO. The alkali ortho-tungstates are obtained by dissolving WO, or WO₃.H₂O in alkali or alkali-carbonate solutions; or by fusing WO₂ with alkalis, alkaline carbonates, or alkali acid sulphates, and dissolving in water. The other orthotung states are generally obtained from solutions of the alkali salts by ppn.; also by strongly heating WO, with metallic oxides or carbonates; also by fusing the alkali salts with metallic chlorides, and washing with water (Manross, A. 81, 243; 82, 356; Geuther a. Forsberg, A. 120, 268; Schultze, A. 126, 56). The orthotungstates are insoluble in water, except the alkali salts and the Mg salt. Soluexcept the alkali saits and the Mg sait. Solutions of the alkali saits give pps. of WO₃.H₂O (yellow) or WO₂.2H₂O (white), with dilute H₂SO₄Aq, HClAq, HNO₃Aq, or H₄PO₄Aq; the pp. by HClAq dissolves in a considerable excess of conc. HClAq (Mallet, C. J. 28, 1228); cold solutions of metatungstates are not ppd. by acids. According to Marignac (A. Ch. [3] 69, 5) the pp. obtained by adding an acid to a solution of an alkali tungstate sometimes contains alkali, and sometimes the ppg. acid, according to the relative quantity of acid used, the dilution, and probably also the temperature. Orthotungstates which are insoluble in water, and the metals of which form carbonates that are insoluble in alkali carbonate solutions, can be brought into solution by fusion with alkali carbonates and treatment with water.

Solutions of orthotungstates give a white pp. with HgNO₂Aq; a bluish-white pp. with Cu(NO₂)₂Aq; a brown floculent pp. on adding K,FeCy,Aq, after adding HClAq; no pp. with tincture of galls until an acid is added, when a copious chocolate-coloured pp. is formed; and a yellow pp. with SnCl2Aq, which pp. turns blue when it is warmed with a little HClAq or H₂SO₄Aq. For the reactions with Zn and acid, and with KCNSAq, Zn and acid, v. Tuyssten,

STECTION OF, p. 798.

Barium orthotungstate BaWO, Prepared by fusing 7 parts BaCl₂ with 4 parts NacPand 2 parts Na₂WO₄, and washing with water; white octahedra (Geuther a. Forsberg, A. 120, 270); fusible with difficulty (Zettnow, P. 130, 256); S.G. 5-0035 at 13-5° (Clarke, Am. S. [3] 14, 281). BaWQ, 2H₂O, by adding four equivalents BaO in a column of BaBO, 208); (2) BaWO, H₂O and BaWQ, 2H₂O, by adding four equivalents BaO in a column of BaBO, 208); (2) BaWO, H₂O and BaWQ, 2H₂O, by adding four equivalents BaO in a column of BaBO. solution to H₂W₄O₃,Aq (Péchard, C. R. 108, 1167).

Cadmium orthotungstate CdWO. Obtained. s a yellow crystalline powder by fusing together as a yellow crystalline powder by using sognificant 11 parts CdCl₂, 16 parts NaCl, and 4 parts Na₂WO₄ (G. a. F., Lc., p. 268; Z., Lc., p. 240). The dihydrate CdWO₄, 2H₂O is obtained by ppg. a solution of a salt of Cdby Na₂WO₂Aq (Anthon, 100). J. pr. 8, 399; 9, 337; Smith a. Bradbury, B. 24, 2935).

Galcium orthetungstate CaWO₄. Occurs native as scheelite, S.G. 6.02 (Bernoulli, J. 13, 783). Obtained by adding K, WO, Aq to CaCl, Aq. Quadratic octahedra are formed by fusing Na, WO, with excess of CaCl, (Manross, A. 81, 243; 82, 348); also by heating the ppd, salt with CaO in a stream of HCl (Debray, C. R. 55,

Chromium orthotungstate $Cr_*(WO_4)_*, 20H_*O_*$. Obtained as a green pp. by adding Na, WO, Aq to $CrCl_*Aq$; loses 13H₂O at 100° (Lotz, A. 91, 66).

Cobalt orthotungstate CoWO .2H,O. violet powder; obtained by ppg. Co salt solutions by K₂WO Aq (Anthon, J. pr. 9, 344).

Copper orthorngstate CuWO, 2H₂O.

green powder, melting at a red heat and cooling to chocolate-coloured crystals? formed by ppg.

Cu salts by Na. WO. Aq (A., l.c.).

Ferrous orthogungstate FeWO. Obtained as opaque crystals by heating WO, and Fe,O, in a stream of HCl (Debray, C. R. 55, 288); also by fusing 2 parts FeCl, 2 parts NaCl, and 1 part Na.WO, (Geuther a. Forsberg, A. 120, 278; Zettnow, P. 130, 30). The trihydrate FeWO.3H O was obtained by Anthon (J. pr. 9, 343) as a brown powder by ppg. a ferrous salt by K₂WO₄Aq. Doublg compounds of the form mFeWO₁...MnWO₃ with the ratios m:n=7:1, 4:1, 3:1, 3:2, 1:2, and 1:7 were obtained by fusing FeCl, MnCl, NaCl, and Na, WO, in varying proportions (G. a. F., l.c. p. 270; cf. Z., l.c. p. 250). Wolframite has approximately the composition FeO.MnO.WO3

Lead orthotungstate PbWO4. Occurs native as scheeletine; obtained, as a white pp., by adding K, WO, Aq to solution of a salt of Pb (A., l.c., p. 342); quadratic octahedra are formed by fusing 10 parts Na₂WO₁ with 47 parts PbOl₂, S.G. 8.245 (Manross. A. 82, 357).

Magnesium orthotungstate MgWQ. Formed, in white octahedra, by fusing 2 parts MgCl, with 2 parts NaCl and 1 part Na, WO, (G. a. F.,

Lc. p. 272).

Manganese orthotungstate MnWO. Garnet-brown, lustrous, rhombic crystals; S.G. 6-7; obtained by fusing 2 parts MnCl., 2 parts NaCl, and 1 part Na, WO. (G. a. F., l.c.; Z., l.c.).

Mercurous orthotungstate Hg, WO. A

yellow pp., formed by adding solution of a mercurous salt to solution of an alkali tungstate (A., l.c.).

(A., L.C.).

Nickel orthotungstate NiWO. Formed by fusing 2 parts NiCl. with 2 parts NaCl and 1 part Na,WO.; brown, lustrous crystals (Schultze, A. 126, 56); S.G. 6.8845 at 20.5°, 6.8522 at 22 (Clarke, Am. S. [3] 14, 281). The hexahydrate, NiWO.6H.O. is obtained by ppn.

Potassium orthotungstate K.WO. . White. Potassium orthotungstate K.WO... White, triclinio needles; obtained by boiling WO. with an equivalent weight of KOHAq or K.CO.3Aq, and evaporating (Marignac, A. Ch. [3] 69, 18: Anthon, J. pr. 8, 399; 9, 337). Decrepitates when heated; melts at sed heat (M. l.c.), taking up CO. (Ulkk; W. A. B. 56 [2], 148; cf. Knorre, J. pr. 27, 89). Various hydrates are electrical by correctlining a solution of WO. obtained by crystallising a solution of WO, in K.CO, Aq under different conditions (M., l.c.; A., l.c.; Riche, A. Ch. [3] 50, 45).

Silver orthotungstate Ag, WO,. Appale-yellow, amorphous pp. by adding Na, WO, A solution of a salt of Ag; malts below redness, and becomes crystalline on cooling; easily soluble in HNO.Aq; soluble in NH.Aq (Zettnow, P. 130, 30; cf. Muthmann, B. 20, 984; Wöhler a.

Rautenberg, A. 114, 120). By evaporating a solution in NH,Aq over CaO and NH,Cl, Wid. mann obtained the compound Ag, WO, 4NH,

(Bl. [2] 20, 64).

Sodium orthotungstate Na, WO, .2H,O. Obtained by crystallising a solution of WO, in the equivalent quantity of NaOHAq or Na₂CO₃Aq. Transparent, colourless, rhombic tablets (Marignac, A. Ch. [3] 69, 22). Effloresces in vacuo, righao, A. Oh. [5] 09, 22). Enforcesces m vacua, or in dry air. Loses all H₂O at 190°. S.G. 3-2588 at 17.5°, 3-2314 at f9°; S.G. of Na₂WO₄. 4-1743 at 20.5°, 4-1833 at 18.5° (Clarke, Am. S. [3] 14, 281). Solubility = 41 at 0°, 55 at 15°. 123.4 at 100° (Riche, J. pr. 69, 10). For S.G. of Na WO Aq of different concentrations, v. Franz (J. pr. [2] 4, 238). For E.C. of Na₂WO₄Aq v. Walden (Z. P. C. 1, 529).

Strontium orthotungstate SrWO4. Obtained by ppn. (Anthon, l.c.); also by fusing 2 parts SrCl₂, 2 parts NaCl, and 1 part Na₂WO₄ (Zettnow, Lc.; Schultze, A. 126, 56).

Zine orthotungstate ZnWO. Colourless tablets; formed by fusing 2 parts ZnCl, with 2 parts NaCl and 1 part Na, WO, (Couther a. Forsberg, A. 120, 270; cf. Zettnow, P. 130, 240).

Paratungstates. A number of acid tungstates have been isolated, the composition of which is expressed by one of the formulæ 3RO.7WO, or ShO.12WO. The former formula was given by Lotz (A. 91, 49) and Scheibler (J. pr. 83, 273); the latter formula by Laurent (A. Ch. [3] 21, 54) and Marignao (A. Ch. [3] 69, 5). The two formulæ represent salts of almost identical composition, and no way has been found of deciding which formula is the better (cf. Knorre, J. pr. [2] 27, 83). The acid tungstates of this series are more easily formed and crystalhse better than the other acid salts; they are generally called paratungstates, following the suggestion

made by Marignac.

The alkali paratungstates are obtained by seturating hot alkali solutions with WO, and crystallising; most of the other paratungstates are prepared by ppn. from solutions of the alkali salts. The alkali salts are soluble in water, the other salts are insoluble. Solutions of alkali paratungstates give, with dilute HClAq, white pps. which become yellow on boiling (WO, 2H, O). Metatungstates, RO.4WQ, are formed by gradually adding HClAq to boiling solutions of paratungstates; meta-salts are also formed by boiling para salts with WO3.H2O. Solutions of paratungstates are not ppd. by SO,Aq, HIAq, bitrie, tartarie, or oxalic acid; but the presence of one of these acids does not hinder ppn. by HClAq. Solutions of alkali paratungstates give pps. with salts of almost all the heavy metals. H₂S reacts with alkali paratungstates in solution to form solutions of thiotungstates which give frown pps. with skids, soluble in (NH.) SAq. Paratungstate: readily react with H.PO, H.Aso., &c., to form complex acids (v. p. 807), solutions of which are not ppd. by soids, except these are added in considerable by sats, sat, whose of paratungstates are, therefore, not ppd by HClAq in presence of H₂PO₄, H₂B₂O₄, &c. For the reactions of paratungstates with PtO₄H₂ v. Rosenheim (B. 24, 2897; the reaction is rather indefinite).

If the simpler (3:7) formula is adopted, the

paratungstates are represented as 3Rt,0.7W0 BRUO.7WO, and Ruy.0.7WO, i.e. as salts of the hypothetical acid H_wW.0.2w therein 6H are replaced by 6R', 3R', or 2R'm; if the less simple formula (5:12) is adopted, the paratungstates of monovalent and divalent metals are regarded as salts of the hypothetical acid $H_1 W_{12} O_0$ $'=12WO_3.5H_2O$), wherein 10H are replaced by [=12WU₃.0H₂U₃, wherein 10H are replaced by 10R¹ or 5R¹¹; paratungstates of R¹¹ must be represented in this scheme by the complicated formula $R^{III}_{lo}(W_{12}O_{4l})_s$. In the paratung states which have been best examined $R^* = NH_{4}$, Li, Hg, K, Ag, and Na; RII = Ba, Cd, Ca, Co, Cu, Pb, Mg, Mn, Ni, Sr, and Zn; and Rin = Al and Cf. The simpler formulæ are employed in the descriptions of the individual salts.

Aluminium paratungstate Al, W,O₂₄.9H,O. A flocculent pp., drying to gum-like lumps; obtained by adding (NH₄)₆W₄O₂₄Aq to a solution of a salt of Al (Lotz, A. 83, 65; Anthon, J. pr.

8, 399; 9, 337).

Ammonium paratungstate (NH₁)_aW,O₂,6H₂O. Obtained by dissolving WO₃,H₂O in NH₃Aq and crystallising at the ordinary, or a little above the ordinary, temperature (Lotz, A. 91, 55). Crystallises in white, rhombic needles (Marignac, A. Ch. [3] 69, 25; Kerndt, J. pr. 41, 190); also in rhombio tablets (M., l.c.); and is, therefore, dimorphous. Solubility = 2.8 to 4.5 at 15°-22°; when the solution is boiled the 'very soluble meta-salt (NH₄)₂W₄O₁₃ is formed. Loses 3.9 p.c. H₂O at 100°; when heated to redness the blue oxide of W remains mixed with compounds containing N (M., l.c.). Marignae (l.c.) gave the formula (NH₄)₁₀W₁₂O₄₁.11H₂O to this salt; Berzelius, and Anthon (l.c.) gave the formula (NH₄)₂W₂O₂,H₂O; and Richo (v. Marignac, l.c.) the formula (NH₄)₂W₁O₁₃·5 or 6H₂O.

Various double salts have been isolated; with Na₆W₇O₂₄ (v. Knorre, B. 19, 821; Gibbs, Am. 7, 236); with $K_0W_0O_2$ (v. Laurent, A. Ch. [3] 21, 59; Marignao, A. Ch. [3] 69, 55); with $Mg_3W_0O_2$ v. M. (i.c.), Lotz (A. 91, 61); with $Zn_3V_0O_2$ v. Lotz (i.c.); with $Cd_3W_0O_2$ v. Lotz (i.c.); with $Cd_3W_0O_2$ v. L. (i.c.); with $Cd_3W_0O_2$ v. Lotz (i.c.); with $Cd_3W_0O_2$ v. Lotz (i.c.); with $Cd_3W_0O_2$ v. Anthon (J. pr. 8, 399; 6 227)

Barium paratungstate Ba₃W,O₂₄.8H₂O. A white pp. formed by adding (NH₄)₆W,O₂₄Aq to excess of BaCl_AA₅, washing and drying over H.SO₄ (Lotz, A. 93, 50; cf. Knorre, B. 18, 327; 19, 826). Forms a double salt with Na₆W,O₂₄ (Scheibler, J. pr. 83, 314).

Cadmium paratungstate Cd, W,O2,.16H2O; white needles, obtained by adding Na, W,O2,Aq to excess of solution of a salt of Cd (Gonzalez,

J. pr. [2] 36, 44).

Calcium paratungstate Ca, W,O2.18H2O; a orystalline pp. formed by ppg. excess of CaCl_Aq by Na₈V,O₂₄Aq, and drying in the air (Knorre, B. 18, 328). Forms a double salt with Na₈W,O₂₄ (Conzalez, l.c.).

Chromium paratungstate Cr, W,O₂₄.9H₂O; a grey powder, obtained by heating CrCl₂ with (NH₁), W,O₂₄; shooluble in water, but dissolves in

CrCl,Aq (Lotz, A. 91, 66), Coralt paratungstate Co, W,O2, 25H2O (Gonzalez, l.c.); forms a double rait with Na, W,O2, (G., l.c.).

Copper paratungstate Cu, W,O24.19H2O; pale-green pp. formed by adding Na W,O MAQ to excess of CuSO,Aq (Knorre, B. 19, 826; v. also Gonzalez, J. pr. [2] 86, 44). Forms a double salt with Na,W,O_{2t} (K., Lc.).

Lead paratungstate Pb₃W,O₂₁; a white pp. formed by adding (NH_.)₂W,O₂₄Aq to Pb(NO₃)₂Aq (Lotz, A. 91, 49). Forms a double salt with Na₂W,O₂₄ (Gonzalez, l.c.).

Lithium paratungstate Li₆W,O₂₁.19H₂O. Large prisms, unchanged in air; obtained by boiling the proper quantities of WO, and LiCO. in water, and allowing to crystallise (Scheibler, J. pr. 83, 321).

• Magnesium paratungstate Mg₃W₂O₂₁, 24H₂O; obtained by ppn. (Knorre, B. 19, 824). Forms a double salt with Na₃W₂O₂₁ (K., l.c.).

Manganese paratungstate Mn, W, O2, 34H, O (Gonzalez, J. pr. [2] 36, 44). ◆ Forms a double salt with Na_eW₁O₂₄ (K., l.c.).

Nickel paratungstate Ni, W,O2,.14H2O (An-

thon, J. pr. 9, 344).

thon, J. pr. 9, 344).

Potassium paratungstate K₄W,O₂₁,6H₂O (Marignac, A. Ch. [3] 69, 33, gave the formula K₁₀W₁₂O₄₁.11H₂O). Prepared by saturating hot KOHAq with WO₂.xH₂O, and allowing to cool; by boiling K₂WO₄ with H₂O; or by fusing wolframite with § of its weight of K₂O₃, boiling the product with water, saturating the aqueous solution with CO₂, and crystallising (M., I). White whombic crystall isong (M., I). Lo.). White shombic crystals, isomorphous with the NH, salt (M., Lo.). Decomposed by melting, to K₂WO₄ and 5K₂O.14WO₃, without forming any meta-salt (Knorre, J. pr. [2] 27, 91). Solubility = 2.15 cold water, 6.6 boiling water.

Various hydrates have been obtained (v. Zettnow, P. 130, 211; cf. Lefort, A. Ch. [5] 9, 93; 15, 321; 17, 470; 25, 200). Forms double

93; 10, 521; 11, $\frac{1}{4}$ (7), $\frac{1}{2}$ (7), $\frac{1}{4}$ (7), $\frac{1}{4}$ (7), $\frac{1}{4}$ (8), $\frac{1}{4}$ (8), $\frac{1}{4}$ (9), $\frac{1}{4}$ (9), $\frac{1}{4}$ (1), $\frac{1}{4}$ (1) excess of AgNO₂Aq (Gonzalez, *J. pr.* [2] 36, 44).

Sodium paratungstate Na₃W₂O₂₄.16H₂O.

This formula is given by Scheibler (J.pr. 83, 285); This formula Na₁₀V₁₀O₄ is given by Laurent (l.c.), Marignae (l.c.), and by Friedheim a. Meyer, (Zeit. f. anorg. Chemie, 1, 81). Prepared by saturating hot NaOHAQ, or Na₂CO₂Aq, with WO₃xH₂O and evaporating to the crystallising point; also by passing CO2 into Na2WO4A o until the reaction is only faintly alkaline. Large, well-formed, white, triclinic crystals (Scheibler, I.c.; Marignac, A. Ch. [3] 69, 39). Effloresces in air; loses c. 3 of its H₂O over H₂SO₄; is dehydrated without decomposition at 300° (S., *l.c.*); heated to dull redness leaves a residue, insoluble in water, containing more than 5WO₂ to Na₂O (M., Lc.; also Knorre, J. pr. [2] 27, 71). Melts above dull redness, giving Na, WQ, and Na, WQ,; (meta-salt). Heated with water to 150° gives much meta-salt (K., Lc.). Solubility 8 to 9 at 35° to 40°; for the salts obtainable from an aqueous solution v. M. (l.c.), and also K. (B. 18, 2362). By boiling a solution with Na₂CO₂ transformation to Na₂WO₄ is complete (v. Schmidt, Am. 8, 16). A hydrate with 21H₂O has been obtained (M., l.c.). Forms double salts with Sr,W,O₂, (Gonzalez, J. pr. [2] 36, 44), and with Zn,W,O₃, (Knorre, B. 19, 823).

Strentium paratungstate Sr,W,O₂,8H₂O

(Knorre, B. 18, 327).

Zine paratungstate Zn.W.Ou.xH.O (Gonzalez, J. pr. [2] 86, 44). METATUNGSTATES or TETRATUNGSTATES METATUNGSTATES OF TETRATUNGSTATES, RIVA, VO, or RIVA, O, Salts of the acid H₂W₂O₁, (v. METATUNGSTIC AGIDS, p. 802). The metatungstates may be obtained by causing metatungstic acid H₂W₂O₁, xH₂O (v. p. 802) to interact with carbonates, chlorides, or nitrates; also by the reaction of a weak soil (H,PO,Aq is the best) with orthotungstates, the acid being added as long as the pp. of WO, xH,O which is at first formed re-dissolves; also from the alkali salts by double decomposition, or better from the Ba salt by interacting with sulphates; the alkali metatungstates are prepared by boiling solutions of the ortho-tungstates for some time with WO, xH,O.

Most of the metatungstates are very soluble in water and are crystallisable from aqueous solutions; aqueous solutions are not ppd. by acids in the cold, but pps, are obtained after long standing or boiling. Metatungstates are changed to orthor salts by excess of alkali; when strongly heated, orthorungstates are formed. Solutions of metatungstates are not ppd. by H2S; (NH4)2SAq gives a blue pp.; pps. are not obtained with salts of the heavy metals except Pb and Hg1; K, FeCy, Aq does not form a

Ammonium metatungstate (NH₁)₂W₁O₁₈BH₂O. This formula is given by Scheibler (J. pr. 83, 303); more complicated formulæ are given by Margueritte (A. Ch. [3] 17, 477), Laurent (A. Ch. [3] 21, 62), and Lotz (A. 91, 55). Obtained by boiling the para-salt (NH₂)₃W₁O₁₈H₂O with WO₂H₂O (Ma gueritte, A. Ch. [3] 17, 477); disc by boiling the para-salt with a little HNO₂Aq (Laurent, A. Ch. [3] 21, 62); also by heating the dry para-salt to 250°-300° (Scheibler, J. pr. 83, 304; cf. l'ersoz, A. Ch. [4] 1, 101; and Marigmae, A. Ch. [4] 3, 71). White octahedra; effloresces in air: Ammonium metatungstate 14] 3, 71). White octahedra; effloresces in air; loses 7H,O at 100°. Solubility in cold water = 120 (Lotz, l.c.), = 286 (Riche, A. Ch. [3] 50, 45). The solution is optically refractive. Insoluble in alcohol or ether. Forms a double

salt with NH₄NO₃ (Marignac, A. Ch. [3] 69, 61).

Barium metatungstate BaW₄O₁₂.9H₂O. Ob-Barium metatungstate Iaw (0,19H,0. Obtained by adding BaCl,Aq to a hot cone. solution of Na, W,O, a acidified by HClAq (Scheibler, J. pr. 83, 304). Crystallises in large, white, tetragonal octahedra; S.G. 4.298 at 14°; loses 6H,0 at 100°; easily soluble in hot water, decomposed by much cold water to WO, and BaW,O, 6H,O, which dissolve spain on heating.

Cadmium paratungstate CdW,O₁,10H₂O.
Lustrous, white octahedra; unchanged in air; obtained by decomposing BaW₂O₁,Aq by CdSO,Aq (S., Le., p. 273).

Calsium metatungstate CdW,O₁,10H₂O.

Quadratic octahedra; obtained by dissolving CaCO, in H.W.O. Ac. Quadratic octahedra; obtained by dissolving CaCO, in H.W.O.Aq and crystallising (S., Lc., p: 314).

Cobalt metatungstate CoW.O. 9H.O (S. l.c. p. 317). Copper metatungstate CuW₄O₁₂.11H₂O (S.,

l.c p. 317). Magnesium metatungstate MgW.O., 8H.O.

(S., Lc.).
Manganese metatungstate MnW,O,s.10H,O (S., l.c. p. 278).

Mercurous metatungstate Hg, W,O,,.25H,O. | Obtained, as a white pp., by adding HgNO, Aq to solution of H.W.O. or a meta-salt (S., l.c.,

Nickel metatungstate NiW.O.s.8H.O (S., l.c.,

p. 273).

Potassium metatungstate K.W.4O,2.8H.O. Lustrous octahedra; obtained by boiling K.W.1O.2.4Q with WO.2.2H.O; very soluble in hot water, considerably less soluble in cold water (S., Marignac (A. Ch. [4] 3, 71).

Silver metatusgstate Ag. W. O.; Obtained,

as a crystalline crust, by adding AgNO₂Aq to Na₂W₄O_{1,2}Aq. evaporating, useparating from Ag₂WO₄, and evaporating again (S., *l.c.* p. 318). Sodium metatungstate Na₂W₄O_{1,2}10H₂O. Obtained by boiling Na₂W₂O_{1,2}Aq with WO₂XH₂O

and allowing to evaporate; white, lustrous octahedra; S.G. 3.8647 at 13°; very soluble in hot, but less in cold, water (S., L.c, p. 303).

Strontium metatungstate SrV 40,3.81120 (S.,

i.c. p. 314). Zinc metatungstate ZnW₄O₁₃.10H₂·20 (S., l.c.

p. 273).

TUNGSTATES OTHER THAN ORTHO-, PARA-, AND META- SALTS.

Ditungstates. Salts of the $\mathbf{R}^{\mathbf{I}}_{2}\mathbf{O}.\mathbf{2}\mathbf{W}\mathbf{O}_{2} = \mathbf{R}^{\mathbf{I}}_{2}\mathbf{W}_{2}\mathbf{O}_{1}.$ Salts of K and Na of this composition were said by Lefort (A. Ch. [5] 17, composition were said by Lettort (A. Ch. [5] 17, 470) to be formed by neutralising cold solutions of K₂WO₄ and Na₂WO₄ by acetic acid; Knorre (J. pr. [2] 27, 83) obtained only metatungstates, B₂W₄O₁₃, by this method.

Two to five tungstates. The existence of salts of the class 2R₂IO.5WO₂=R₁IW₂O₁₇ is doubtful. Marignac obtained a salt to which he gave the formula Na WO (11M O along mith

gave the formula Na₄W₅O₁,.11H₂O along with the para-salt Na₅W₇O₂,.16H₂O (A. Ch. [3] 69, 50). The same salt scems to have been obtained by Lefort (l.c.; cf. Forcher a. Gibbs, J. 1880. 341) by adding acetic acid and alkali to Na, WO, Aq and allowing to stand for some time (cf. also Schmidt, Am. 8, 16).

Three to eight tungstates. A salt $(NH_4)_aW_aO_{22}.8H_2O=3(NH_4)_2O.8WO_3.8H_2O$ secms to have been prepared by Marignac (A. Ch. [3]

69, 61).

Tritungstates R¹¹O.3WO₃ = R¹¹W₃O₁₀.

Lefort (A. Ch. [5] 17, 470) prepared a salt to which he gave the formula Na₂W₃O₁₀cH₂O, by pouring a boiling solution of Na₂W₃O₁₀CH₂O (contained by adding acetic acid to Na₂WO₄Aq until the liquid shows an acid reaction) into boiling acetic soid, allowing to cool, separating the lower syrupy layer, and crystallising it. (A corresponding salt K,W,O₁₀,2H₂O was obtained by a similar method; and a series of tritungstates was prepared by mixing equivalent quantities of the Na salt and metallic acetates, in solution, and adding alcohol. L. de cribes the tritungstates as easily decomposing in aqueous solutions to diand tetra- salts. The following salts were formed and tetra saits. The flowing saits were then by L.:

— BaW₂O_{1.0}4H₂O; CdW₂O_{1.2}4H₂O; CaW₂O_{1.0}6H₂O; CoW₂O_{1.0}4H₂O; FeW₂O_{1.0}4H₂O; PbW₂O_{1.0}2H₂O; MgW₂O_{1.0}4H₂O; MnW₂O_{1.0}5H₂O; NiW₂O_{1.0}4H₂O; Al₂O; PsyV₂O_{1.0}6H₂O. Kaorre's experiments led him SrW₂O₁₆,5H₂O. Knorre's experiments led him to regard Lefort's tritungstates as mixtures (J. pr. [2] 27, 83).

Penta- and octo- tungstates.

of K and Na of the composition R.W.O. and R₂W₈O₂₅ are said to have been isolated, former by fusing mixtures of R₂WO₄ and WO₃, the latter by fusing R₂W₄O₁₃ with R₂WO₄ (Knorre, J. pr. [2] 27, 81, 91).

A few tungstates that do not find places in any of the foregoing classes have been described by different observers (v. especially Lefort, A. Ch. [5] 9, 93; 15, 324; 17, 470; 25, 200; also Schreibler, J. pr. 83, 237; Gonzalez, J. pr. [2] 36, 44; Knorre, J. pr. [2] 27, 93; Lotz, A. 91, 49; Feit, B. 21, 133; Cleve, Bl. [2] 43, 170; Högborn,

Bl. [2] 42, 2).

PERTUNCSTATES. By boiling a solution of the paratungstate Na₆W₁O₂₁.16H₂O with H₂O₂Aq, and then evaporating in vacuo, Péchard (C. R. 112, 1060) obtained small white crystals of a salt to which he gave the formula Na O.W.O, 2H,O= NaWO, H₂O; and by treating (NH₂), W₂O₂, 6H₂O in a similar way he isolated the corresponding NH, pertungstate. According to P. these salts are decomposed by alkalis with evolution of O; solutions of them set free I from KIAq, and

react with HClAq, giving off Cl.

TUNGSTEN BRONZES. Bright-coloured, lustrous, metal-like, crystalline solids, obtained by the action of reducers—such as H, coal-gas, Sn, or Fe-on tungstates of Li, K, or Na; also by the electrolysis of these tungstates when molten. The composition of these compounds, which are known as bronzes and are used as pigments, is represented by the formula $M_r(WO_s)_p$, where M = Li, K, or Na. The constitutions of the compounds are not known; they may be represented as compounds of tungstates with WO, by the general formula xM2O.yWO3.zWO2; they may also be represented as compounds of M2O with a radicle composed of W and O in a ratio greater than W:20 and less than W:30-that is, as compounds of M₂O with oxides intermediate between WO₂ and WO₂. The tungsten bronzes are insoluble in most acids, also in alkali solutions.

Sodium tungsten bronzes. These compounds are formed by the interaction of Na tungstates and H (Wöhler, P. 2, 350), Sn (Wright, A. 79, 221), coal-gas (Schnitzler, D. P. J. 211, 484), Zn or Fe (Zettnow, P. 130, 261), or by electrolysing Na tungstates (Scheibler, J. pr. 83, 321). According to Philipp (B. 15, 499), the different processes yield the same bronze if the same tungstate is used, and the more WO, there is in the tungstate employed the richer in WO, is the broaze produced. All the compounds are insoluble in acids or alkalis; they dissolve in NaClOAq; heated with NH,Aq and AgNO,Aq they give Ag and WO, (cf. P. a. Schwebel, B. 12, 2234; 15, 500; Knorre, J. pr. [2] 27, 51). These compounds are slowly oxidised to tungstates by heating to redness in air (K., l.c.). Philipp (l.c.) gave S.G. of all the sodium Bronzes as 7.2 to 7.8 at 16° to 18°.

Purple-red bronze Na, W₂O₂ = Na, O.2WO₃, WO₃ = Na₂O, W₂O₃ = Na₂WO₄, W₂O₄. Prepared by fusing for c. haff an hour a mixture of 10.9 g. fusing for c. half an hour a mixture of 10.9 g. Na₂CO₃, 71.7 g. WO₃ and 0 g. tinfoil, and boiling successively with H₂O, NaOHAq, and HOlAq. Red cubes; the powder transmits green light when suspended in water (P., l.c.).

Red-yellow bronze Na₄W₃O₁ = 2Na₂O.3WO₂2WO₂ = 2Na₂O.W₃O₂... Prepared by

melting 60 to 80 g. of a mixture of Na₂WO₄ and WO₄ in the ratio 2Na₂WO₄WO₃, adding 30 g. finfoil, and keeping molten for 1 to 2 hours feed-yellow cubes; the powder is brownish yellow, and transmits blue light when suspended in water (P., l.c.).

10 Water (T., 5.0.).

Gold-Bellow bronze Na, W.O., =

5Na,O.7WO_1.5WO_2 = 5Na,O.W. 20,1.

Prepared by heating Na, W.2O, to dull redness in H, powdering and again heating in H, and then boiling with H.O. HClAq, and Na, CO, Aq successively. Golden yellow, crystalline powder (P., l.c.; cf. Wöhler, P. 2, 350; Wright, A. 79, 221).

Blue bronze Na₂W₃O₁₅ = Na₂O.4WO₃, WO₂ = Na₂O.W₃O₄₄. Prepared by fusing Na₃WO₄ with more than 2WO₂, and adding tinfoil; also by melting Na,W,O₂₄ (paratungstate) and electro-lysing with 6 Zn-Pt elements P., Lc.; Scheibler, J. pr. 83, 321; cf. Knorre, J. pr. [2] 27, 49; and Zettnow, P. 130, 261). Dark-blue cubes, with a red sheen: S.G. 7.28 at 17°.

Potassium tungsten bronzes. $K_2W_4O_{12} = K_2O.3WO_3.WO_2 = K_2O.W_4O_{11}$ pound seems to be the only one of this class that has been isolated. Prepared by fusing K₂WO₄ with WO₃ and adding tinfoil; also by fusing K₂CO₄ wo, and adding timoli; also by tusing K.O., with from 3WO, to 4WO, and reducing by H or coal gas; also by electrolysing a molten mixture of K, WO, and WO,. Reddish-violet prisms, giving a blue powders which transmits greenish light when suspended in water; S.G. c. 7-1 (Laurent, A. Ch. [2] 67, 219; Zettnow, P. 130, 262; Knorre, J. pr. [2] 27, 63).

Lithium tungsten bronzes. A compound of this class, probably Li₂W₃O₁₅, is obtained by fusing Li₄W₂O₂₄ (paratungstate) with tin. Darlablue crystals (Scheibler, J. pr. 83, 321; Knorre, I.c., p. 69; Feit, B. 21, 133).

A potassium sodium bronze and a potassium lithium bronze have been obtained (Knorre, l.c.

p. 66; Feit, l.c.).

TUNGSTIC ACIDS AND COMPLEX SALTS. Tungstic oxide WO, combines with several anhydrides, e.g. B.O., P.O., As.O., SiO., &c., and water, to form acidic compounds, and also with these anhydrides and basic oxides to form salt-like compounds; the whole of these compounds are usually grouped together as complex tungstic acids and complex tungstates, and they are divided into such classes as arsenotungstates, phosphotungstates, &c.

ANTIMONOSTUNIORITIC ACIDS AND SALTS. According to Lefort (A. Ch. [5] 17, 487), the compounds Sb₂O₃.5WO₂.4H₂O and Sb₂O₃.5WO₂.8H₂O are formed by dissolving tarter emetic in Na₂O.3WO₂Aq and Na₂O.2WO₂Aq respectively. Gibbs (Am. 7, 392) obtained 4BaO.6Sb₂O₂22WO₃36H₂O and 6K₂O.4Sb₂O₂12WO₂25H₂O.

ARSENOTUNGSTIC ACIDS AND SALTS. Compounds of the form As₂O₃16WO₃.xH₂O have been 6b-tained by Kehrmann (A. 245, 45; cf. Fremery, B. 17, 296); and series of compounds of As.O. with WO, and basic oxides (Na.O. K.O. BaC. &c.), in which the ratio of As.O.: WO, is 1:6 and 1.3, have been described by Gibbs (Am. 7, 313). Compounds of WC, with As.O, and bases, and finely with As.O, and bases, and finely with As.O, and P.O. and bases, are described by Gibbs (Lc.).

BOROTUNGSTIC ACIDS AND SALTS. Two com-

pounds of B.O. and WO. have probably been isolated, in which the ratios of the oxides are 1:14 and 1:9 respectively; compounds of each of these with bases are known (Klein, A. Ch. [5] 28. 350).

Borotungstic acid and salts

B₂O₂.14WO₂.eH₂O. A solution containing B₂O₃ and WO₂ in the ratio 1:14 is obtained by boiling and WO, in the father 1.14 is considered by bothing N_a , WO_a , Aq with B_2O_aAq , ppg. by $HgNO_aAq$, decomposing, the pp. by H_aS , and expelling H_aS from the filtrate by warming (for actuals $x \in K$, Lc.). Compounds of the form $xMO.B_2O_s.14WO_s.yH_2O$ have been formed, where x=2, 3, and 4, and M is Ba, K_2 , Ag_2 , Na_2 , Ag_2 , Na_3 , Ag_3 , Ag_4 , Ag_3 , Ag_4 , and Sr.

Tungstoboric acid and salts. The compound B₂O₂.9WO₂xH₂O, usually known as tungstoboric acid, is obtained in yellowish octahedra by evaporating the solution of borotungstic acid. A considerable number of compounds of bases A considerable number of compounds of bases with B₂O₂ and WO₂, in the ratio B₂O₂9WO₃, has been obtained; most of them are of the form 2MO.B₂O₂9WO₃.wH₂O₄ M= (NH₁)₇, Ba, Cd, Ca, Co, Cu, Li₁, Mg, Mn, H₁G, Ni, K₂, Na₂, Tl₁; a few salts 2M₂O₂.B₂O₃.9WO₂.xH₂O₄ (M-Al or Cr) are also described by Klein (l.c.).

FLUOTUNGSTATES and allied compounds; v.

TUNGSTOXYFLUORIDES (p. 799).

IODOTUNOSTATES. Blomstrand (J. pr. 40, 327) described a compound 2K,0.1.0, 2V 43.3H,0, obtained by adding the calculated quantity of HIO, to K.WO, Aq.

Phosphotungstic acids and salts. The oxides WO, and P2O, combine in several proportions, in presence of H2O, to form complex acids which contain large quantities of WO, relatively to the P₂Q₃. A great many compounds are known containing WO₃ and P₂O₅ combined with basic oxides

Phosphotungstic acids. Compounds of the form $P_2O_*xWO_*yH_*O$; compounds wherein = 24, 21, 20, 16, and 12 seem to have been isolated. The existence of these compounds was made known by Scheibler (B. 5, 802); they have been investigated chiefly by Gibbs (Am. 2, 217, 281; 4, 377; 5, 361, 391; 7, 313, 392; Péchard, C. R. 109, 301; 110, 754; and Kehrmann, B. 20, 1805, 1811; 24, 2326; 25, 1966; A. 245, 46; Zeit, f. anorg. Chemie, 1, 428; also Drechsel, B. 20, 1452; and Brandhorst a. Kraut, A. 249, 373). The phosphotungstic acids are obtained by boiling HaPO Aq with HaW,O13.xH2O meta-acid); by decomposing the merourous salts by HClAq; and by boiling Na,W,O₃,xH,O (para-salt) with Na,HPO,Aq decomposing by HClAq, and dissolving the acids thus formed in other. The phosphotungstic acids are unchanged in solutions in dilute acids; these solutions are scarcely acted on by H2S, and very slightly by zinc they give phosphates and tungstates when hoiled with alkalis; characteristic pps. are produced with alkaloids, urea, albumen, &c.

Phosphoduodecitungstic acid and salts

Phosphoduodecitungstic and and salts estimated by August 19,0,24W0,xH,0. The acid is obtained by evaporating a solution of H,PO, and H,W,O,,xH,O iff the proper proprition (Péchard, l.c.); by boiling a solution of tungstate and phosphate of Na, in the ratio 24Na,WO,:2Na,HPO, acidulating with HNO,Ad, decomposing the Hg salt hy pg. by HgNO, Aq, decomposing the Hg salt by HClAq, filtering, and evaporating in vacue

(Gibbs, Am. 2, 217); by boiling H,PO,Aq with BaWO, in the proper proportion, decomposing by a small excess of H.SO.Aq, removing H.SO. by BaOAq, filtering, and evaporating (Sprenger, J. pr. [2] 22, 418). The acid crystallises in white, regular octahedra, or cubes. The value for x in the formula P.O. 24WO. xH2O varies according to different observers, from 40 to 53, 59, and 61. The salts yMO.P.O.24WO.xH.O are obtained by mixing tungstates (normal or para-salts) with H,PO,Aq or a phosphate, and decomposing by slight excess of HClAq, HNO,Aq, or H.SO, Aq; in most cases the salts ppt. as fine. white powders; in some cases it is advisable to evaporate to dryness, extract with alcohol and ether, and evaporate. The saits have been described by Gibbs (i.c.); Kehrntann (Zeit. f. anorg. Serined by Gross (1.2.1), Rentmann (200.), Lattory, Chemie, 1, 430); K. a. Freinkel (B. 24, 2327); Sprenger (J. pr. [2] 122, 418); and Brandhorst a. Kraut (A. 249, 373). Salts have been obtained wherein MO = (NH₂), BaO, CuO, K₂O, Ag₂O, and NaO, and and 1.2, and 2.3, and 2.3, and 3.3, and Na₂O, and y=1, 2, and 3.

Phospholuteotungstic acid and salts. P₂O₅.16WO₃.xH₂O and yMO₂.P₂O₅.16WO₃.xH₂O. The acid is obtained by boiling Na₂WO₄Aq₁.with He acid is obtained by boiling Na, Wo, Adwith H, PO, Aq. acidulating with HNO, Aq. adding NH, Cl and boiling, crystallising the pp. from NH, ClAq. evaporating the NH, salt thus produced with agata regia, and crystallising the acid so formed from water (for details v. K., I.c.). To an acid obtained by decomposing the K salt by H₂SiF₂Aq, or the Ag salt by HClAq, K gives the formula P₂O₂.18WO₁.xH₂O; and he says that the salts are yMO.P₂O₂.18WO₂.xH₂O. The acid forms citron-yellow, six-sided tablets; it melts by the heat of the hand, and is very soluble in water. According to K. (B. 20, 1805; A. 245, 45), salts of this series are obtained by boiling any phosphotungstates with excess of H,PO,Aq in presence of an alkali salt. It is probable that two series of salts exist -one with 16WO, and another with 18WO₃ (cf. Gibbs, l.c.; and Péchard, l.c.). Salts have been obtained wherein MG = (NH₁)₂O, BuO, CaO, CuO, PbO, and K₂O, and y = 1, 3, 4, and 6.

Other phosphotungstic acids and salts.

I. Salts of the form yMO.P.O.,22WO, xH_O have been obtained, wherein MO = (NII), O, BaO, and K_O, and y = 2, 3, 4, and 7 (v. K. a. F., B. 21, 2327; 25, 1966; K. //cit. f. anorg. Chemie, 1, 435; Sprenger, l.c.; Gibbs, l.c.).

by c

Sprenger, i.e.; Gibbs, i.e.).

II. An acid of the form P₂O₂.21WO₃.xH₂O, and salts yMO.P₂O₂.21WO₃.xH₂O, where MO = (NH₂)₂O₂. K₂O, and Ag₂O and y = 3, have been isolated (K₁ a. F., i.e.; K₁, i.e.).

III. The acid P₂O₂.20WO₃.xH₂O and a salt 6BaO.P₂O₂.20WO₃.xH₂O were obtained by effectand (i.e.) and Gibbs (i.e.).

IV. For the acid P₂O₂.12WO₃.xH₂O and the salts yMO.P₂O₃.12WO₃.xH₂O, where MO = (NH₂)₂O₃. Back CaO, CuO, PbO, Li₂O, Mg₂O, Hg₂O, K₂O, Ag₂O, Na₂O, Tl₂O, and ZnO, v. Féchard (C. R. 110, 754).

V. A few salts of the form

V. A few sults of the form yMO.P.O., TWO, xH2O have been obtained (MO = (NH4), O. **BaO, CaO, Hg2O, Na2O; y doubtful) (Gibbs, L.c.; K., L.c.).
VI. Compounds of alkali phosphates with

WO_s, and with phosphoric acids and WO_s, have been isolated; also compounds of alkalis with H.PO. and WO., and with H.PO. and WO., 2Na, 0.P.O. 24WO, xH.O.

are described by Gibbs (Am. 5, 361; 7, 318, 892).

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PLATINITUNGSTATES, v. this vol., p. 283,

SILICOTUNGSTIC ACIDS AND SALTS. Three compounds of SiO, with WO, and H,O, which react as acids, have been isolated, and many compounds of bases with SiO, and WO, Rave been obtained (Marignac, A. Ch. [4] 3, 5).

Silicoduodecitungstic acid, and SiOr.12WO_{3.07}H_{2.0}; as most of the salts contain 4M₂O (or 2MO) the acid is usually written 4H₂O.SiO_{2.12}WO_{3.07}H₂O (=H₂SiW_{1.2}O_{4.07}H₂O). According to Drechsel (B. 20, 1452), the acid is most easily obtained by dissolving Na, WO, in boiling water, nearly neutralising with HNO.Aq, boiling water, nearly neutralising with HNO₂Aq, dissolving the crystals that separate in cold water, boiling this solution with gelatinous SiO₂xH₂O until HClAq ceases to give a pp., filtering, evaporating, adding a large excess of H₂SO₂Aq, extracting with ether, separating the lowest layer and evaporating (for details v. D., l.c.). Large, colourless, dimetric octahedra (with x = 29); loses 25H₂O at 100°, and all H₂O at 350°. Very soluble in water and alkali colutions. Most of the salts of this acid have the composition 4MO.SiO.12WO.xH.O. or the composition 4M₂O.SiO₂12WO₃.xH₂O, or 2MO.SiO₂.12WO₄.xH₂O; M₂O = (NH₄)₂O, Hg₂O, K₂O, Na₂O; MO = BaO, CaO, MgO; x varies from 7 to 28 (Marignao, Lc.).

Tungstosilicic acid, and salts. is generally given to an acid containing SiO, and WO, in the same ratio (1:12) as silicoduodecitungstic acid. The formula of the acid is generally written 4H₂O.SiO_{...}12WO_{...}20H₂O. The acid is obtained by evaporating a solution of silicodecitungstic acid to dryness, taking up with water, filtering from separated SiO2, evaporating to a syrup, and allowing to crystallise. Forms short, white, triclinic prisms; melts under 100°, giving off 16H,O and again solidifying. salts of this acid are obtained by dissolving carbonates in a solution of the acid, and evaporating; they are more soluble and less easily crystallised than the salts of the duodeci-acid; the salts are of the forms

(1) $2MO(4M_2O).SiO_2.12WO_3.xH_2O$, where $M \neq Ca$, or $M_2 = K_2$; (2) $2M_2O.2H_2O.SiO_2.12WO_3.xH_2O$, where

M2 = K, or Na2; some more complex salts have also been isolated (Marignac, l.c.).

Silico-lecitungstic said, and selts. The acid 4H₂O.SiO₂:10WO₂:xH₂O (x probably = 3) is obtained by decomposing the Ag salt by HClAq, filtering, and evaporating in vacuo; the Ag salt is prepared by adding AgNO, Aq to the Ag salt is prepared by adding AgNO₂Aq to the NH₄ salt which is obtained by boiling an acid tungstate of NH₄ with SiO₂xH₂O, filtering, and evaporating. The acid forms a clear, yellowish, glassy solid, which does not wholly dissolve in water; loses 3H₂O at 100°; on boiling with water most of the SiO₂ separates, and the filtrate contains tungstosilicie acid. A few salts have been obtained, they are difficult to prairie have been obtained; they are difficult to purify from silicotungstates and tungstosilicates (Marignac, l.c.).

STANNIPHOSPHOTUNGSTATES. 892) obtained the salt 2(NH₄)₂O.P.O. 2SnO₂.22WO₃.15H₄O by the reaction of SnCl₄.2NH₄Cl and

TITANOTUNGSTIC ACIDS. Two acids. IH_O.TiO_12WO_xH_O and

1H₂C.TiO₂.10WO₂.xH₂O, are described by Lesarme (v. Klein, Bl. [2] 36, 17).

parme (v. Klein, Bl. [2] 30, 11).

Vanadorungstic acids and salts. Several compounds of WO₃ with V₂O₃ and H₂O have seen described by Gibbs (Am. 4, 377; 5, 361, 391) and Bosenheim (A. 251, 197); hey belong to the forms V₂O₃,10WO₃,xH₂O₄, V₂O₃,18WO₂,xH₂O₄, and V₂O₃,4WO₃,xH₂O. Compounds of these with yM₂O and yMO are the described; and a great variety of compounds of these with yM₂O and yMO are also described; and a great variety of com-pounds coming under the general formula mMO.nV.O.pWO.xH.O have been obtained (cf. Friedheim, B. 23, 1505; and Rothenbach, B.

Tungsten, exybromides of. Two exybromides, WO Br. and WOBr, are formed by the reaction of Br on WO, and in other ways. The formula WOBr, is very probably molecular, from the malogy of WOCl4.

TUNGSTEN DIOXYDIBROMIDE WO2Br2. ained by heating WO, in a stream of Br vapour, ulso by passing vapour of WBr, over heated VO, (Roscoe, C. N. 25, 73); also by heating VS, or a mixture of WO, and C in Br (Borck, 7. pr. 54, 254). Red, transparent, prismatic rystals; appearing black when hot, and giving yellow powder. Volatilised at red heat with rystats; appearing with yellow powder. Volatilised at red heat with artial decomposition to WO₃ and WOBr.

TUNGSTEN OXYTETRABROMIDE WOBr. Ob-

ained by passing Br vapour over a hanixture of equal parts of WO, and W, autiously distilling from less volatile WO₂Br₂ Roscoe, C. N. 25, 73). Also formed by passing Br aixed with some Ooverheated W, or by heating a nixture of WO, and C in Br vapour (Blomstrand, . pr. 82, 430). Brownish black, lustrous, rystalline needles; melts at 277' and boils at 27°. Heated in moist air gives WO, and HBr. nd is decomposed to the same products by water.

Tungsten, oxychlorides of. Two oxy-hlorides, WO₂Cl₂ and WOCl₄, are formed by Two oxyeating W in Cl mixed with some O, and in other

eactions.

TUNGSTEN DIOXYDICHLORIDE WO.Cl., TUNGSTEN DIOXYDICHLORIDE WO.Cl.. Obained by heating WO. in a stream of Cl, and ubliming (Roscoe, C. N. 25, 63); also by pasing CO. over a mixture of WO. and CaCl. heated o redness (Schultze, J. pr. [2] 21, 439). Also ormed, along with WOCl., by heating W in Cl aixed with O; by heating WO. and C in Cl; by leating WO. in CCl. (Watts a. Bell, C. J. 33, 42); and by heating WO. with PCl. (Schiff, 4. 97, 185; cf. Tungsten trioxide, Reactions, io. 10, p. 801). Yellow, four-sided tablets; ublimes without melting at c. 266°, with pulling at c. 266°, ublimes without melting at c. 266°, with partial ecomposition to WO, and WOCl. Not decomosed in moist air, nor by cold water (R., l.c.). leated in dry NH, gives off NH, Cl and leaves VO, (Rdeal, C. J. 55, 48); in this reaction VO, Cl, behaves like CrO.Cl, (R., C. J. 49, 367) eccording to Smith a. Shinn (Zeit. f. anorg. hemie, 4, 881), a black compound W, O, N, H, is ormed by heating WO2Cl2 in dry RH,

TUNGSTEN OXYTETRACHLORIDE WOCI,. 841.04. Formed by heating W in Cleconaining a little O; siso by passing Cl over a hot nixture of WO, and C; by heating WO, in CCl, Watts a. Bell, C. J. 33, 442); by heating VCl, or WCl, in O and Cl; by heating WCl, with

H₁C₂O₄; and by heating WO₂Cl₂. Prepared by passing vapour of WCl₂ over heated WO₂ in a current of Cl (Boscoe, C. N. 25, 63). Also by heating WO₂ and PCl₃, in the ratio WO₂:PCl₃ or WO₂:PCl₃, distilling off POCl₃ and the small quantities of WCl₃ and WCl₃ that are formed, washing the reddish residue with a little cold CS (15, 2000). CS, (to remove WCla), then dissolving in a larger quantity of warm CS, evaporating, and carefully heating the residue in a stream of CO, whereby the more volatile WOCl, is separated from WO, Cl., (Schiff, A. 197, 185).

WOCI, forms suby-red, transparent needles; melts at 210.4°, and volatilises at 227.5°, forming a yellow vapour (Ref.c.). V.D. 170-2 to 175-8 at 850°, 171-5 at 440° (R., l.c.; of. Debray, C. R. 60, 820). Exposure to air produces a crust of yellow Wo.Cl.. Heated in NH, probably gives W.N. (Rideal, C. J. 55, 43). Decomposed by water, with a hissing sound, to WO, and HClAq

(Roscoe, l.c.). Tungsten, oxyfluorides of. No compound of W with O and F has been isolated, but com-pounds are known which may be regarded as containing WO.F.. These compounds, ontaining WO.F., These compounds, WO.F., 2MF and WO.F., MF, and also a compound WO.F., 2KF, are described under Tungsr-OXYPLUORIDES (p. 799).

Tungsten, phosphides of. By heating W in vapour of P, a dark-grey powder was obtained by Wohler a. Wright (A. 79, 214), to which they gave the composition W₂P_e. By heating a mixture of WO₂ and P₂O₃ in a graphite crucible, W. a. W. (l.c.) obtained large, dark-grey, lustrous, six-sided prisms; S.G. 5.207; insoluble in acids, including aqua regia, soluble in a molten mix-ture of Na₂CO₃ and NaNO₃; unchanged by heating in air, but burns brilliantly in O. From an estimation of the P, W. a. W. gave the formula W.P.

Tungsten, salts of. No salts have been isolated by replacing the H of oxyacids by W. Except the halides, the only salts of W that are known are those wherein W forms part of the

negative radicle.

Tungsten, selenides of. By saturating a solution of Na.W.O., with H., Se, and then adding dilute H., SO.Aq, Uclsmann (A. 116, 125) obtained a black pp., to which he gave the formula WSe, (one estimation of W is given); by heating this in a tube a grey solid was obtained, said by U. to be WSe, (no analyses). WSo, is said to be easily soluble in solutions of alkalis, alkali sulphides, or alkali selenides.

Tungsten, sulphides of. Two compounds of Wand S are known, WS, and WS,; the latter is saidic, forming salts M.WS. The V.D. of

reither has been determined.

TUNGSTEN DISULTRIDE WS. Obtained by heating WO, to whiteness in vapour of S or in H.S (Berzelius); also by leating W and S; also by heating WO, with 6 pts. HgS out of contact with air (Borck, J. pr. 54, 254). According to Carnot (Bl. [2] 32, 164), WS, is usually formed when a compound of W is heated in a stream of dry H.S (v. also von Uslar, A. 94, 256; Corleis, A. 232, 262). A dark-grey, graphite-like, lustrous, crystalline powder (v. Riche, d. Ch. [8] 50, 26). Is said to decompose steam at a full red heat: reduced to W by very long continued heating in H.

TUNGSTEN TRISULPHIDE WS. Obtained by | tusing powdered wolframits with 2 pts. C. 3 pts. S, and 3 pts. Na₂CO₃, dissolving in water, decomposing the Na₂WS₄Aq thus produced by HClAq, washing the pp. completely out of contact with O, and drying at 100° (von Uslar, A. 94, 256; Corleis, A. 232, 264). A black powder; slightly soluble in water, more soluble on boiling, probably with partial decomposition. Soluble in alkali sulphide solutions, forming thio- salts (v. TUNGSTEN, THIO- ACIDS AND SALTS OF, infra). By adding to Na₂WS₄Aq a little more HClAq than was needed to combine with the Na. Winssinger (Bl. [2] 49, 452) obtained a colloidal form of WS.

Tungsten, sulpho- acids and salts of, v. next article.

Tungsten, thio acids and salts of. saturating (NH₄)₂WO₄Aq and K₂WO₄Aq with H₂S, Berzelius obtained (NH₄)₂WS₄ and K₂WS₄ (P. 8, 267); these salts were more fully examined by Corleis (A. 232, 258), who also obtained Na,WS, and also some thio-oxy-tungstates. All the thio-tungstates that have been isolated are ortho-salts, i.e. salts of H₂WS, Very dilute solutions of thiotungstates can be titrated with IAq in presence of KHCO₃ (C., l.c.).

Ammonism thiotenystate (NII₁)₂WS₄. Ob-

tained by passing H.S for four or five hours into solution of 10 g. WO3.H2O in 100 c.c. NHAQ S.G. 94, +20 c.c. water, allowing to stand for some hours in a closed vessel, and washing the crystals that separate with alcohol and ether. Forms orange-yellow prisms, isomorphous with (NH4), MoS4; very easily decomposed in moist air; easily soluble in water, slightly soluble in alcohol. Heated in CO2 gives WS, (B., l.c.;

Ammonium dithio-oxy-tungstate

(NH₄)₂WS₂O₂. Obtained by passing H₂S into a solution of 10 g. WO₃H₂O in 40 c.c. NH₃Aq S.G. 90, + 10 c.c. water, until the liquid becomes *turbid, and washing the crystals that form with alcohol and ether. Forms yellow, prismatic orystals. When dry, the salt is unchanged in Decomposed by re-crystallising from water, giving paratungstate (NH,),W,O24.6H2O (C., l.c.).

Potassium thiotungstate K.WS. Obtained by warming (NH₁)₂WS₄ with KHSAq, adding alcohol, and crystallising from conc. KHSAq. Forms yellow, prismatic needles; easily soluble in water. By continued boiling with KHSAq paratungstate is formed, K_aW,O₂,6H₂O (C, l.c.). Forms a double salt with KNO₃, with the composition K. WS. KNO, (B., l.c.).

Potassium trithio-oxy-tungstate K,WS,O.H,O. Obtained in citron-yellow, quadratio tablets, by passing H₂S for three or four hours into a solution of 10 g. K₂WO₄ in 10 c.o. water, and evaporating in vacuo, or precipitating by alcohol (C., l.c.).

Potassium monothio-oxy-tungstate K, WSO, H,O. Obtained, in almost colourless, very hygroscapic, crystalline masses, by passing H,S, into a solution of 10 g. K,WO, in 5 c.c. water until the liquid is turbid, filtering, adding 4 to 5 vols. alcohol, separating the under layer of liquid, allowing to crystallise, and washing with alcohol and ether (C., Lc.).

Sodium thiotungstate Na.WS. Obtained.

but not pure, by Corleis (Le.), by decomposing (NH₄)₂WS₄ by NaHSAq.

Tungsten, thiochloride of. By heating W to redness with S₂Cl₂, Smith a. Oberholtzer (Zcit. f. anorg. Chemie, 5, 63) obtained a red, crystai. line sublimate, unstable in air, probably W.S.Cl. M. M. P. M.

TUNGSTEN BRONZES v. under TUNGSTEN охудствы, р. 806.

. TUNGSTIC ACIDS v. TUNGSTEN OXYACIDS, p. 802; also Tungsten THIO-ACIDS, supra

TUNGSTOXYFLUORIDES v. under Tung-

STEN FLUORIDES, p. 799.
TUNGSTEN, ORGANIC COMPOUNDS OF. Tungsten, heated with MeI at 240°, forms WMe,I₂ [110°], which crystallises in tables, and is converted by Ag O into WMe,O, which dissolves in acids Riche, C. R. 42, 203; Cahours,

A. 122, 70).
TUNICIN v. Animal Cellulose, vol. i. p. 718. TURMERIC. The root of Amomum Curcuena.

It contains curcumin (q. v.) and turmerol.

TURMERIC ACID C₁₁H₁₄O₂. [35°]. A product of oxidation of turmerol by cold KMnO₄ (Jackson a. Menke, Am. 6, 77). Needles, sl. sol.

water, v. sol. alcohol.—CaA', 3aq. S. (of CaA',)
1-28 at 16°. White needles.—AgA',

TURMEROL C₁₁H₂₀O (?). (193°–198° at 60
mm.). S.G. ¹⁷ 902. [a]₀ = 33·5°. An oil occurring in turmetic. Distils with decomposition at 285°-290° (Jackson a. Menke, Am. 4, 368; 6, 77). Dextrorotatory. Does not combine with NaHSO₃. KMnO₄ oxidises it to acetic, terephthalic, turmeric, and apoturmeric acids. PCl, forms C₁₉H₂Cl, which is also got by henting turmerol with conc. HCiAq at 150°. Sodium forms C₁₀H₂,ONa, whence isobutyl iodide forms oily C₁₉H₂,OC,H₃.

Apoturmeric acid C₅H₈(CO₂H)₂(?). [221°].

Woolly mass, sol. boiling water.

TURPENTINE. Semi-fluid resins exuding from coniferous trees. They consist of resin dissolved in oil of turpentine. On distillation oil of turpentine passes over and colophony remains behind. The various oils of turpentine are described under TERPENES. The chief constituent of colophony is abietic anhydride (v. ABIETIC ACID and Sylvic ACID). On oxidation by dilute HNO, colophony yields isophthalic, trincellitic, and terebic acids (Schreder, A. 172, 93). On the products of distillation of colophony v. RESINS

v. Resins.

TURPETHIN C₁₄H₂₆O_{1s} [c. 183°]. Occurs in the root of Convolvulus Turpethum (Ipomea Turpethum) (Boutron-Charlard, J. Ph. 8, 131; Spirgatis, J. pr. 92, 97; A. 139, 41). Purgative yellewish-brown resin, v. sol. alcohol, insol. ether (difference from jalapin). Conc. H.804 forms a red solution. Boiling alkalis convert it into turpethic acid. Boiling dilute mineral acids yield glucose (3 mols.) and turpetholic acid (1 duol.).

Turpethic acid C₁₁H₂₀O₁₅. Amorphous yellowish mass, v. sol. water. Split up by boiling HClA'u into glucose and turpotholic acid.—BaA".—BaH₂A'₂c'dried at 100°).

acid.—BaH.—BaH.A., dried at 100°).
Tarpetholic acid C. H., O. [c. 88°]. Minute reedles (from dilute alcohol.), sl. sol. ether.—NaA' (dried at 100°).—BaA'. Amorphous.—AgA'. Amorphous pp. A'. Amorphous pp. Ethyl ether Eth'. [72°]. Plates.

TYLOPHORINE. An alkaloid in Tylophora asthmatica (Hooper, Ph. [3] 21, 617). Crystalline, al. sol. water, sol. alcohol and ether.

TYPE METAL. An alloy of 15-20 parts Sb with c. 70 parts Pb, and 10 to 15 parts Sn; v.

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LEAD ALLOYS, vol. iii. p. 124.

TYPES. The object of classification is to put together like things, and to put apart things that are unlike. A perfect system of chemical classification would place side by side those elements and compounds that are chemically similar, and it would also indicate the relations that exist between all the elements and all the compounds. Inasmuch as the object of chemistry is the study of the connections between composition and properties, and between changes of composition and changes of properties, a com-plete scheme of chemical classification must indicate the relations of the substances classified, both as regards composition and also as regards properties. To connect composition with properties necessitates a thorough knowledge of both, and this knowledge can be gained only by comparing one substance with other substances. But, because of the large amount of detailed investigation that is required before the chemical properties of an element or a compound are known, chemists have often forgotten the larger issues of their labours, and have busied themselves rather with the examination of individual bodies than with the comparative study of many bodies. And, because of the imperfection of chemical knowledge at any time, those who have attempted the classification of chemical substances have generally paid chief. attention either to the composition or to the properties of the substances to be classified. Hence systems of classification have sometimes prevailed that were founded chiefly on similarities of composition, and at other times classifica-tory schemes have been in vogue that rested mainly on similarities of properties. But there has always been a desire, and generally an effort, to classify on the bases of composition and pro-perties. To classify satisfactorily demands the recognition of a simple class-mark, which shall also be clear, definable, and invariably applicable. It is probably correct to say that none of the larger classes of chemical compounds has a class-mark of this description. Hence the main difficulty in chemical classification. Take, for instance, the great class of acids. What is the class-mark? What must be known about the composition of a compound before it is put into the class of acids? There is no single and sufthe class of acids? ficient class-mark to be gained by studying the compositions of acids. What, then, about the properties of acids? Here, too, no simple, definable, and applicable property has been found nnane, and applicance property has been touted which serves to distinguish acids from all other compounds. Acids, it is usually said, are compounds containing replaceable hydrogen. But the expression replaceable hydrogen has not been, and cannot be, exactly defined. Hence, all that can be done is to set up an ideal or typical acid, and to place in the class acids those compounds which fairly closely approach this type as regards both properties and composition. And as with acids so with other classes of compounds. A classification by means of types ounds. becomes inevitable in such a science as chemistry,

but a typical classification cannot be final in any exact science.

Lavoisier's system of classification rested on oxygen; compounds were regarded as formed by the union of oxygen with other elements or groups of elements; the non-oxygenated part of a compound was called by Lavoisier the rest or radicle; compounds of oxygen with certain radicles were bases, compounds with other radicles were acids, and salts were formed by the union of bases with acids. Lavoisier used the term radicle to include elements and groups of elements.

J'al dejà fait observer, que dans le règne minéral presque tous les radicaux exitables et aciditables etalent simples; que dans le règne vegétal au contraira, et surtout dans le règne aqui me existait presque paqui ne fussent composes au moins de deux substances, d'hydrogene et de carbone; que souvent l'acte et le phosphore s'y reinfissaient, et qu'il en résultait des radicaux à quatre bases. — Tratié élémentaire de Chime, [1793], p. 251.

About twenty-four years after Lavoisier made this statement Berzelius repeated it.

Nachdem wir den Unterschied zwischen den Pro-ducten de organischen und der unorganischen Natur, und de verschiedene Art und Weise wie ihre entfernteren und die verschiedene Art und Weise wie ihre entfernteren Bestandtheile untereinander verbunden sind, niher kennen gelerut, haben wir gefunden, dass dieser Unterschied eigentlich darin besteht, dass in der unorganischen Natur alle oxyditten Körper ein einfachs Radical haben, während Hagegen alle organischen Suffeianzen aus Orgden mit zusammengestiem Radical be-tehen, "Lehrbuch der Chemie, 2 Auff. [Stockholm, 1817], vol. 1, p. 644.

Why do acids and bases unite to form salts ? What is the cause of the formation of compounds by the union of radicles, either simple or compound? These questions were answered by Berzelfus by appealing to the fact that the electric current very often resolves compounds into two parts, and in many cases also effects the combination of elements or groups of elements. Radicles combine, said Berzelius, because the negative electricity on one is thereby neutralised by the positive electricity on the other. Thus arose the electro-chemical conception of dualism (v. Dualism, vol. ii. p. 415; cf. Radical, vol. iv. p. 393).

In 1832 Liebig and Wöhler made an exhaustive study of compounds obtained from bitteralmond oil; they showed that the relations of composition and properties of these compounds were brought together, and expressed in a consistent conception by supposing that all the compounds contained a radicle having the composition C,H₂O(C = 12, O = 16); this group of elements, common to all the derivatives of bitteralmond oil, they called benzoyl. The work of Liebig and Wöhler marked a great advance in chemical classification; it was the actual working out of the connections between composition and properties of a number of compounds, and the expression of these connections in clear and definite language. The term scalels became henceforth the expression of a vivifying conception. The compounds derived from bitteralmond oil had certain common properties, and they had also a common composition; they belonged to the same type. The compounds of belonged to the same type. The compounds of benzoyl examined by Liebig and Woller included such compounds as these: C,H,O,OH, C,H,O,H, C,H,O,C,N, C,H,O,NO, The medicle C,H,O is common to all; this radicle is united with H, Cl, NO, CN, or some other radicle, in the different compounds; neverthe-

less, the properties of the compounds are so similar that all are said to belong to one type. To what extent, then, it was asked, may the properties of one radicle differ from those of another before the replacement of one of these by the other carries with it a change of type? The answer generally given to this question was: If the replacing radicle is chemically similar to the radicle replaced the type will not be destroyed. In 1834 Dumas, from the study of the action of chlorine on various organic compounds, an-nounced the empirical laws of substitution as follows: (1) When a compound containing hydrogen is subjected to the dehydrogenating action of chlorine, bromine, iodine, oxygen, &c., one atom of chlorine, bromine, indine, or oxygen, is taken up for each atom of hydrogen lost by the compound. (2) The same rule applies, without modifications, when the compound contains oxygen. (3) If a hydrogenised compound contains water the hydrogen of the water is given up without replacement, and then another quantity of hydrogen is absorbed, so that the final result is a replacement of hydrogen. A year or so later Laurent propounded a theory of substitution, which asserted that when equivalent substitution of hydrogen by chlorine or bromine occurs the chlerine or bromine takes the place of the hydrogen, and to a certain extent plays the same part as the hydrogen, and hence the chlorinated or brominated product must be similar to the compound from which it has been prepared. Laurent's views were much opposed, for a time by Dumas himself; but they gradually prevailed, and chemists became familiarised with the notion of the replacement of such a decidedly electro-positive element as hydrogen by an element so decidedly electro-negative as chlorine, resulting in the production of a compound of the same chemical type as the original substance.

About 1839 Dumas sought to distinguish 'mechanical types from chemical types. Compounds formed one from the other by the replacement of a certain number of equivalents of one radicle by the same number of equivalents of another radicle, and having their radicles similarly combined, and exhibiting similar properties, were said to belong to the same chemical type. Compounds were said to belong to the same mechanical type when they were composed of equal numbers of equivalents of radicles, but differed essentially in their properties. Dumas at this time regarded the properties of com-pounds as conditioned more by the arrangement than by the nature of their parts. He compared compounds to planetary caystems, the planets being represented by the atoms of the compounds. One atom, he said, might be replaced by another atom, or an atom by a group of atoms, without destroying the system; if the number of replacing atoms, or radicles, were the same as the number of atoms, or radicles, replaced, and the relative arrangement of all the atoms or radicles were not altered, the compounds belonged to the same type. By some such development as this the theory of types came to include the older theory of radicles.

It is evident that the terms used by Dumas and others to express the conceptions of the theory of types are vague and incapable of

exact definition. The expression 'equivalent radicles' cannot be defined, nor can an exact and invariable connotation be given to the expressions 'radicles similarly combined' and compounds having similar properties. But if it had been possible to classify chemical substances in an ideally perfect way the theory of types would not have arisen. If there is to be a typical classification the language whereby that classification is expressed must be more or less vague. Whether a compound formed from another by replacing equivalents of one kind by an equal number of equivalents of another kind does or does not belong to the same type as the parent compound can be determined only by a careful study of the properties of both compounds and by a comparison of the compounds one with another. The application of the theory of types was possible only when the properties and the compositions of compounds were exhaustively compared. The theory of types produced much fruit, because it suggested and demanded much inquiry into the fundamental

problem of chemistry.

In 1849 Wurtz prepared two compounds which resembled ammonia in their prominent characters. These compounds were found to have the compositions C_2H_1N and C_1H_1N respectively (G=6). The similarities between the properties of these compounds and ammonialed Wurtz to regard them as substituted ammonias, and to express this conception by the formula these compounds were prepared consisted in treating methyl and ethyl bromides (C₂H₃Br and C_iH_aBr ; $C=\vec{0}$) with ammonia, and then decomposing the products by potash. These reactions suggested the view that the new compounds were derived from methylic and ethylic ethers (C,H,O and C,H,O, according to the notation then used) by substituting NH₂ for O. Both views agreed in representing the new compounds as C₂H₃,NH₂ and C₄H₃,NH₂ respectively. But the properties of the compounds resembled those of ammonia; hence the view that Wurtz's compounds were derived from ammonia prevailed. This view was expressed by saying that these compounds belonged to the ammonia type, and by comparing the formula of the typical compound with the formula of the compounds formed after that exemplar; thus:

Type: Derinatives: Ammonia NH, H. Methylamine NH, C, H, Ethylamine NH, C, H,

Very soon after Wurtz's preparation of methylamine and ethylamine Hofmann argued that it should be possible to substitute each of the three atoms of hydrogen in NH, by the radicles three atoms of hydrogen in AH_1 by the radices C_1H_2 and C_1H_3 , and so to obtain the compounds $NH(C_2H_3)_2$, $N(C_2H_3)_3$, $NH(C_4H_3)_4$, and $N(C_4H_5)_4$ ($C^{\underline{o}\underline{o}}$ 6), all which compounds ought to results ammonia in their properties. Hormann fulfilled his own prophecy by preparing diand tri-methylamine and diand tri-ethylamine and diand tri-ethylamine and diand tri-ethylamine. amine; and, basing his methods on the concep-tion of the ammonia type, he prepared a large series of ammonia-like compounds derived from NH₃, 2NH₃, &c., by substituting for H various radicles composed of carbon and hydrogen. The ammonia type was thus established.

TYPES.

About the year 1850 Williamson studied the relations of ether to alcohol. The formula of ether was then written C_4H_3O (C=6, O=8), and that of alcohol $C_4H_4O_2$. Williamson heated that of alcohol C₄H₆O₂. Williamson heated potassium alcoholate (C₄H₅KO₂) with ethylic odide (C.H.I), expecting to obtain ethylated alcohol (OH, (C.H.JO₂); but he obtained common ether. Williamson suggested that the formula then accepted for ether should be doubled, and written (C.H.), O. He also found that by heating common alcohol with sulphuric acid, and adding methylic alcohol to the hot mixture, an etherlike compound was obtained, the simplest formula of which was C_2H_4O (C=6, $O_2=8$). Williamson argued that if common other is C.H.O. then the ether of methylic alcohol must be C.H.O, and that, in the reaction of sulphuric acid with ethylic and methy to alcohols simultaneously, a mixture of these two ethers might be expected to be produced. To account for the facts he had observed Williamson proposed to double the formulæ of the two ethers and to write them $(C_4H_3)_2O_2$ and $(C_2H_3)_2O_2$; and for the formula of the ether formed by the action of sulphuric acid on the two alcohols simul-taneously he proposed the formula C₄H₃(C₂H₃)O₂ $[=2C_0H_1O]$. Williamson compared the relations between the alcohols and ethers with the relations between water, potash, and potassium oxide. These relations are made clearer if the formulæ are expressed in terms of the atomic weights C = 12 and O = 16; thus:

Type: Water H.H.O Derivatives:
Alcohol C,H,HO
Ether C,H,C,H,O
Potash K.H.O
Potassium oxide K.K.O.

Thus arose the water type. To this were referred such compounds as acetic acid C₂H₂O.I.O., anhydrous acetic acid C₂H₂O.C₂H₂O.O, and many others.

Gradually the greater number of compounds, both organic and inorganic, came to be referred to four fundamental types—the hydrochloric acid type HCl, the water type HHO, the animonia type NHHH, and the marsh gas type CHHHII. To these were added so-called condensed types and mixed types; sulphuric acid, for instance, SO₂.OH.OH, was said to belong to the double water type.

Oxamic acid CO.NH, CO.OH was regarded by Wurtz as derived from the water-ammonia type.

Thus: $\begin{array}{ccc}
H \\
H \\
H \\
N
\end{array}$ $\begin{array}{ccc}
H \\
H \\
H \\
H
\end{array}$ $\begin{array}{cccc}
H \\
H \\
H
\end{array}$

The great danger attending the development of the theory of types was, that careful investigations into the reactions of compounds might easily be abandoned in favour of a superficial examination of a compound, followed by a relegation of it to this or that type. The theory began by being very vague and eelastic; she adoption of a few definite types rendered it more axect; but the temptation to manipulate for

mulæ on paper, and to invent condensed types and mixed types, gradually led chemists to see that the theory had done its work, and that it must give place to wider views, which should also be more accurate, regarding the connections between composition and properties.

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The conception of types carried with it, from the first, more or less vague notions regarding the arrangements of the atoms in those collocacompounds; at any rate, this conception was bound up with the general conception of atomic arrangement. The reacting units of compounds that showed similar properties were thought of as composed of atoms similarly arranged. Moreover, the type was said to be maintained when an atom, or a group of atoms, in the parent compound was replaced by an equivalent number of atoms, or groups of atoms. These two conceptions, that of equivalency, and that of atomic arrangement, led gradually to the representation of the reacting unt, or molecule, of a compound as a definitely arranged group of atoms he'd together by actions and reactions between individual atoms; these conceptions led to the wider conception of valency, and to a system of classification based on the notion that each kind of atom is capable of directly com-bining with a limited, and determinable, number of other atoms. The formula given to chloro-sulphonic acid, with the object of connecting the composition with the properties of this compound. and of suggesting relations between this and other compounds, may be taken as an example of the merging of the notion of types into that of valency. This acid was regarded as derived both from water and hydrochloric heid; it was supposed to belong to the mixed water-hydrochloric acid type. Hence the formula, ClSO,H, was written thus:-

The radicle SO₂ was regarded as equivalent to 2H; and it was said that the residues of the two parts of the mixed type, i.e. Cl and OH, were bound together by the radicle SO₂. Again, monochlorhydrin, C₃H,ClO₂, was regarded as a derivative of the triple type HHO.HCl.HHO, and was said to be formed by the binding together of the three residues OH, Cl, OH by the radicle C₃H, regarded as equivalent to 3H. Thus:

The moment the conceptions underlying these formule, and formule like these, were expressed in the language of atoms and molecules, the nation of atomic valencies was gained. The group of atoms SO, replaces two atoms of hydrogen, one atom in the molecule HCl and one atom in the molecule HIO; and as the atomic group SO, is capable of directly combining with two atoms of hydrogen, or such a number of atoms as is equivalent to two atoms of hydrogen, this group binds together the atom Cl and the atomic group OH, and so the new molecule

S14 TYPES.

SO_rOH.Cl is produced. This statement contains the fundamental conception of atomic valency; it also contains the conception of types, and that of radioles.

The radicles were compared at regards their equivalency, generally in terms of hydrogen; then the elementary atoms were compared, and arranged in classes, such that all in one class were exchangeable, any number of one kind for the same number of another kind.

kind for the same number of another kind.
When the atoms had been classified in accordance with the number of atoms of hydrogen, or atoms equivalent thereto, with which each was capable of combining, the loundations had been laid of a system of classification which was more accurate than that based on the notion of types, and which at the same time included the essential characters of the typical system. article CLASSIFICATION in the first edition of this Dictionary cepresents the stage which had then (1863) been reached in the process of fusion of the theories of radicles, types, and valency. The system of classification developed in that article is based (1) on the compesitions of compounds interpreted by help of the theory of valency, and (2) on the properties of the compounds interpreted by the help of the theory of types ; the study of the properties of a compound is used to determine the fadicles that the compound contains, and a knowledge of the valencies of these radicles determines the form of the compound, and, taken along with the reactions of the compound, the type to which it is to be referred.

Although the introduction of the principle of atomic equivalency widened the conception of chemical types, it also tended towards a method of classification which was based on too slight a study of the bodies to be classified. A super-ficial examination of a compound generally sufficed to bring out some similarities between it and a well-known typical substance; the new compound was at once referred to its type; the form of the type determined the form of the compound under examination; it was then only necessary to manipulate the empirical formula by arranging the elements in groups, or radicles, and to assign to each radicle such a valency as satisfied the general rules that had been deduced from the study of a few typical compounds. The conception of types became very mechanical in its applications, so mechanical indeed that it was in danger of becoming metaphysical. New radicles were easily invented, and their valencies were deduced by a priori arguments. Kekulé recalled chemists to the study of properties by insisting that the properties of a compound are conditioned by the properties of the atoms which composithe molecule of the compound; and at a later date Mendeléeff made the same demand by asserting that the properties and the compositions of all compounds are periodic functions of the atomic weights of the elements.

The notion of types plays an important part in the classification of elements and compounds that has arisen from the practical examination of the meaning of Mendeléeff's periodic law. The periodic classification of the elements lays considerable stress on the study of the typical oxides, hydrides, hydroxides, &c., of each group of elements; for instance, the highest salt-forming oxide of Group L belongs to the type R.O.

that of Group II. to the type R₂O₂, and so on. But the word *type* is not used here with quite the same connotation as was given to it by the theory of types. All that is implied in statements such as those just made is, that the elements of Group I. combine with oxygen in the ratio of two atoms of element to a single atom of oxygen, that these oxides are salt-forming, and that they are characteristic of the elements of this group. The typical oxide-form of each of this group.

The omposition of that oxide which contains the greatest number of atoms of oxygen relatively to one atom of the group-element, and which oxide reacts either with acids or with alkalis to form corresponding The oxides that belong to the typical oxide-form of a group may be acidic or basic, or some of them mae be acidic and some basic; all that is asserted of their properties is that they are salt-forming. The properties of the typical oxide of any individual element are conditioned by the general character of the group, and the general character of the series, wherein the element is placed; by the special character of the element itself; and by the position of the element in the whole periodic system of classification. The term type is used in the nomenclature arising from the comparative study of the elements and compounds based on the periodic law with a wider, and at the same time a more exact, meaning than that which was given to it when the notion of types was made the basis of chemical classification. In the older classification the conception of types was the basis of the system; the conception was of necessity vague, and hence it was necessary sometimes to widen, and sometimes to narrow, the application of the conception. The modern system of classification is based on the relative weights of the atoms of the elements, and the conception of types plays a subsidiary part; the form of the typical oxide, or hydroxide, or other compound, is determined, as the compositions of all the compounds are determined, by the relative masses of the atoms of the elements; and the general character of the typical oxide, hydroxide, &c., of each group is determined, as the special character of each compound of each element is determined, also by the relative masses of the atoms of the elements.

The periodic classification of the elements and compounds makes use of the notion of types in another way, by applying the conception to certain elements. The elements placed in series I and 2, viz. H, Li, Be, B, C, N, O, and F, exhibit almost the whole range of properties of all the elements. The properties of the succeeding elements may almost be said to be but variations on the theme announced in the change from hydrogen to fluorine. These eight elements are types of all the others. In a comewhat narrower sense the element lithium summarises the range of properties shown in Group I.; beryllium summarises the range of properties of Group IV.; nitrogen, the properties of Group VI.; and fluorine, the properties of Froup VII. Each of the seven elements is the typical element of its group. Objections have been raised to this use of the term typical, on the ground that each

of the elements in question differs more from any member of its group than any other two members of the group differ from one another. But if an element is to summarise the properties of some ten or eleven other elements, it must differ considerably from each of these, while at the same time it resembles them all. The question of typical elements, and also that of typical oxide-forms, &c., are discussed in the article Periodic LAW (vol. iii. p. 808); that article should be consulted.

The older classification by types prepared the way for the wider conception of valency, which took up and utilised the permanent features of the typical arrangements of elements and compounds. The study of valency led chemists to see the importance of examining the properties of the atoms of the elements and thus made them ready to accept the more elastic, and more exact, generalisation of the periodic law. The theory of types developed into the theory of valency, and the theory of valency has been included in the theory of the periodicity of the connection between the atomic weights of the elements and the compositions and properties of the compounds of the elements. The general conception of types remains; we are still obliged to picture to ourselves a typical acid, a typical base, a typical salt, a typical alcohol, a typical amide, and so on. But this conception is no longer the basis of chemical classification. We have gone deeper down, and laid the foundations of our system on the firmer basis of the atomic weights of the elements. M. M. P. M.

An alkaloid TYPHOTOXINE C,H,, NO. obtained from pure, cultures of the typhogen bacillus (Gautier, Bl. [2] 48, 13).

TYROSINE C. H., INO, i.e.
C. H., (OH), CH, (NIL.), CO. H. p. Oxy-a-amido-menul-premious acid. Mol. vs. 121 (1925)

phenyl-propionic acid. Mol. w. 181. [235°]. S.G. 1 456 (Siber, B. 17, 2837). S. 04 at 20°; 65 at 100°. S. (90 p.c. alcohol) 0074 in the cold. H.F. 156,400. H.C.v. 1,070,800. H.C.p. 1.071.200 (Berthelot a. André, Bl. [3] 4, 227). $[a]_D = -8^\circ$ in HClAq at 16° ; -9° in KOHAq at 20° (Mauthner, M. 3, 843).

Occurrence.—Occurs abnormally in the liver and urine (e.g. in cases of poisoning by phosphorus (Frerichs a. Städeler, J. 1855, 729; 1856, 702; Blendermann, H. 6, 242), in the cutaneous scales in pellagra (Schmetzer, Dissert., Erlangen, 1862), in cochineal (De la Rue, A. 64, 35), in 1802), in cochineat (De la Ruc, A. 04, 53), in sprouting pumpkin seeds (Schulze a. Barbieri, J. pr. [2] 20, 401; 32, 457), in the roots of Stachys tubesiera (Planta, B. 23, 1699), in dahlia bulbs (Leitgeb, C. O. 1888, 1897), in alcoholic extract of woad leaves (Schunck, C. N. 37, 223), and in beetroot molasses (Lippmann, B. 17, 2835).

B. 17, 2835).

Formation.—1. By potash fusion from casein (Liebig, A. 57, 127; 62, 269), globulin, feathers, hairs (Leyer a. Köller, A. 68, 332), and albumen (Nencki, J. pr. [2] 17, 97).—2. By the action of boiling dilute H.5O, on ox-horn (Hinterberger, A. 71, 72), on fibrin (Städeler, A. 111, 12; 116, 57), and on silk (Weyl, B. 21, 1529).—3. By putrefaction of yeast A. Müller, J. pr. 57, 162; Báchamp, C. R. 74, 115, 184), albumen and gelatin (Jearmeret, J. pr. [2] 15, 853).—4. En amall quantity by heating conglutin with HClAq small quantity by heating conglutin with HClAq (Siegfried, B. 24, 419).—5. From p-amido-

phenyi-alanine and HNO, (Friediander a. Mahly, B. 16, 854; Erlenmeyer a. Lipp, A. 219, 161)

Properties .- Stellate groups of slender silky needles (from water), insol. alcohol and ether, m. sol. NH, Aq and KOHAq. Lævorotatory. Its solution is not ppd. by lead acetate or subacetate until NH, Aq is added. Boiling Hg(NO₂), containing HNO, turns its solution red, forming a brownishred pp. (R. Hoffmann, A. 87, 123; L. Meyer, A. 132, 156). After warming with conc. H. SO., diluting with water, and neutralising with BaCO₃, the solution is turned violet by FeCl., Tyrosine gives off less N, when its solutions are decomposed by NaOH and III in presence of NH₃ than when the NH₃ is absent.

Reactions.—1. At 270° it splits up into CO₂

and C.H.(OH).CHI. CHI...NH. (Schmitt a. Nasse, A. 133, 211).—2. Polash-jusion forms p-oxybenzoic and acetic acids (Barth, A. 136, 110; ost, J. pr. [2] 12, 159; Baumann, II, 4, 304). 3. KClO₂ and HClAq form tetra-chloroquinone.—4. By putrefactive fermentation it is converted into hydro-p-coumanic acid, and inally into p-cresol and phenol (Weyl, B. 12, 1450), 5. Hild and P at 150° from NH, and p-oxy-phenyl-propionic acid (Hüfner, Z. [2]) 4, 391; 6, 113). Conc. HClAq and HBrAq at 240° have no action.—6. Conc. H₂SO₄ (4 pts.) at 100° forms crystalline C₂H₁₀(SO₂H)NO₂, v. sl. sol. cold water, which also occurs in a hydrated son con water, which also containing 2aq). He yields (NH,)||fA" aq, Ba(HA"), 4aq, and Ca(HA"), 5aq (Städeler, A. 116, 57). BaC, H,NO, 3aq is obtained from the product of the action of H2SO4 \$10 pts.) on tyrosine (1 pt.).—7. MeOH, potash, and Mef yield crystalline C, H, NIO, K, sol. and Met yield crystalline C_{1,111,8}NlO₂K, sol. water, decomposed by warm KOHAg into NMe, and the methyl derivative of p-coumaric acid (Körner a. Menozzi, G. 11, 550).—8. Potassium cyanata added to boiling water containing tyrosine forms tyrosine-hydantoic acid C_{6,11,1}(OH).CH₂.CH(NH.CO.NH₂).CO₂H crystallising from water in needles, insol. ether (Jaffé, H. 7, 310). This body legisles to melt at 1553 H. 7, 310). This body begins to melt at 1552, being decomposed above 170°. It gives a red colour and pp. on warming with Millon's reagent. KA'aq, crystallising from alcohol-It forms KA'aq, crystallising from alcohol-benzene. 9. Tyrosine administered to a dog appears in the urine as tyrosine-hydantoin C_oH₄(OH).CH₂.CII NH.CO [275°-280°], which crystallises from water in needles, and is decomposed by heating in sealed tubes with baryta-water into CO,, ammonia and tyrosine. Other products found in the urine of a rabbit after a dose of tyrosine are hydro-p-coumaris and p-csy-phenyl-acetic acids and phenols (Blendermann, H. 6, 251).

nn, H. 0, 251).
Salts. — Na₂C₆H₆NO₅. — CaC₆H₆NO₅. —
C₆H₆NO₆2aq. Prisms, more sol. cold than BaC,H,NO,2aq. Prisms, more sol. cold than hot water.—Cu(C,H,NO,),. S. 99 in the cold; 4 at 100°. Got by adding Cu(OH), to a boiling solution of tyrosine (Hofmeister, A. 189,6). Insolution of tyrosine (Holmeiser, A. 189, 0). Insol. alcohol. Deposits black cupric oxide
on boiling with water.—C.H., NO. (HgO), 2aq.—
C.H., NO. (HgO), 2aq.—
(Vintschgau, J. 1869, 985).—Ag.C.H., NO. aq:
amorphous pp.—AgC.H., NO. 4aq: crystalline
powder.—B'H.PtCl. (Gintl, Z. [2] 5, 704).—
B'H.FO. Standar needles, decomposed by
water.—B'H.PtCl. (Gintl, Z. [2] 5, 704).— B'H2SO4. Slender needles, not coloured by FeCla

Di-bromo-tyrosine C,H,Br,NO, 2aq. S. ·46 at 16°; 4 at 100°. Formed from dry tyro-sine and Br vapour (Gorup-Besanez, A. 125, 281). Needles or tables (from water), sl. sol. alcohol. Ag, C, H, Br₂NO, 2aq. — B'HCl 1 aq. — B'HBr. — B'₂H₂SO₄. Prisms, sol. water and alcohól.

Mitro-tyrosine C₀H₁₆N₂O₃ i.e. C₀H₁₆(NO₂)NO₃. Formed from tyrosine (1 pt.), water (4 pts.), and nitric acid (4 pts. of S.G. 1·3) in the cold (Strecker, A. 73, 70; Städeler, A. 116, 77). Pale-(Siffector, 2. 70, 70, Business, 1. 17), 17). Lawyyellow needles, sl. sol. cold water. — Salts: Ba $(C_bH_bN_2O_b)_2$ (dried at 100°). Blood-red amorphous mass.— $^{-1}A_5C_bH_bN_2O_a$; orange ppohanging to a red powder.—B'HOl $_2$ loq. Tufts of lemon-yellow needles.— D'HNO $_2$. S. 20.

Lemon-yellow needles.-B'.H.SO.. Yellow needles or granules.

Di-nitro-tyrosine C₂H₂(NO₂)₂NO₂. [115°]. Formed by warming nitro-tyrosine with dilute HNO. Golden CaC,H,N,O, 3aq. Golden plates (from water). - Salts; Golden six-sided tables. BaC.H.N.O. 2aq. Ruby-red prisms with vellow reflex, exploding when heated.

Reference.—Amido-tyrosine.

TYROTOXICON. A poisonous substance formed in milk, containing the butyric acid ferment, which has stood for some days. Occurs also sometimes in cheese (Vaughan, Ph. [3] 18. 479; H. 10, 146). When its alcoholic solution is mixed with PtCl, and evaporated violent explosion takes place.

sol. chloroform, insol. ether. Poison, paralysing respiration (Bradford, J. Physiol. 8,79). Possibly identical with sytisine. -B'HCl. Deliquescent.

D'H.PtCl....B'2HAUCl..
ULTRAMABINE. The blue-coloured material contained in lupis-lazuli. Until 1828 ultramarine was obtained by powdering and washing lapis-lasuli; but since that year it has been manufactured by heating to bright redness mixtures of Al silicate (china clay), Na2CO3 (carbonated soda ash), S, and charcoal, and washing, powdering, drying, and sifting the product. (For details of the manufacture v. Dierronany of APPLIED CHRMISTRY, vol. iii. p. 891.) The constituent elements of ultramarine are Al, Na, Si, S, and O. Treated with HClAq, ultramarine gives off H₂S; the solution contains NaCl AlCl₃, and FiO₂, and the residue consists of SiO₂, S, and some Al2O3; these reactions point to ultramarine being a compound of silicates and polysulphides. Much work has been done on the constitution of ultramarine, but the results obtained have not finally settled the question. From analyses and investigations made in 1891, Brögger a. Bäckström (W. J. 1891. 454) conclude that the composition of the essential colouring compound in natural ultramarine is represented by the formula Na₁[A'(S₃Na)]Al₂(SiO₄)₂. They also conclude that artificial ultramarines may be expressed by the following formula:-

 $Na_3Al_3Si_3O_{12} = N$ $\begin{array}{l} Na_3Al_3Ol_3Ol_2= \Lambda \\ Na_2Al_2Sl_0Ol_2= \Lambda \\ Na_4[Al(SNa)]Al_2Sl_3Ol_2= U(S_1) \\ Na_4[Al(S_Na)]Al_2Sl_3Ol_2= U(S_2) \\ Na_4[Al(S_Na)]Al_2Sl_3Ol_2= U(S_3). \end{array}$

The main constituents of the different varieties of blue ultramarine are N, A, and $U(S_1)$; of green ultramarine $U(S_2)$ and N; and $U(S_1)$ is the main contituent of white ultramarine, according to B. a. B. Formulæ more or less approaching those given above have been assigned to ultramarine by other observers; thus Silber in 1880 represented blue ultramarine as Si₂Al₄Na₂S₄O₂₀ (B. 13, 1854). On the other hand,

ULEXINE C. H., N.O. [1519]. An alkaloid some chemists have regarded the essential conin the seeds of common furze (Ulex europeeus) stituent of ultramarine as a sodium thiosilicate; (Gerrard a. Symons, Ph. [3] 17, 101, 229; 19, 1029; 20, 978, 1017). Deliquescent crystals, v. S.Si(ONa), as the composition of 'ideal ultra-S.Si(ONa), as the composition of 'ideal ultra-marine blue'; and he regards artificial ultramarine as a mixture, the only essential part of which is sodium thiosilicate. Clarke (Am. 10, 126) suggested a formula for ultramarine which should indicate the relations of this body to various natural silicates; in this respect Clarke's formula is important (v. this vol. p. 451).

White ultramarine is obtained by completely white utrimarine is obtained by completely cutting off air during the roasting of the materials; it is changed to blue by heating in O, SO, or Cl (v. Ritter, W. J. 1160. 226; cf. Philipp, B, 9, 1109; 10, 1227; Böttinger, A. 182, 311; R. Hoffmann, A. 194, 1).

Red ultramarine was observed by Scheffer, in 1873, to be formed in preparing the ordinary substance in a muffle furnace very strongly heated and freely exposed to the air; it contains less Na and more Al than the blue variety (B. 6, 1450; v. also Bächner, D. P. J. 231, 446; Zettner, B. 8, 259, 353).

Yellow ultramarine is formed by heating the red variety in the air a little above 360°, for a short time (R. Hoffmann, A. 194, 1). According to Büchner (B. 7, 990), both the yellow and red forms are produced by heating blue ultramarine red and then to yellow. If Cl is passed over ultramarine before the formation of the blue variety is completed, at 410°, the colour goes green, and then reddish-yellow (Zettner, B. 8, 259, 353); by heating the product with alkali. all CF is removed and a violet ultramarine is produced. This variety goes to the red form when heated in vapour of HNO or HCl at 130°-150° (Zettner, l.c.).

Green ultramarine is formed when a little Sa'ls used in the roasting process; it is converted into the blue substance by roasting with S. This form seems to be intermediate between white and blue ultramarine. According to Philipp (B. 9, 1109), S is not taken up in the change from green to blue; by heating the green form in sealed tubes with water, at 100°, he obtained the blue the material the blue the tained the blue, the water removing a very small quantity of sodium compounds.

Sabstituted ultramarines. Blue to green, and reddish-grey, substances have been formed by hesting ultramarine with AgNO, Aq, and by treating the product of this reaction with KI, LiI, BaL, ZnI, &c. These substances, known as silver ultramarine, potassium ultramarine, &c., probably contain Ag, K, Li, Ba, &c., in place of Na (v. Unger, D. P. J. 212, 224, 301; Philipp, B. 10, 1227; Heumann, A. 199, 253; 201, 262; Forerand a. Ballin, Bl. [2] 30, 112). By heating silver ultramarine with various alcofictio iodides, Forerand (C. R. 88, 30) obtained ultramarines containing alcoholic radicles, such as cethyl ultramarine, amyl ultramarine, &c. Selenion and tellurium ultramarines have also been produced, wherein S is substituted by Se or Te (v. Leykauf, W. J. 1876, 555; Guimet, A. Ch. [5] 13, 102; Pliequa, Bl. [2] 28, 518; Morel, Bl. [2] 28, 522). Various substituted ultramarines have been examined by Wunder (Chem. Zeit. 1890, 1119).

M. M. P. M.

ULMIC ACID. C. 66-4-63-9; H. 46-4-5; O. 29-31-5. C₁₂H₁₁O₂ or C₁₂H₁₂O₃. 11.C. 1983, 200. H.F. 266,200. Formed by action of HCl on cane sugar. Is an anhydride or mixture of anhydrides C₁₂H₁₂O₄ (humic anhydride) (Berthelot a. André, Bl. [3] 7, 441, 451). Turnsyllow in air and sunlight, giving off CO₂. The same thing happens with the humic acid extracted from vegetable mould by KOHAq and ppd. by HCl. Dilutte alkalis cause it to swell up, forming insoluble satts and a small quantity of a soluble basic salt. When cone. KOHAq is used a salt is formed, from which two-thirds of the alkali can be removed by washing, leaving KC₁H₁₁O₄, aq, and is reconverted into the acid. C₁₂H₁₂O₄ by HClAq. Animonia converts humic anhydride (ulmic acid) into an amido-acid C₃₄H₁₁O₄ wh₁₁ whence HCl sets free C₃₄H₁₁NO₄. Salts. -KC₁₅H₁₅O₄ aq. Hard, black, in-

Salts. – KC₁₈H₁₈O, aq. Hard, black, involuble mass, yielding a brown powder. The ulmin of Malaguti. Forned by shaking the anhydride with KOH (1 pt.) and water (120 pts.). – NaC₁₈H₁₃O, aq. – Na₂C₁₈H₁₃O, xaq.

References.—HUMIG, SACCHARUMIG, and SACCULMIG ACIDS.

UMBELLIC ACID C. H.O. i.e. [4:2:1] C.H.(OH), CHI:CH.CO.H. Mol. w. 132. Dr. oxy-cinvante acid. Formed by warming its lactone, umbelliferone with KOHAq (Tigmann a. Reimer, B. 12, 994; Posen, B. 14, 2745). Yellowish powder. Turns brown at 240°, and decomposes below 260°. Sol. alcohol and warm water, insol. ether. Resinified by boiling its aqueous solution. Reduces warm ammoniacal AgNO₂, forming a mirror. FeCl. gives a brown pp.

Methyl derivative C₁₆H₁₆O₄. [180²₂-185⁵]. Got by heating herniarin with alcoholic potash at 160° (Barth a. Herzig, M. 10, 165). Needles (tagg. water).

(a) Di-methyl derivative

C.H. (OMe), CH:CH.CO.H. [138°]. Formed by
the action of MeI and KOH in MeOH on the
methyl derivative of umbelliferone in the cold

(W. Will, B. 16, 2115; 19, 1277). Needles, v.
sol. alcohol and ether. Converted into the
(8)-isomeride by boiling alone or with HCIAq.
Both isomerides are reduced by sodium-amalgan
to the same C.H. (OMe), CH, CH, CO, H, and are
oxidised by KMnO, to the same C.H. (OMe), CO, H.

—CAA', 2aq: crystals.—BaA', 2aq: needles.

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(3) Di-methyl derivative. [1847]. Formed as above, and also by saponification of its methyl ether C.H.(OMe). CH:CH.CO.Me [877], which is got by evaporating methyl-umbelliferone (1 mcl.) with NaOH (2 mols.) nearly to dryness, and digesting the residue with McI and McOH (Tiemann a. Will, B. 15, 2079). Needles, sol. alcohol and ether. Sl. sol. cold water.

(a)-Di-ethyl derivative [4:2:1] C.H. (DEI), C.H., CO.H. Di-ethyl-umbellic acid. [107°]. Formed by mixing ethylumbelliferone (5g.) with Etl (10g.) and a solution of KOH (4g.) in alcohol (Will a. Bock, B. 19, 1780). Small plates, v. 201. alcohol, ether, and benzene.

(β) Diethy' derivative. [200°]. Formed by boiling the (a) Asomeride for some time, and also by heating ethyl-umbelliferone (10 g.) with EtI (9 g.) and a solution of Na (2\) g.) in alcohol for six hours at 150°. Crystals, m. sol. alcohol, sl. sol. water.

UMBELLAFERONE C,HO, i.e.

C_H_3(OII) C_CO. Mol. w. 162. [224]. S. 1 at 100°. Formed by the dry distillation of various resins, chiefly those derived from umbelliferous plants, e.g. galbanun, sagapenum, and asafactida (Sommer a. Zwenger, A. 115, 15; Mössmer, A. 119, 260; Hlasiwetz a. Grabowski, A. 139, 100; Hirschsohn, C. C. 1877, 182). Formed by heating malic acid (1-mol.) with resorcin (1 mol.) and H_SO, (Pechmann, B. 17, 932). Prepared by distilling the alcoholic extract of gum galbanum (Tiemann a. Reimer, B. 12, 993). Needles, sl. sol. cold water and ether, v. sol. alcohol. Dissolves in acids, without charge. Alkalis above 50° form embellic acid. Its solution in dilute alkalis shows blue fluorescence. It SO, forms a solution with green fluorescence. Reduces AgNO₃ on boiling. Yields (4,2,1)-di-oxy-benzoic acid on oxidation (Tiemann a. Parrisius, B. 13, 2354). Funning JiNO₃ and H SO₄ form C₉H₃(NO₂),O₃ [216°] (Posen, B. 14, 2744).

Acetyl derivative C₁₁H_aO₄. [140°]. Formed by acetylation, and also by boiling di-oxy-benzoic aldeliyde with Ao₄O and NaOAe (Tiennann, B. 10, 2216; 12, 995). Needles, sl. sol. water.

Methyl derivative C, H,O, i.s.

C.H. (OMe) < CH: CH [114°]. Formed by heating umbelliferone with KOMe and MeI (T. a. R.). Ledlicts, nearly insol. water. Appears to be identical with herniarin [118°], which is extracted by alcohol from Herniaria hirsuta (Barth a. Herzig, M. 10, 161).

Ethyl derivative C₁₁H₁₀O₂. [88°]. Plates y. sol. alcohol (Will a. Beck, B. 19, 1779). Oxim of the methyl derivative

[4:2:1] C.H. (OMe) CHI.TH [138°]. Formed from the methyl derivative of thio-umbelliferone and hydroxylamine (Aldringen, B. 24, 3465). Reedles, v. sol. hot water and alcohol. Fell. colours its solution brownish-red.

Phenyl-hydraside of the methyl defivative C.H.(OMe) CHCH [115]. Yellow needles, giving a blue colour with H.8O.

Thio-umbelliferone. Methyl derivative C.H. (OMe) CH:CH. [114°]. Formed by heating the methyl derivative of umbelliferone with P₂S₃ (Aldringen, B. 24, 3465). Needles, sol. alcohol, v. sl. sol. water.

References .- BROMO- and MPTKIYL- UMBEL-

LIFERONE.

UMBELLOL C_sH₁₀O. (216°). V.D. 4·29. Occurs in the volatile oil of the Californian laurel (Stillmann, B. 13, 629). Oil, sol. H.SO., with red colour, becoming black. Attacked by

UMBELLULICA ACID v. HENDECOÏC ACID. UNDECANE v. HENDECANE. UNDECOTO ACID v. HENDECOTO ACID. UNDECOLIC ACID v. HENDECINOIC ACID. UNDECYLENE v. HENDEGYLENE.
UNDECYLENIC ACID v. HENDECENOIC ACID.

UNDECULIC ACID v. HENDECOIC ACID. URACIL CO NH.CH CH. , Di-oxy-pyr-

imidine. Derivatives of this compound are formed by the action of accetoacetic ether on urea, thio-urea, and guanidine (Behrend, Ar 229, 1; 240, 6; List, A. 236, 1; Jüger, A. 262, 365;

Amido-uracil C₄H₁N₂O₂, by reducing nitro-uracil (Behrend), and by boiling di-brono-pyruvuramfde vith baryta-water (Fischer, A. 239, 193). Yellow needles, sol. water. Converted by evanic acid into oxyxanthine C,H,N,O,, which crystallises in needles, sl. sol. water, sol. alkalis, gives with Cl the murexide reaction, may be oxidised to alloxantin, and gives some alloxan with bromine water.

Acetyl derivative C, H, N,O, and Prisms. Nitro-uracil v. NITRO-DI-OXY-PYRIMIDINE. Bromo-nitro-oxy-uracil. Dihydride

C₄H₄N₂O₅Br i.e. CO<NH.CH(OH)>CBr(NO₂).

, Formed by adding Br to nitro-uracil suspended water (Behrend, A. 240, 11). Crystalline mass, sl. sol. cold water and alcohol. Boiling with water produces brominated nitro-methanes and a crystalline compound C,H,N,O,, formed by the action of urea upon nitro-uracil. Tin and HCl reduce it to amido-uracil.

Methyl-uracil v. DI-OXY-METHYL-PYRIMIDINE. Nitro-methyl-uracil C₃H₃N₃O₄. Prepared by nitrating methyl-uracil with HNO₃ (S.G. 1.5) mixed with an equal volume of H₂SO₄ (S.G. 1.82) (Behrend, A. 240, 3). Prisms or tables (from water), al. sol. lot alcohol.

Isomeride v. Nitro-di-oxy-mewiyl-pyrim-

Nitro-di-methyl-uracil v. NITRO-DI-OXY-DI-METHYL-PYRIMIDINE.

Di-chloro-oxy-methyl-uracil. · Dünydride $\operatorname{CCr} <_{\operatorname{CO}}^{\operatorname{CMe(OH).NH}} > \operatorname{Co}.$ i.e. Formed by the action of chlorine on methyluracil suspended in water (Behrend, A. 236, 59). Tables (from water); slowly decomposed by boiling water. M. sol. alcohol; not decomposed by boiling alcohol. M. sol. ether. A solution of SnCl, in HClAq at 100° reduces it to chloromethyl-uracil O₂H₂ClN₂O, which crystallises from water in needles. Fuming HNO, gives diahloro-barbituric acid.

Di-bromo-oxy-methyl-uracil C.H.N.Br.O. i.e. CBr₂ CMe(OH).NH . From methyl-uracil (or bromo-methyl-uracil), and bromine water (Behrend, A. 229, 18; 236, 57). Cubes (from hot water). Boiling alcohol converts it into bromomethyl-uracil CaH, N2BrO2. Fuming HNO2 forms di-bromo-barbituric acid.

Di-chloro-oxy-tri-methyl-uracil. Dihydride $CO \stackrel{NMe.CO}{\sim} COl_2$ [144°]. by passing Cl into an aqueous solution of trimethyl-uracil (Hagen, A. 244, 14). Crystals, sl. sol. hot water. Reduced by boiling with SnCl. to chloro-tri-methyl-uracil, which crystallises in prisms, m. sol. hot water.

Nitro-ethyl-uracil v. Nitro-di-oxy-ethyl-

PYRIMIDINE.

Methyl-ethyl-uracil v. DI-OXY-METHYL-ETHYL-PYRIMIDINE.

Nitro-methyl-ethyl-uracil v. NITRO-DI-OXY-METHYL-ETHYL-PYRIMIDINE.

Amido-uracil carboxylic acid v. Di-oxy-AMIDO-PYRIMIDINE CARBOXYLIC ACID.

References .- THIO-METHYL-URACIL and UR-AMIDO-CROTONIC ACID.

URAMIDO - ACETIC ACID v. HYDANTOÏO ACID.

p-URAMIDO-BENZENE SULPHONIC ACID NH₂.CO.NII.C_aH₄.SO_aH. Formed by evaporating a solution of p-amido-benzene sulphonic acid and potassium cyanate (Pellizzari, A. 248, 156), and also by heating dry p-amido-benzene sulphonic acid (1 mol.) with urea (1½ mols.) (Friedel, C. R. 112, 868). Pearly plates (from dilute alcohol), v. sol. water. -BaA', 3aq; mono-

clinic prisms, sol. Aq.
o-URAMIDO-BENZOIC ACID C₈H₈N₂O₃ i.e. NH₂.CO.NH.C₆H₄.CO₂H. Formed from potassium cyanate and the hydrochloride of o-amido-

beingoic acid (Griess, J. pr. [2] 5, 371; B. 11, 1730). HNO₃ yields only one di-nitro-derivative. n. Uramido-benzoic acid CH_mN_O. S. 1 at 10°. S. (96 p.c. alcohol) 72 at 16°. S. (ether) 127 at 16°. Occurs in urine after a dose of m-amido-benzoic acid (E. Salkowski, H.

7, 113).

Formation.—1. By adding potassium cyanate to a boiling saturated solution of the sulphate of m-am do-benzoic acid (Menschutkin, A. 153, 84; Z. [2] 4, 275).—2. By fusing m-amido-benzoid acid with urea (Griess, Z. [2] 5, 312; B. 2, 47). . By boiling m-cyanamido benzoic acid with

HClaq (Traube, B. 15, 2122).

Properties.—Small prisms (containing aq),
v. sl. sol. hot water. At 200° it yields v. sl. sol. hot water. At 200° it yields CO(NF, C₄H, CO₂H), On distilling m-uramido-benzoic acid (4 pts.) with P₂O₃ (1 pt.) m-amido-benzoic nitrile [54°] is formed (Griess, B. 8, 224). Boiling KOHAq splits it up into m-awido-

Benzoic acid, CO₂, and NH₃.

"Salts.— NH₁A'aq. — KA'. — CaA'₂4aq. —
PbA'₂2aq.—AgA': curdy pp., becoming crystalline.

Ethylether Eth'. [176°]. Formed from m-amido-benzoic ether and KCyO (Griess, J. pr. [2] 4, 293). Plates, sl. sol. hot water.

'Amido C,H,N,O. Formed from m-amido-benzamide and KCNO (Monschutkin). Scales

(from water), decomposed by fusion, al. sol.

p-Uramido-benzoic acid C₈H₈N₂O₃. Formed in like manner (Griess, J. pr. [2] 5, 369). Plates, almost insol. cold water, v. sl. sol. hot water, m. sol. hot alcohol. Yields some p-amido-benzonitrile [86°] on distilling with P₂O₃.—BaA'₂. Plates, v. e. sol. cold water.

Di.uramido-benzoic acid C,H,ON,O4 i.e. (NH,CO,NH),C,H,CO,2H. Formed by fusing diamido benzoic acid with urea (Griess, B. 2, 47). Small granules, v. sl. sol. hot water.— InAA's (dried at 130°). Noulles, v. sol. hot water.

References.—Amno-, Nitro-, and Oxy. UR-

AMIDO-BENZOIO ACIDS.

• URAMIDO-BENZOYL v. OXY-QUINAZOLINE.
p-URAMIDO-BENZYL-UREA C.H.,2N,O2 i.c.

NH₂CO.NH.C₂H₄CH₄NH.CO.NH₂, [197°], p-a-Di-uramido-toluene. Formed by heating toge-ther p-amido-benzyl-amine, hydrochloride (1 mol.), and KCNO (2 mols.) in aqueous solution (Amsel a. Hofmann, B. 19, 1289). Small needles. Sol. hot water.

URAMIDO-ISOBUTYRIC ACID v. ACETON-

TRAMIC ACID.

o-URAMIDO-CINNAMIC ACID Cullin N.O., i.e. NH .. CO.NH.C H .. CH: CH.CO .. H. Formed from o-amido-cinnamic acid and aqueous KCNO (Rothschild, B. 23, 3341). Sol. NII Aq and hot HClAq.
(β)-URAMIDO-CROTONIC ACID C₂H₈N₂O₃

i.e. CH, C(NH. CO.NH.): CH. CO.H. The ether is converted by NaOHA into the salt NaA', which crystallises in needles, v. sol. water; but on adding acids to this salt di-oxy-methyl-pyr-imidine Q₂H₁N₂O₂ is produced. Methyl-uracil is reconverted by NaOHAq into sodium uramido-

crotonate (Behrend, A. 229, 5).

Ethyl ether EtA', [166]. Formed from acctoacetic ether and urea. Needles, v. sol. ether, m. sol. alcohol. Decomposed by warm HCIAq into urea, acetone, CO., and alcohol. Alcohol forms CH., C(NH.CO,Et):CH.CO,Et [29°] (Meister, A. 244, 234).

CH3.C(NH.CO.NH2):CH.CO.NH2. Amide [131°]. Crystals (containing EtOII) (Meister). Amido-uramido-crotonic acid. Lactam.

Amido-methyl-uracil. Methyl-uracil (v. DI-oxy-METHYL-PYRIMIDINE) is converted by Br in CS₂ into crystalline bromo-meth fl-uracil C, H, DrN, O, whence conc. NH₃Aq at 150° forms amidomethyl-uracil (Behrend, A. 231, 250). Satiny plates (from water), in Iting near 250. Sol. alcohol. The hydrochloride is converted by potassium cyanate into oxy-methyl-xanthine G₄H_AN₄O₂2aq, crystallising from water in prisms.—B'HCl aq. Monoclinic crystal •; a:b:c =1:629:1:2·345; β · 52° 57',—B'₂H₂PtCl₆2uq:• needles, v. sol. water.

scetyl derivative C.H. (NHAc)N.O. 1 Rg. Formed from oxy-methyl-xanthine and Ac.O at 170°. Thick trimetric prisms (from water). Decomposes near 210° without melting. Sol.

alkalis and reppd. by acids.
URAMIDO-ETHANE SULPMONIC ACID NH, CO.NH.CH, CH, SO.H. Taurocarbanic acid. Occurs in small quantity in urine after as dose of taurine (E. Salkowski, B. 6, 744, 1191). Formed by evaporating a solution of taurine with KCyO. Formed also by the action of B. 22, 1142). Dimetric plates, v. sol. water, sl. sol. alcohol, insol. ether. Decomposed by baryta-water at 140° into CO, taurine, and NH₂.—BaA'₂: tables (from alcohol).—AgA'. Radiating tufts of crys-

URAMIDO - HEXOIC ACID C,H,,N,O, i.e. NH, CO.NH.CH(C,H,e),CO,H. [200°]. Formed by boiling isobutyl-hydantom with baryta-water (Pinner a. Spilker, B. 22, 696). Needles, v. sol. alcohol and hot water. - BaA'a: nodular groups of prisms.

Ethyl ether EtA'. [135°]. Formed by heating isobutyl-lydantoïn with KOH and EtBr. Needles, v. sol. alcohol and flot water.

Nitrile. NJL.CO.NH.CH(C.H.o.).CN.

Formed by heating the cyanhydrin of isovaleric aldehyde with urea (Pinner a. Lifschütz, B. 20, Oil, sol. alcohol and ether. On warming with HClAq it yields isobutyl-hydantoin C,H,,CH

CO,NH [210°].

Amide NILCO.NH.CH(C,H,),CO.NH.

[170°]. Formed from the nitrile (1 pt.) and cone. H.So. 3 pts.) in the cold. Crystals, v. sol. water and alcohol.

URAMIDO-HIPPURIC ACID C10H11N,O Formed by fusing m-amido-hippuric acid with urea (Griess, J. pr. [2] 1, 235). Nodules, v. e. sol. hot water. Decomposed by boiling conc. HClAq into glycocoll and m-uramido-benzoic acid.—AgA'. Crystalline pp.
URAMIDO-NITRO-AMIDO-PHENOL

C,H,N,O, i.e. C,H,(NO,)(NH,)(NH.CO.NH,).OH. Formed by reducing di-nitro-oxy-phenyl-urea with a monium sulphide (Griess, J.pr. [2] 5, 1). Reddish-brown needles, sl. sol. hot water and alcohol.—B'HCl: white scales.—BaA', 3\angle actel-blue needles, v. sol. hot. water. Boiling HClAq converts it into amidocarboxamidonitrophenol C.H.N.O., which yields BaA', xaq and B'HClaq, and is reduced by tin and HClAq to diamidocarboxamidophenor C,H,N,O, which yields B'HCl, crystallising in plates.

URAMIDO DI NITRO-PHENOL v. DI-NITRO-OXY-PHENYL-UREA.

p-URAMIDO-PHENYL-ACETIC ACID NH, CO,NH.C,H, CH, CO,H. [174°]. Formed by boiling p-cyanamido-phenyl-acetic acid with HClAq (Traube, B. 15, 2122). Small crystals

(containing 1 aq), sol. water, alcohol, and ether, a Uramido-phenyl-acetic acid. Ethyl her NH. CO. NH. CHPh. CO. Et. [130]. Formed by the action of aqueous KCyO on the hydrochloride of a-amido-phenyl-acetic ether (Kossel,

B. 24, 4150). V. sol. alcohol and hot water.
Nitrite NIL.CO.NH.CHPh.CN. [17 [170°] Formed by heating the cyanhydrin of benzoic aldehyde with urea (Pinner a. Lifschütz, B. 20, 2351). Converted by acids into C.H.N.O. [1827], crystantising in scales, v. sol. alcohol and hos water. water.

ter. g. uramido-phenyl-crotonic Acid. Nitrile CHPh:CH.CH(NH.CO.NH.).CN.

[160°]. Formed by heating urea with the cyanhydrin of cinnamic aldehyde (Pinger a. Lifschütz, B. 20, 2351). Needles, v. sol. hot alcohol. Boiling HClAq converts it into di-oxy-styryl-pyrazole (q. v.).

Amide CHPh:CH.CH(NH.CO.NH.).CO.NH. Formed from the nitrile and cold cone. H.SO bromine-water on ethylene-v-thio-ures (Gabriel, (Pinner a. Spilker, B. 22, 692). Microorystalline powder, decomposing at 210°-220° with evolu-tion of NH,. Sol. alcohol, al. sol. hot water. a-URAMIDO-PROPIONIO ACID C,H,N,O,

i.e. CH, CH(NH.CO.NH₂).CO.H. Lacturanic acid. [155°]. Formed by evaporating a solution of alanine sulphate mixed with KCyO (Urech, A. 165, 99). Formed also by boiling lactyl-urea with baryta-water (Heintz, A. 169, 128). Prisms, sl. sol. cold water and alcohol, insol. ether .-BaA'2 aq (dried at 100°).—PbA'2aq -AgA': needles, m. sol. water.

Nitrile CH, CH(NH.CO.NH,).CO.H. [106°] (Franchimout a. Klobbie, R. T. C. 7, 16). Amide CH, CH(NH.CO.NH,).CO.NH,

[196°]. Small needles (from a rohol), sol. water. URAMIDO-SUCCINIC ACID. Amic acid Amic acid NH, CO.CH, CH(NH.CO.NH,).CO.H. [138°] (G.); [157°] (P.). Succinuranide. Amido-succinuric acid. S. 54 at 23°. Formed by evaporating the mixed solutions of asparagine KCyO (Guareschi, G. 7, 404; B. 10, 1747). Dextro-asparagine gives a hevo-compound, while levo-asparagine gives a dextro-compound (Piutti, B. 19, 1693). Prisms, nearly in ol. alcohol and ether. According to Piutti, the dextroand lavo- compounds both melt at 157°.

Reactions.-1. Decomposed by fusion, with formation of malyl-ureide C.H.N.O. [230°-235°], which is also formed by heating urea with asparagine at 125° (Grimaux, Λ . Ch. [5] 11, 400) and Erystallises from water in pointed Phombohedra.—2. Boiling HClAq (S.G. 1-12) forms malyl-ureidic acid C₅H₆N₁O₄, which is also got by heating aspartic acid with urea at 130°. Malyl-uredic acid crystallises in orisms [215°-220°], S. 25 at 100°, which yields BaA', aq and is converted by heating with bromine-water into C,H,Br,N,O,, S. 3 at 100°, C,H,Br,N,O,, S. 25 at 100°, C,H,Br,N,O,, which is v. sol. water, C,H,BrN,O,, S. c. 6 at 100°, and C,H,Br₂N₂O₃, S. 10 in the cold and c. 22 at 100°

URAMIDO-THIO-FORMIC ACID v. THIO-

ALLOPHANIC ACID.
DI-URAMIDO-TOLUENE v. URAMIDO-BENZYL-

DI-p-URAMIDO-DI-o-TOLYL-SULPHIDE [2:1:4] S(C,H,Me.NH.CO.NH,), Thio-p-tolyl-di-[151°] (when containing benzene of crystion). Formed by heating the hydrotallisation). tallisation). Formed by nearing the hydrochloride of di-p-amido-di-tolyl-sulphide with KCNO (Trehlar, B. 20, 669). Crystallises from benzene in white silky needles (containing

URAMIL C.H.N.O. i.e.

CO NH.CO CH.NH. Dialuramide, Amidobarbituric acid. Amido-malonyl-urea. Murexan. Mol. w. 148. Formed by boiling alloxantin with NH.Cl (Liebig a. Wöhler, A. 26, 310; Grimaux, O. R. 87, 752) and by boiling ammonium thion-urate with HClAq. Formed also by reducing nitro- or nitroso- barbituric acid with HIAq (Baeyer, 4. 127, 223). It is also a product of the action of acids on murexide (Beilstein, 4. 107, 188).

Properties.—Silky needles, sl. sol. hot water, insol. alcohol and ether. Sol. conc. H.SO, and re-ppd. on dilution. Ats alkaline solution turns red in air, forming purpurates; thus it is converted in ammoniacal solution into murexide by boiling with air or HgO. Conc. HNO, forms alloxan. Bromine at 85° forms orange C,H,BrN,O, (Mulder, B. 14, 1060).

URAMILIC ACID C.H.N.O. (?). S. 14 in the cold; 33 at 100°. Formed by heating uramil with H₂SO, and water, or by evaporating ammonium thionurate with some H₂SO, (Liebig a. Wöhler, A. 26, 314; Gregory, P. M. 24, 187). Transparent, four-sided prisms, sl. sol. cold water. Converted by boiling cone. HNO, into nitro-barkituric acid.

URANATES v. URANIUM, OXYACIDS AND SALTS or, p. 826.

URANIUM. U. At. w. 239 (not determined with very great accuracy). Mol. w. unknown. M.P. not determined accurately; between red heat and white heat. S.G. of fused U at 18° = 18.685 (Zimme...ann, B. 15, 851). S.H. at $100^{\circ} = .0276$ (Z., *l.c.*). S.V.S. 12.8.

Historical.-In 1789 Klaproth prepared some compounds of a new element from pitchblende; to the characteristic element of these compounds he gave the name uranium, from oùpavos = the heavens, in allusion to the planet Uranus which had been discovered a few years before (Crell's A. 1789 [2] 400). The compounds of U were A. 165 [2] 400). The compounds of 6 were examined by Richter (Gehlen's A. 4, 402), Buchholz (Gehlen's A. 4, 17, 134), Lecanu (J. Ph. 9, 141; 11, 279), Brande (S. 44, 1), Berzelius (P. 1, 359), and Artveison (P. 1, 245). In 1840, Péligot showed that the substance supposed till then to be U was really an oxide of U (A. Ch. [3] 5, 5); P. isolated the metal, and determined the at. w. to be 120. Mendeléeff in 1872 (A. Suppl. 8, 133; cf. C. N. 41, 39 [1880]) proposed to double the at. w. of U, making it 240; this proposal was completely justified by the determina-tion of S.H. of pure U by Zimmermann in 1882 (B. 15, 851), and by the determination of the V.D. of UCl, and UBr, (Z., A. 216, 2 [1883]).

Occurrence.—Never uncombined. A minerals containing compounds of U are found sparsely distributed and not in large quantities; the chief of these is pitchblende, which consists of U₃O₃ along with SiO₂ and oxides of Sb, As, Ca, Cu, Fe, Mg, V, &c. Carbonate, sulphate, phosphate, niobate, tantalate, and various other compounds of U are also found in varying quantities in several rare minerals (v. Zimmermann, A. 232, 300; Ridden a. Mackintosh, Am. S. [3] 38, 474; Hillebrand, Am. S. [3] 38, 329; 40, 384). Lockyer (Pr. 27, 49) stated that some of the lines in the emission-spectrum of U coincide with lark lines in the solar spectrum. Hutchins a. Holden (P. M. [5] 24, 325) think there is no trustworthy evidence in favour of the existence of U in the solar atmosphere.

Preparation .- 1. A mixture of UCl., NaCl, and Na is strongly heated in a closed iron cylinder. Zimmermann (A. 116, 14) used a cylinder of soft iron with walls c. 3 centim. thick, bored from a larger cylinder (similar to that employed by Nilson a. Pettersson for preparing Be; B. 11, 383) fitted with a cap which could be screwed on tightly. He placed a layer of pure fused NaCl in the cylinder, then small pieces of Na (c. 3 to 4 pts. for 10 pts. UCl.), then UCt (which must be put into the cylinder as quickly as possible, as it is hygroscopic), and covered the whole with a layer of fused NaCl. Z. raised the cylinder to a white heat, kept it at

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that temperature for some time, cooled, and washed the contents with dilute alkali solution, and then with water. According to Z, the metal as thus prepared is quite pure $(v.\ infra)$,—2. Moissan $(C,R.\ 116,\ 847)$ obtained U, containing from 5 to al. 5 p.c. C, by mixing the oxide prepared by strongly heating $UO_{\cdot}(NO_{\cdot})_2$ with excess of charcoal, compressing the mixture in a carbon crucible, imbedding this in MgO, and heating for 10–12 minutes in an electric furnace, using a current of 60 volts and 450 ampères.

UCl₄ is obtained by heating the nitrate $UO_2(NO_s)_2$ in air, mixing the oxide thus obtained (chicfly U_3O_s) with C, and heating in a stream of Cl (v. Uranium tetrachloride, p. 823). The nitrate is obtained from pitchblende by powdering the mineral, walking with water, drying, and washing to remove S and As, dissolving in HNO, Aq, evaporating to dryness, dissolving in water, filtering from Fe₂O₃, PbSO₄, &c., evaporating a little, and allowing to crystallise. The crystals of UO, (NO,), thus obtained are purified by draining in a funnel, washing with a little cold water, drying in the air, dissolving in ether in a wide-mouthed bottle, crystallising by spontaneous evaporation, and re-crystallising from hot water; the crystals of UO2(NO3), are then dissolved in water so as to form a conc. solution, UO2-C2O, is ppd. by adding H.C.O.Aq to this solution, the 14p. is washed with boiling water, and then decomposed by heat, and the UO, thus produced is digested with conc. HClAq, washed, dissolved in HNO3Aq, and the solution is crystallised (Poligot. A. Ch. [3] 5, 5; 12, 258; cf. Ebelmen, A. 43, 286; Wertheim, J. pr. 29,

The oxide U₂O_a used by Zinnmermann (v. supra) for the preparation of UCl₁, from which pure U was obtained, was prepared by him as follows. A warm solution of commercial uranium hydroxide in HClAq was saturated with H₂S; after standing for some time the liquid was filtered off, NH₄Aq and (NH₄)₂CO₄Aq were added in excess, the liquid was warmed and (NH₄)₃SAq was added; after standing the liquid was filtered, saturated with HClAq, and boiled till CO₂ was removed, then mixed with NH₄Aq and (NH₄)₃SAq and heated on the water-bath till most of the (NH₄)₂S was removed; the pp. of UO₂ was collected, washed, and heated over the blowpipe; the U₂O₆ thus formed was dissolved in HNO₂Aq and the solution was crystalised; the crystals of UO₂(NO₂)₂ were dissolved; in ether, the solution was poured off from insoluble substances, evaporated to dryness, and the residue was again dissolved in HNO₂Aq, and the orystals that formed on evaporation were dissolved in ether, and the cthereal solution was evapotated to dryness and the residue decome evapotated to dryness and the residue decome posed by heating.

Properties.—A lustrous, hard, silver-white metal; S.G. 18:685 at 150 (Zimmermann, B. 15, 851); if UCl, is reduced by Na at a red heat, U is obtained as a greyish-black powder. S.H. at 100 = 0.276 (Z., &c.). U is somewhat malleable, but cannot be hammered into third plates. The emission-spectrum, obtained by the aid of electric sparks, shews only a few lines, the most marked being one in the yellow (Thalén, A. Ch.

[4] 18, 289). For the fluorescence, phosphorescence, and absorption-spectra of U compounds v. Beoquerel (A. Ch. [4] 27, 589), also Morton a. Bolton (Am. Ch. 3, 361, 401). U melts towards a white heat; according to Moissan (C. R. 116, 1429), the metal is volatilised by heating in an electric furnace using a current of 350 ampères and 75 volts. After long standing in the air the surface of U becomes covered with a steel-blue to black film of oxide; U that has been fused burns brilliantly when heated on Pt foil in the air; palverulent U burns at 150°-170° in the air; pulverulent U burns at 150°-170° in the air. U combines directly with Ol or Br, also with S; the metal dissolves in dilute H. SO, Aq or HClAq; it is not acted on by acctic acid, nor by KOHAq, NaOHAq, or NH, Aq.

The at. w. of U has been determined (1) by determining U and Cl in UCL (Peligot, A. Ch. [3] 5, 12 [1842]; Rammelsberg, P. 95, 318; 56, 125 [1842]; Q by analyses of UO₂C.O. H₂O (Ebelmen, A. Ch. [3] 5, 191 [1842]; Peligot, A. Ch. (3] 20, 341 [1846]); (3) by analyses of UO₂(C.H₂O₂)...2H₂O (Peligot, Lc.; Wertheim, J. pr. 29, 207); (4) by analyses of the double salt UO₂Na(C.H₂O₂), (Wertheim, Lc.); (5) by transforming UO₂ into U₂O₃, and UO₂Na(C₂H₂O₂), into Na₂UO₄ (Zimmermann, A. 232, 117, 273 [1886]); (6) by determining S.H. of U (Zimmermann, B. 15, 851 [1882]); (7) by determining V.D.s of UBr₄ and UCl₄ (Zr, A. 216, 21883)).

The at. w. of U was formerly taken as c. 120; in 1872 Mendeléeff adduced reasons for doubling this value, based on a comparative study of the properties of compounds of U to which he was led by considering the periodic arrangement of the ekements (A. Suppl. 8, 178; C. N. 41, 39). When the at. w. of U was taken as 120, the formulæ given to the chief oxides, chlorides, and salts of this element were UO, UCl, USO, &c.; U₃O₄; U₂O₃, UOCl, UO₂(NO₃), &c.; and Ü was classed with the iron metals. Mendelégif • pointed out that U was very much heavier than the iron metals, that the oxide U2O, did not form salts similar to those derived from Fe₂O₃, that the salts of UO, i.e. USO4, U(NO3)2, &c., were not isomorphous with the salts of MgO, FeO, NiO, &c. Mendelceff also drew attention to the existence of a chloride which would have to be fepresented as U_2Cl_3 if U=120 and that this chloride was obtained by heating UCl_3 in H. Mendeléeff proposed to double the value then accepted for the at. w. of U, and, following on this, to write the formula of the chlorides, oxides, and salts as UCl, UO₂, U(SO₄), &c.; U₅O₄; UO₅(NO₆), &c.; and UCl, It was pointed out that many of these formulas are analogous to those of the corresponding compounds of Cr, Mo, and W; and it was shown that the properties of compounds of U more nearly resemble those of compounds of Cr. Mo, and W than of any other elements. Especial stress was laid by Mendeléeff on the acidic charetrees was laid by Mendeleen on the actue character of the highest oxide of U., Finally, Mendeléen showed that an element with the properties of U, and an at. w. equal to c. 240, finds its proper place in Group VI, series 12, of the periodic arrangement of the elements. Mendeléen suggested that the S.H. of pure U should be determined; that the V.D. of the volatile chloride should be found; that the action of H

on the chloride then taken to be UCl, should be studied; that salts of the lower oxide (UO if U=120, UO_2 if U=240) should be examined, especially as regards their iso.norphism with salts of ThO₂, SnO₂, ZrO₂, and TeO₂; that the crystalline forms of corresponding compounds of MoO₃, WO₃, and UO₃ (U=240) should be studied, and that an especially thorough crystallographic examination should be made of the compounds R₂UO₂F₄; and that the physical properties of compounds of Cr, Mo, W, and U should be compared. Since the publication of Mendeléeff's mercoir, the S.H. of U, and the V.D.s of UBr, and UCl, have been determined, the action of H on UCl, has been examined, and something has been done in the study of the crystalline forms of compounds of U, including those of the form R2UO,F4; the results of all these invertigations fully confirm the justness of Mendeléeff's view that the at. w. of U is c. 210. and that this element must be classed with Cr. Mo, and W. The exact value to be given to the at. w. of U has not been yet determined; Zimmermann's measurements gave 238.75 from the ratio $UO_2:U_2O_3$, and 238:67 from the ratio $UO_2:Na(C_2:I_3:O_2)$; $Na_2:UO_4$ (O=15:96). The mol. w. of U is not known.

U is the last member of the even-series family of Group VI.; this family also contains, besides O, the elements Cr. Mo, -, and W. The chromium elements are both metallic and nonmetallic in their chemical relations; they form oxides MO, that are acidic, and some of the lower oxides are basic. The oxide UQ, forms some corresponding salts; a series of salts of the form Uo2X is also known, where X ESO, &c. Several series of uranates M₂UO₅, M₂U₂O₇, &c., are known. The haloid compounds are UX, UX, and UX, (For a comparison of the metals of the Cr family v. Curomum group of ELEMENTS, vol. ii. p. 168; cf. CLASSIFICATION, vol.

ii. p. 207.)
The atom of U is tetravalent in the gaseous

Reactions and Combinations .- 1. Heated in air U is burnt to a voluminous deposit of UaOs (perhaps containing also UO2), which stops the further oxidation of the metal. Pulverulent U burns when heated in air to 150°-170°. 2. U burns brilliantly when heated in chlorine, forming UCl.; heated in bromine to c. 240° part of the metal is changed to UBr₁.-3. Heated in sulphur vapour US₂ is produced.-4. It is generally said that J does not react with water; but, according to Moissan (C. R. 116, 347), the metal obtained by him by reducing the oxide by char coal in an electric furnace decomposed water at the ordinary temperature; this specimen of U contained from 5 to 13.5 p.c. C .- 5. J dissolves in dilute sulphuric acid, rapidly on warming, forming USO, and giving off H; pulverulent U dissolves in hot conc. H.SO,, giving off SO2; the compact metal is scarcely acted on by conc. H.SO. -6. U dissolves in hydrochloric acid, dilute or conc., rapidly on warming, forming a hyacinth-red solution of UCl, which goes green on shaking in air, and then cortains UCl,—
7. Conc. nitric acta, even when hot, scarcely acts on U that has been fused; the pulyerulent metal is quickly oxidised by hot conc. HNO, Aq to U.O. 8. Several metallic salts in solution are reduced by U, with ppn. of the metals, e.g. HgNO₃, AgNO₃, CuSO₄, SnCl₂, PtCl₃, AuCl₃, Detection and Estimation.—Uranyl salts

UO, SO, &c.) are formed by heating uranates with acids, also by the reactions of acids with UO3, and also by oxidising uranous ralts (salts of UO). K_LreCy_AAq givos a brownish-red pp. with uranyl salts, soluble in HClAq or in (NH₁)₂CO₂Aq; this reaction is said to be extended delicate; H₂O₂Aq and alcohol give a brown pp. (Fairley, C. N. 62, 227); carbonates give yellow pps., soluble in excess, forming yellow liquids; NaOHAq or KOHAq forms yellow pps., NH,ClAq does not interfere with the ppn., but in presence of sugar or tartario acid pps. are not produced. Uranous salts are produced by reducing uranyl salts in solution by Zn and HClAq. After reduction the solutions give green pps. with KOHAq or NaOHAq, the pps. becoming brown and then yellow in the air; with (NH₄)₂SAq green pps. are formed, quickly becoming dark green, and black on boiling; K,FeCy,Aq produces yellow-green pps. becoming red in the air (v. Zimmermann, A. 213, 285).

U is generally estimated as UO_2 or U_3O_8 (v. Zimmermann, A. 232, 209). Solutions may be reduced by Zn and H.SO, Aq, and then titrated with KMnO,Aq, the quantity of O used corresponding with the change of UO₂ to UO₃ (Z., l.c.; v. also Belohoubek, J. pr. 99, 231).

Uranium, arsenates of. A compound, probably UO Ac O. to it leaving the liberty of the compound of the co

bably UO. As.O. 4aq, is described by Rammels-berg (P. 59, 26). Werther (J. pr. 43, 321) describes UO. H. As.O. 3aq, and various doubte salts of this compound with arsenates of Ca, Cu, and Na.

Uranium, bromides of. UBr₄ is formed by heating U₃O₅ mixed with C in Br vapour; and UBr₄ by heating UBr₄ in H. Zimmermann (A. 216, 5) failed to obtain a compound with more Br by heating UBr, with Br to 230° in a sealed

URANIUM TETRABROMDE UBr., (Uranous bromide.) Mol. w. 558. Prepared by strongly heating a mixture of U3Os and sugar, mixing with sugar charcoal that has been heated to redness, placing the mixture in a tube, and heating it first in a stream of thoroughly dried CO2, and then in Br vapour, and allowing to cool in CO. the Er used must be perfectly freed from Cl, HBr, and H₂O by distillation from KBr, MnO₂, and P₂O₅ (Zimmermann, A. 216, 2; Alibegoff, A. 232, 132; cf. Hermann, J. 1861, 260). UBr, forms block furth leafter, velocities track heat forms black, fusible leaflets; volatile at red heat, giving a vapour with V.D. 281 (Z., l.c.); very hygroscopic; dissolves in water, with a hissing sound, forming a green liquid.

By evaporating a solution of UO.xHO in HBrAq, Rammelsborg (P. 59, 12) obtained green crystals of hydrated UBr₄, probably UBr₄,8H₂O.

Uranoxybromides. (Bromoxy-uranates.)
UO₂Br₂-2MBr or M₂UO Br₁. By the reaction of HBrAq with K. O₂ and (NH₂)₂UO₂ respectively, Sendtner (A. 195, 325) cobtained yellowish, 'vgrosopoic tablets of the composition M₂ UO₂Br₂-2H₂O, where M = NH₂ and K.

URANIUM TRIBROMIDE UBr₂. Mol. w. not determined. Obtained by Alibegoff (A. 233, 119; of Zimmermann. A. 216. 5) by passing dry H

cf. Zimmermann, A. 216, 5) by passing dry H over molten UBr. Dark-brown fieedles; easily

volatilised; not changed by continued heating in H; very hygroscopic; warmed in H,S, in complete absence of air, forms U2S3.

Uranium, chlorides of. By heating U in Cl both UCl, and UCl, are produced; and by heating UCl, in H, UCl, is formed.

URANUM PENTAGILLORIDE UCl₃. Mol. w. not determined; formula probably molecular, from analogy of MoCl₃ and WCl₃.

Preparation .- 1. By heating U in excess of Cl. -2. A slow stream of dry Cl is passed over a mixture of charcoal and any oxide of U, or UO.Cl., heated to dull redness in a glass tube; dark-green octahedral crystals of UCl, are formed near the heated part of the tube, and in front of these needle-shaped xystals of UCl, are deposited, mixed with a loose brown powder, which is also UCl₅. If the stream of Cl is rapid, most of the UCl, is produced as a light-brown, mobile powder (Roscoe, C. J. [2] 12, 933).

Properties and Reactions .- UCl, crystallises in long, dark, needle-shaped forms; the crystals are lustrous, and reflect greenish light, in trans-mitted light they are dark ruby red. Both the crystals and the brown powder are very hygroscopic. Dissolves in water, with a hissing sound, forming a yellow-green liquid and giving off HCl. Decomposed to UCl, and Cl when heated, either alone of in CO, of Cl; decomposition begins at 120° in CO2, and is complete at 235'. ing in NH, probably produces a nitride (Roscoc, l.c.; no amalyses given).

Combination. -A compound UCl₃, PCl₃ is described by Cronander (J. 1873, 222) as an amorphous, yellow solid; formed by heating UO₄ with excess of PCl₃ in a sealed tube for a long time.

URANIUM TETRACHLORIDE UCI, (Uranous

chloride.) Mol. w. 380-48.

Preparation. -1. U is heated in Cl. -2. A mixture of charcoal and an oxide of U, or UO Cl. is heated in a slow stream of dry Cl (Péligot, A. 43, 258; cf. Roscoe, C. J. [2] 12, 933). The crystals that form nearest to the heated part of the tube are again heated in a stream of dry CO₂, whereby traces of UCl, are volatilised and removed (Zimmermann, A. 216, 8).—3. A solution of ammonium uranate in HClAq is reduced by Zn, and the solution is evaporated and crystallised. Arendt a. Knop (C. C. 1857, 164) reduced, by boiling the solution for 15 min. with Cu and a little PtCl, Aq; they then filtered, saturated with H.S. filtered, boiled off H.S. and crystallised.

Properties and Reactions. - Dark green, lustrous, regular octahedral crystals; volatilises at red heat, in complete absence of moisture, giving a red vapour (Péligot, l.c.) with V.D. 192 (Zimmermann, l.c.). Very deliquescent; fumes much in air, giving off HCI; dissolves in water, with a hissing sound, forming a green, water, with a missing sould, nothing a green, solution that is unchanged in air; gives green, amorphous UCl, by evaporation in vacuo, but is decomposed by evaporation in the air. When UCl, Aq is drouped into boiling water all the U is ppd. as UO, xH₂O. Solution of UCl, reduces salts of Au and Ag to the metals, and FeCl, to FeCl., &c. By heating in dry H one-fourth of the Cl is remared and UCl, remains (Péligot, A. 43, 286). According to Péligot (Le.), UCl, com-

bines with several metallic chlorides to form double salts.

Uranozychlorides. (Chloroxyuranates.)
UO_CL_2MCl.2āq, or M_UO_Cl_2aq. Salts of
by cl_2mcl.2āq, or M_UO_Cl_2aq. Salts of
by the reaction of large excess of HClAq with
uranates of NH, and K, (Péligot, A, 43, 279).
The K compound is also formed by acting on
UO_Cl, with excess of KClAq, and separating
the KCl that crystallises with the K_UO_Cl, mehanically Bargaline D_L_1@1. The chanically (Berzelius, P. 1, 366). The K compound forms thick plates (for crystalline measurements b. de la Provostaye, A. Ch. [3] 6, 165); easily loss water; gives off HCl at a little above 100°; melts at red heat, giving off Cl, and leaving UO, and KCl. The ammonium compound forms very deliquescent rhombohedra.

URANIUM TRICHLORIDE UCl3. Mol. w. not determined. Obtained by Péligot (t.e.) by heating UCl₄ in day H as long as HCl was given off. Also formed in solution by long-continued reduction of uranyl salls by Zn and HClAq (Zimmerranni, A. 213, 300). A brownish-red solid; dissolves very readily in water, forming a red solution, which gives off 11 and becomes green (v. P., l.c.; Z., l.c.; also A. 216, 12).

Uranium, ferrocyanides of. Various compounds are described by Wyruboff (A. Ch. [5] 8, 444) and Atterberg (Bl. [2] 24, 355) as obtained by ppg. K,FeCy,Aq by solutions of salts of U. The following formule are given:

(2) UzKzFeCya. 6aq;

(1) U_FeCy_a. 10aq; (3) (UO₂)₄K₂(FeCy_a)₂. 6aq; (4) (UO₂)₅K₆(FeCy_a)₄. 12aq.

Uranium, fluorides of. Only mie compound, UF, has been isolated with certainty.

URANIUM TETRAPLUORIDE UF, (Uranous fluoride.) Mol. w. not determined; formula probably molecular, from analogy of UBr, and UCI, Prepared by adding HFAq to U,O,, boiling, pouring off the yellow solution (which contains UO,F,), washing the green powder that remains, first on a filter and then by decantation, until free from HFAq, and drying at 100° (Smithells, C. J. 43, 125; cf. Bolton, Z. [2] 2, 353). The process of washing is very tedious, and occupies many days. UF, is a green powder; insol. in water and dilute acids; slowly dissolved by cone. acids; boiling NaOHAq produces UO. Heated in a Pt crucible with the lid on, a small quantity of a white, bulky sublimate is obtained; this sublimate is UO.F. (Smithells, l.c.); the residue in the crucible is chiefly UO. Heated on Pt foil, UF, leaves

chieffy U.O., Heated on Pt foil, U.F. leaves

U.O. (S., l.c.).

Double salts.—Bolton (l.c.) obtained the
compands U.F. K.F and U.F. NaF—as green
powders, insoluble in water and dilute acids, giving UO., KF (or Nal), and HF when heated ground out, he for reary, and his waen heated to redness, in closed vessels—by the action of formic or oxalic, acid on UO.F., SKF or UO.F., NaF (v. infra) in sunlight. These combounds may be called uranoflucyides, and written KHE and M. ME

KUF, and NaUF,

Uranium hexafuoride UF, was said by Ditte (C. R: 91, 115) to be formed by heating U,O, with HFAq, evaporating the yellow liquid, and heating the crystals of UF, 8HF thus obtained; but Smithells (C. J. 43, 125) has shown that the substance obtained by avacation 1. that the substance obtained by evaporating the

solution formed by heating U.O. with HFAq is

UO.F. (v. Uranum extriuoride, p. 828).
Uranoxyfluorides. (Fluoxy-uranates.)
These compounds may be regarded either as double, salts of UO,F, with alkali fluorides, or as salts derived from hypothetical ticids H, UO,F, The compounds are formed by adding alkali fluorides to solutions of uranous nitrate, and crystallising under different conditions (v. Bolton, Z. [2] 2, 353; Baker, C. J. 35, 763). The compounds that have been isolated belong to compounds that have been isolated belong to several series: (1) MF.UO.F., xaq = MUO.F., xaq, where M = Na ard x = 2 and 4 (Bolton); (2) 3MF.UO.F., = M, UO.F., where M = NH. and K (Bolton; Baker); (3) 3KF.2UO.F., 2aq — K, U.O.F., 2aq (Baker); (4) 5KF.2UO.F., 2aq (Bolton). Two other series were described by Ditte (C. * R. 91, 166), 4MF.UO.F., and 4MF.UO.F., xaq; but the experiments of Smithells (C. * J. 43*, 131) have shown that these compounds do not exist. compounds do not exist.

Uranium, haloid compounds of. U combines directly with Br and Cl, but not with I'; no iodide, indeed, has been isolated. The haloid sompounds of U belong to the form UX₃, where X = Br or Cl; UX_1 , where X = Br, Cl or F; and UX_2 , where X = Cl. The compounds UBr_1 and UCI, have been gasified, and the formule are molecular. From the analogy of WCI, and MoCI, the formula UCI, is probably molecular; this compound decomposes to UCl, and Cl when heated, either alone or in CO, or Cl. From the analogy of CrCl, it may be supposed that UCl, and UBr₃ are molecular formule. No haloid compounds of U have been isolated corresponding with the chlorides of Cr, Mo, and W, MrCl2. No haloid compounds of U are known containing each more than one halogen. Various oxyhaloid compounds, chiefly UO X, and compounds of these with alkali haloids, are known. , Uranium, hydroxides of, v. Uranium, oxides and hydrated oxides of (infra); also Uranium

OXYACIDS, AND SALTS OF (p. 826).

Uranium, iodides of. No compound of U and I has been isolated. Hermann (J. 1861. 260) and Sendter (Verbind. des Uraniums, Erlangen, 1877) failed to obtain an iodide by heating a mixture of UO, and C in I vapour or

in HI.

Uranium, nitride of, U₁N₁. A greyish-blao'-powder; obtained by heating UCl₄ in NH₃, then mixing with NII,Cl and heating for a long time in a stream of NII, (Uhrlaub, Verbind. einiger Metalle mit Stickstoff, Göttingen, 1853). Roscoe (C. J. [2] 12, 933) states that a nitride is formed by heating UCl, in NH, but no analyses are

Uranium, oxides and hydrated oxides of. When U is burnt in air the product is U.C.; when U is burne in air ine product is y_0 , by heating this oxide with reducers, or for a long time in a stream of N or CO_2 , UO_2 is formed; UO_4 is produced by fusing U_2O_4 with $KCIO_3$, also by heating $UC_1(NO_3)_2$; by adding H_2O_2Aq to $UO_4(NC_4)_2$, Aq a hydrate of $UO_4(NC_4)_3$, Aq or $UO_4(NO_3)_2Aq$ a hydrate of UO_4 is obtained. Besides these four oxides, others, intermediate between UO, and UO, perhaps exist. No definite hydrate of UO, har been isolated; the pp. formed by adding NH,Aq to UCl,Aq, or to solution of a uranous salt (U(SO), &a.), is either a hydrate, or a

mixture of hydrates, of UO₂. A hexahydrate of U₂O₂ probably exists. Uranic acid is the monohydrate of UO₂. UO₂ dissolves in some acids to form corresponding salts; U.O. is said to react with conc. H.SO, or HClAq to form both uranous salts UX₂, and uranyl sales UO₂X, where X = a divalent acidic radicle. UO₂ interacts with several acids to form uranyl salts UOIXII; UO, also reacts as an acidic oxide with strong bases, forming uranates, di-uranates, &c., M¹₂UO₄, M¹₂U₂O₇, &c.

According to Guyard (Bl. [2] 1, 89), two oxides having the compositions UO and U₂O₂ exist; but the more accurate investigations of Zimmermann (A. 213, 301) showed that the substances examined by Guyard were not definite compounds. Péligot described a black oxide U2O3; Zimmermann (A. 232, 273) has shown that the substance is a mixture, in variable proportions, of UO. and U,O,.

URANIUM DIOXIDE UO. (Uranous oxide.)
Mol. w. not known. This oxide was supposed to be the element U until 1840, when Péligot proved the presence of O in the substance

(A. Ch. [3] 5, 5).

Formation.—1. By heating U₃O₈ with such reducing agents as H (Arivedson, P. 1, 245), NH Cl and S (Hermann, J. 1861, 258), a little C (Buchholz, Gehlön's Ann. 4, 17, 134), oxalic acid (Wertheim, J. pr. 29, 211), &c. -2. By heating U.O. for a long time in a stream of N

or CO₂ (Zimmermann, A. 232, 283).—3. By strongly heating UO₂.C₂O₄ in absence of air (Berzelius, P. 1, 359), or in a stream of H (Péligot, A. Ch. [3] 5, 5; Ebelmen, A. Ch. [3] 5, 189).

Preparation.—A mixture of UO.Cl. and

excess of NaCl and NH₄Cl is strongly heated in absence of air; and the product is washed thoroughly with water, and dried (Wöhler, A. 41, 345; cf. Hillebrand, Zeit. f. anorg. Chemie, 3, 243). If air is not excluded during heating, 3, 213). If air is not excluded during heating, some UO, is obtained (H., l.c.). This process gives UO, as a black crystalline powder. In place of using UO₂Cl₂, a solution of ammonium uranate in HClAq may be mixed with excess of NaCl and NH,Cl, and evaporated to dryness, and the residue heated. By fusing any oxide of U with borax for 24 hours, and washing with water and then with dilute acetic acid, or dilute HClAq, Hillebrand (c.c. p. 249) obtained jet-black octahedra of UO, isomorphous with ThO,

Properties .- Prepared by heating Proper tes.—Frepared by neating UO₂(2.0, UO₂) is a dark-brown, pyrophoric powder; if the temperature has been kept high the oxide is lustrous, reddish-black, and not pyrophbrio; prepared by heating UO₂Cl₂ with NaCl and NH₂Cl, UO₂ forms black, non-pyrophoric, octahedral crystals. Púligot gave S.G. 10.15 - according to Hillehrand (I.c.) has fix is 10.15; according to Hillebrand (l.c.), the S.G. is norly 11. UO, is insoluble in water, Hellaq, and dilute H.SO,Aq; it dissolves in HNO,Aq, and in conc. H.SO, in presence of a little water. UO, is oxidised to U.O. by heating in air.

Reactions.—I. Heated in air or oxygen

U.O. is produced; UO, burns brilliantly in the O. H. findine (Clarke, C. A. 62, 853).—2. Heating in chlorine produces UO₂Ol₂; when mixed with carbon and heated in chlorine, UCl₂ and UCl₄ are formed. UBr₄ is produced by heating UO₂ mixed with carbon in bromine vagour.—3. U₂O₂ is formed by heating UO₂ in voater vagour [Regnault, A. Ch. [2] 62, 358).—4. Heating in vapour of carbon disulphide produces $U_{c_0}S_{c_1}$ (Hermann, J. 1861. 258; H. Rose, G. A. 73, 139). UO_a is said to be unchanged by heating in hydrogen sulphide (Arfvedson, P. 1, 245).—5. A solution of UO_a in cone. sulphuric acid gives green crystals of $U(SO_a)_a$ on evaporation.

HYDRATES OF URANSUM DIONIDE. No definite hydrate of UO, has been isolated; NH, Aq produces a reddish-brown pp. when added to UC!Aq or solution of a uranous salt, this pp. becomes black on boiling; when washed with air-free water and dried in vacavo it forms black, coherent lumps. A black pp. is also produced by dropping UC!, Aq into boiling water. These black pps. contain UO,; they are probably hydrates of this oxide. The name vacaous hydroxide is often given to the pp. obtained by either of the processes described; the pp. dissolves in dilute H₂SO₄Aq, HNO₂Aq, and HClAq.

URANOSO-URANIC OXIDE U₃O₃. (Olive-green oxide of uranium. Uranyl uranate UO₂.2UO₃.) Mol. w. not known.

Occurrence.—In combination with SiO₂, and oxides of Sb, As, Ca, Cu, Fe, Mg, &c., in pitch-blende.

Preparation. — U, or a decomposable U compound, e.g. UO₂(NO₃)₂, is heated in the air and then in a stream of O, and s allowed to cool in O (v. Zinnnetmann, A. 232, 283). For a method of preparing U₂O₈ from pitchblends v. URANIUM, Preparation of (p. 821).

Properties.—A dark olive-green powder, sometimes almost black, but always showing a green streak when rubbed on unglazed porcelaif (Z. Lc.). S.G. 7-2 (Karsten, S. 65, 394); 7-31 (Ebelmen, J. pr. 27, 385). S.H. 07979 (Donath, B. 12, 742). Insoluble in water; slightly soluble in dilute HCIAq or H_SO_Aq; soluble in HNO_Aq, also in H_SO, with a little water.

Reactions.—1. Gives off O when heated in air or in an indifferent gas; the final product of heating in N or CO_is UO_2 (Zimmermann, A. 232, 283).—2. Reduced to UO_by heating with hydrogen, carbon, sulphur, potassium, or sodium.
3. Heated in vapour of curbon disulphide U_3O_8, is formed.—4. Heated with conc. sulphuric acid, or with hydrochloric acid to 180?—200°, gives both uranous and uranyl sulphates, or chlorides; reacting as UO_2UO_3 (Z., A. 232, 287).—5. Silver nitrate solution is slowly reduced to Ag (Isambert, C. R. 80, 1087).

HYDRATE OF URANOS-URANIC OXIDE. By adding NH₂Aq to UCl₂Aq and allowing the pp. to oxidise in the air, and drying in vacuo over H₂SO, Rammelsberg (P. 55, 319) obtained a greenish-black solid which may have been a hydrate of U₂O₃; one determination of water only is given which agrees fairly with U₂O₄.62q.

URANIUM TRIONIDE UO₂. (Uranic arible. Uranic anhydride. Uranyl oxide (UO₂)(O.) Mol. w. not known. This oxide is obtained by carefully heating the hydrate UO₂H₂(O. infra) to 800° (Ebelmen, A.Ch. [2] 5, 199); to 250°, temperature being gradually raised (Jacquoline Ph. C. 1845, 183). The oxide is also formed by heating UO₂OO₂2(NH₂)₂CO₃ to 800° (E., Lc.). The preparation of UO₂ may be conducted by heating UO₂(NO₂)₂ in a Pt basic until decomposition begins, then transferring to glass tubes

and heating these in an oil-bath to 250° so long as acid fumes are given off.

UO_I is a chamois-yellow powder. S.G. 5.02 to 5.26 (Brauner a. Watts, P. M. [5] 11, 60). Ebelmen (L.c.) described UO₂ obtained by heating UO₂ CO₂ 2(NH₁) CO₃ as a sealingwax-red powder. When UO₃ is heated to redness it gives off O and U₂O₃ remains (E., L.c.; cf. Read, C. J. 65, 313 (1894)); the oxide seems to be somewhat volatile at the temperature of a porcelain oven (Elsner, J. 1866, 35).

UO, reacts with many acids as a basic oxide, but the salts formed are always basic salts of the forms UX, 2UO, where X = the radicle of a monobasic acid, and UX, 2UO, where X = the radicle of a dibt3ic acid. It is customary to write the formule of these basic salts as UO, Xi, and UO, Xi, and to call them urany! salts

 $(UO_2 = uranyl)$; thus $U(NO_3)_a \cdot 2UO_2 = UO_2(NO_3)_a$,

and U(SO,), 2UO, = UO (SO,).

WO, behaves towards strong bases as an acidic oxide, forming uranates M₂UO, and diuranates M₂UO, &c.; these salts are generally formed by fusing U compounds with bases and O, and by ppg. uranyl salt solutions by strong bases. When KOHAQ, NaOHAQ, NII₃AQ, BaOAQ, or CaOAq is added to a solution of markingly salt, e.g. to UO₂(NO₃)₂Aq, the pp. consists of a uranate of the metal of the base. Alkali carbonates ppt. alkali uranates, but the pps. contain also CO₂; the pps. dissolve in excess of the alkali carbonates forming double carbonates of uranyl and the allisti metal, e.g. UO₂CO₂(NII₁),CO₂. Addition of alkali or alkali carbonate to solutions of uranyl salts containing other metallic salts causes ppn. of a uranate of the metal of the salt present, generally mixed with alkali uranate (cf. Uranium, oxyacids, and salts thereof, p. 826).

By adding KOIIÂq to a cold solution of TCI, or UO₂(NO₃), and dialysing, Graham (T. 1861. 213) obtained a solution, free from acid and alkali, which he regarded as a loose compound of sugar and UO₃, and which he called sucrate of peroxide of uranium.

Hydrates of Uranium Trioxides. Pure hydrates of UO, are not obtained by progurany salt solutions by alkalis (v. supra); but according to Ebelmen (A. Ch. [3] 5, 199) UO, xH_O is produced by boiling an aqueous solution of UO, CO, 2(NH), CO, until a yellow pp. is formed, and allowing this pp. to stand for a long time. By the continued action of sunlight on UO, (CO,) in presence of water, UO, xH_O is said to be formed; after washing and drying in the air, the solid basethe composition UO, 2H_O; and after dwying in vacuo the composition is UO, H_O (E., Ic.). Berzelius (B. J. 24, 118) obtained UO, H_O by heating UO (NO,) on a sand-bath until acid fumes ceased to be given off, washing sile residue with boiling water, and drying in air. The same hydrate is said to be formed by heating U,O, with KClO, until fusion begins, boiling out with water, and drying in air (Dreaksmann, J. 1861, 256). The best method of preparing UO, H,O seems to be that given by Malsgut (A. Ch. [3] 9, 463), viz. boiling a solution of UO₂(NO₂), in absolute alcohol as long as

reaction proceeds, washing the yellow solid that | separates with water, and drying in air or in vacuo; EtNO₂, N₂O₃, C₂H₄O, and H.CO₂H are

formed in the reaction.

UO.H.O is described as a yellow powder; S.G. 5.93 at 15° (Malaguti, l.c.); needens litmus paper; when hot it absorbs CO₂ from the air; heated to 250°-800° water is given off and UO₄ remains (Ebelmen, l.c.; Jacquelin, A. Ch. [3]5, 199); heated to redness gives off O and leaves U.O. UO.H.O is generally called uranic acid; U. URANIUM OXYACIPS, AND SALTS THEREOF (infra).
URANIUM PEROXEE. By adding UO. (NO.)...Aq

to a mixture of H.O.Aq and Q. large excess of H.SO.Aq, and allowing to stand for a considerable time, Fairley (C. J. 31, 13. [1877]) obtained a small quantity of a heavy, crystalline, almost white pp., which when dried (? in air, or at dilute H₂O₂Aq to solution of UO₂(NO₃)₂ or UO₂(C₂H₂O₂)₂, free from acids, Fairley (l.c. p. 127) obtained a yellowish-white pp., which when dried by pressure between filter paper had the composition UO,4HLO, and when dried at 200° the composition UO,2HLO.

Zimmermann (A. 232, 273 [1886]) failed to obtain the tetrahydrate UO, 4H₂O; according to him the dihydrate UO, 2H₂O is very hygroscopic, and begins to decompose at 115°. Alibegoff also obtained only UO, 2II,O; he failed to prepare the anhydrous oxide UO₄ (A. 233, 123 [1886]).

Hydrated uranium peroxide, dried at 100°, is a yellowish-white powder; decomposed by heat, giving off O and leaving much $U_3\tilde{O}_8$; reacts with alkal solutions to give UO, xII,O, and a solution from which alkali peruranate 2M2O.UO. 8aq, crystallises (Fairly, Lc.; v. Peruranates under URANIUM OYYACIDS, AND SALTS

тивнеог, р. 827).

Uranium oxyacids, and salts thereof. UO, H2O = H2UO, reacts with strong baser as an acid, forming uranates M'2UO; di-uranates M'2UO, are also known, and a few tri- and hexa-uranates. A few peruranates are derived from hydrated uranium peroxide UO,xH,O.

The compounds of UO,X, with MX (X=Br, Cl, or F) may be regarded as bromoxy-, chloroxy-, and fluoxy-uranates. The substance known as uranium red is perhaps UO..ONH .SNH, i.e. the ammonium salt of an oxythic uranic acid.

(v. Uranium oresulphides, p. 828).

Uranic acid H₂UO₄. This compound is obtained as a yellow powder, which reddens litmus paper, and is decomposed to UO₃ and H₂O at 250°-300°, and to U₃O₆ and O at a higher temperature, by boiling a solution of UO (NO₃), in absolute alcohol, washing the solid that separates with water, and drying in air or in cacuo. (For other methods of preparation, and mose details v. Hydrates of uranium trioxide, p. 825.) The salts of H₂UO₄, are prepared indi-

URANATES, DY. URANATES, &c. Salts derived from H. 100,; salts derived from the hypothetical actus H. 120, H. 120, H. 120, H. 20, are also

known.

URANATES. Salts of the composition M. UO, and M. UO. These salts are propared by ppg. solutions of uranyl salts by bases in solution, or by adding alkali solution to a mir-

ture of a uranyl salt and a metallic oxide in solution; also, in many cases, by oxidising, U,O, or UO, in presence of a base or a salt of a base. The uranates are insoluble in water, and are not readily decomposed by heat except the ammonium salt. Carson a. Norton (Am. 10, 219) have pointed out that analyses of uranates always show considerable differences between the percentages of U found and calculated; they hate found the same anomaly in analyses of uranates of ammonium and several ammonium

derivatives, such as NEtH₃, NEt₂H₂, &c.
Ammonium uranates. The pure salt does not • seem to have been isolated. An impure uranate containing c. 90 p.c. UO₃ ((NH₁)₂ŪO₄ requires 84:66 p.c. UO₃) is obtained by adding NH₃Aq to a solution of a urangel salt (Péligot); it is a yellow powder, which loses H₂O and NH₂ above 100°, very slightly soluble in water, and insol. NH, Aq (Arfvedson, P. 1, 245). An impure salt is also obtained by adding NH, ClAqor (NH,) SO, Aq to boiling Na, UO, Aq, as long as NH, and CO, are given off, washing the pp., and drying at a low temperature (Anthon, D. P. J. 156, 211). Heated to reduces gives U₃O₄; many of the compounds of U are prepared from ammonium uranate.

Potassium uranate K₂UO₄. Prepared by heating 6 g. U₃O₉ with HClAq and HNO₃Aq, adding 4 g. KCl and 16 g. NH₃Cl, evaporating to dryness, heating very strongly until the fused mass is orange-yellow, and washing with water (Zimmermann, A. 213, 290). The salt is said to be formed also by strongly heating UO, HPO. (obtained by ppg. a uranyl salt by a phosphate) with K.SO, (Grandeau, A. Ch. [6] 8, 223), Orange-yellow, rhombic tablets; insol. water, cold or hot; easily sol. acids (Zimmermann,

Lc.).
Sodium uranate Na.UO₄. Prepared by fusing U₃O₃ with NaCl and Na.CO₃, or with NaCl with gradual addition of NaClO₅, and washing the state of with water; resembles K2UO, (Zimmermann,

Lithium uranate LizUO, has been prepared similarly to K.UO,; it is said to be decomposed by liot water (Z., l.c.). Uranates of Bs, Ca, and Sr-MUO₄- are said by Ditte (C. R. 95, 988) to be formed by heating the chlorides of these metals with U,O,.

DI-URANATES. Salts of the composition

M. U.O. and M. U.O. The formula may also be written M. U.O. and M. U.O., and M. U.O., if the formula by Barium di-uranate Baul.O., Formed by ppg. UO. (C.H.O.). Aq by BaOAq (Berzelius, P. 1, 359); also by heating to redness UO. Ba(C.H.O.). (Wertheim, J. pr. 29, 207). A yellowish-red

Calcium di-uranate CaU₂O₂. Formed, eac-cording to Ditte (C. R. 95, 988), by strongly heating U₃O₈ with Ca(ClO₃)₂; a yellowish-green solid.

Copper di-uranate CuU2O2. This salt is said to be formed, as a green crystalline powder,

said to be formed, as a green crystaline powder, by fusing Cu(UO_PO₁), saq_with Na_CO₂, and vashing with water (Debray, A. Ch. [3] 61, 451).

'Lead di-uranate PbU_O. Cormed by diegesting UO_(O_H_O), Aq with freshly ppd. PbCO₂ (Wertheim, J. pr. 29, 207); also by adding NH_Aq to a mixture of UO_(NO₂), Aq and Pb(NO₂), Aq (Arfvedson, P. 1, 258). A yellowish-

red powder, becoming green when heated; strongly heated in H, gives a pyrophoric mixture

of Pb and UO.

Potassium di-uranate K,U;O,. Formed by melting together UO, and K,CO, and washing with water; also by strongly heating UO₂.K₂(CO₃)₂ or UO₂.K(C,H₂O₂)₃ (Berzelius, P. 1, 359). A yellowish-red powder.

Silver di-uranate Ag₂U₂O₂. Obtained by

adding amorphous K, UO4 to molten AgNO3, and washing with ice-cold water (Alibegoff, A. 232, 129; 233, 117, 143). Also by strongly heating UO₂-Ag(C₂H₁O₂), (Wertheim, *J. pr.*, 29, 221; cf. Rammelsberg, *P.* 59, 10). An amorphous, yellowred solid; easily sol. acids; decomposed by hot

water (Alibegoff, l.c.).

water (Alloegoit, i.e.).
Sodium di-uranate Na. J.O., Gaq. Obtained
by ppg. uranyl salts by NaOlIAq (Patera, J. pr.
51, 125; cf. Stolba, Fr. 3, 74). Loses water of
crystallisation over H.SO. A light-yellow to
darkish-yellow powder. Known commercially darkish-yellow powder. Known commercially as uranium yellow (v. Dictionary of Applied CHEMISTRY, vol. iii. p. 893).

Di-uranate of strontium SrU₂O₇ is said also to exist (Ditte, C. R. 95, 988).

TRI-URANATES. The only salt that has

been isolated is sodium tri-uranate Na₂U₃O₁₀; it is prepared by fusing UO.(SO₄) with NaCl, and boiling out with water. This salt forms yellow leaflets resembling mosaic gold; S.G. 6:912; hygroscopic; insol. water, sol. acids (Drenkmann, J. 1861, 255).

HEXA-URANATES. The potassium salt, U₀O₁₉ 6aq, is described as a yellow micro-K2U6O19

water at 300°-400°; prepared by melting $UO_2(SO_4)$ with KCl (Drenkmann, J. 1861, 255). PER-URANATES. By adding excess of alkali and H₂O₂Aq to solutions of uranyl salts, Fairley (C. J. 31, 134) obtained salts which may beformulated as MI4UO,. xaq and MI2RIIUO,. xaq

where $M = NH_1$, K, or Na, and $R = UO_2$

Ammonium uranyl peruranate (NH₄)₂(UO₂)UO₃, Saq. The formula may also be written (NH₄)₂O₄U₂O₅, Saq, or

(NH1)20.UO2.UO4. 8aq, or, regarding the compound as a double peroxide of U and NII, as 2UO, (NH4).O. Saq. The salt is prepared by 2UO, (NH.).O.8aq. The salt is prepared by adding excess of NH3Aq and H2O2Aq to a solution of a uranyl salt and ppg. by alcohol; it is an orange-yellow solid, readily soluble in water. The quantity of KMnO, in solution decolourised shows that the ratio of U to 'peroxide oxygen' in the salt is U.30.

Potassium per-uranate K, UO, 10aq. salt may also be looked on as a double peroxide of U and K (UO, K.O., 10aq), or as K.O. UO., 10aq, It is prepared by adding alcohol to a solution obtained by treating UO₂(NO₂), Aq with KOHAq and excess of H₂O₂Aq, and rapidly drying the orange-yellow pp. by pressure in filter paper. The salt rapidly absorbs CO₂ from the air and lease O₂ it is regilled decompand by host silicated. loses O; it is easily decomposed by heat, giving

loses U; it is easily decomposed by hear, givingoff H₁O and O. Experiments showed that the
ratio of U to 'peroxide oxygen' is U:3O.
Sedium perurahate Na₁UO₁, 8a₂ The
formula may also be written U₁O₁, Na₂O₂, 8a₃ or
Na₁O₂O₃ O₄ The salt u O₂, Na₃O₄, 8a₃ or 2Na,O.UO, 8aq. The salt is prepared by dissolving 'ordinary uranic hydrate,' or UO, xaq, in excess of NaOHAq along with excess of H₂O₂Aq, allowing to crystallise if conc. solutions

are used, or ppg. by a little alcohol if dilute solutions are used, and drying by pressure in filter paper. Poleck (B. 27, 1051 [1894]) obtained this salt by adding sodium superoxide to solution of a salt of U. The salt is golden-yellow and lustrous; its lowly absorbs CO, from the air, and gives off O. When heated, alone or in CO, it gives off 30; it also loses 30 in contact with acidified Kyno, Aq or other unstable O compounds. The ratio of U to 'peroxide oxygen' is U:30 as measured by the quantity of KMnO. decolourised by a solution of the salt.

Sodium-uranyl per-uran to Na.(UO.)UO. 614. The formula may also be written Na.O.U.U., 6aq or Na.O.UO.,UO. 6aq; or, regarding the compound as a double peroxide of U and Na, as 2UO, Na,O., 6aq. The salt is prepared similarly to Na, UO, Saq, but using only the minimum quantity of NaOllAq required for solution, and adding alcohol, when it separates as a red oil which slowly rystallises to a red solid. The quantity of KMnO, in solution decolourised by a solution of the salt showed that the atio of U to 'peroxide oxygen' is U:30.

Uranium, oxybromide of, UO_Br. (Uranyl bromide.) In preparing UBr, by heating a mixture of U₃O₃ and C in Br vapour, Hermann (J. 1861, 260) obtained a yellow, easily volatile sublimate, which was probably an oxybromide. By heating UO, with Br and water, also by dissolving UO, in HBrAq, a colourless liquid is obtained, which on evaporation gives yellow needles of the hydrated oxybromide UO,Br., 7aq (Sendtner, A. 195, 325). This compound combines with NII, Br and KBr to form UO, Br, 2MBr

(c. Uganoxygromides, p. 822). Uranium, oxychloride of, UO.Cl., (Uranyl chloride.) Formed by strongly heating UO, in Cl; a yellow, crystalline solid, easily fused, but volatilised only at a high temperature; heated with K forms UO and KCl (Péligot A. Ch. [3] 5, 5). By dissolving UO, H.O in HClAq, also by oxidising UCl, by HNO,Aq, and evaporature, yellowish-green crystals of UO.Cl. xII O are obtained (Klaproth, Crell's A. 1789 [2]. 387).

By dissolving UO2Cl2 in other and evaporating, Regelsberger (A. 227, 119) obtained yellow needles of the compound UO₂Cl₂2Et₂O.

UO, Cl. forms compounds with NH, Cl and KCl of the form 2MCl.UO2Cl, (v. URANOXXCHLORIDES,

UO₂Cl₂ combines with MH, to form UO₂Cl₂xNII₃, where x = 2, 3, and 4. The first of these compounds, UO₂Cl₂NII₃ is formed by passing dry NH₃ into UO₂Cl₂ dissolved in ether, adrying the voluminous yellow pp. that forms, and then placing it in vacuo over H.SO, until and then placing if in vacuo over H.SO, until all other is removed; the second compound, UO₂Cb₂3NH₃, is formed by the action of NH₃ on UO₂Cl₂2NH₄; and a mixture of UO₂Cl₂3NH₃ and UO₂Cl₂4NH₄ is produced by passing NH₃ over solid UO₂Cl₂. When strongly heated in air these compounds give off all NH₄ and Cl and deave U₂O₂; heated out of contact with air they give UO₂ (Regelsberger, A. 227, 119). The three compounds are called by R. uranylaminonium and their formulæ are written

""" uO₂(NH₂Cl)(NH₂NH₂Cl), and

""" water reacts thus: chlorides, and their formul UO,(NH,Cl), UO,(NH,Cl)(NE UO,(NH,NH,Cl), Water (1), 3UO,(NH,Cl), + 3H,O = (NH,), U,O, + UO,Cl, + 4NH,Cl;

(2) UO₂(NH₂Cl)₂ + 2H₂O = UO₂(OH)₂ + 2NH₄Cl; the second reaction takes place quickly with

warm water.

Uranium, oxyfiuoride of, UO₂F₂. fluoride.) This compound is produced by boiling U₂U₃ with HFAq, filtering off UF₄ (v. URANIUM TETRAFLUORIDE, p. 823), and evaporating the filtrate; it is also formed, in small quantities, by heating UF, in a closed Pt crucible. The compound differs according to the method of preparation (Smithells, C. J. 43, 125).

a-Oxyftuoride. About 1 gram UF, is heated in a Pt crucible with the lid on, temperature being raised as quickly as possible; after five minutes the crucible is allowed to cool, the light, bulky sublimate is removed, And the crucible is again heated for five minutes, and these processes are repeated several times (S., l.c. p. 129). This form of UO₂F₂ is a very bulky, light, white, crystalline solid; it is very soluble in water,

forming a yellow diquid; heated in air it is gradually changed to U₂O₄.

\$-Oxylluoride. U₂O₄ is the ated with boiling HFAq in a leaden vessel, the yellow solution is poured off from green UF₄, heated until the excess of HF is driven off, and allowed to evaporate; evaporation may be completed over H₂SO₄ and CaO in vacuo; the residue is dried at 100° (S., l.c. p. 130). This form of UO,F, is we fellow saponaccous mass; in one instance the preparation had a semi-crystalline appearance, forming yellow, lustrous scales; it is very soluble in water or alcohol; heated on Pt foil U,O, is formed; heated in a closed crucible probably forms a compound with HF; by evaporating a solution of U₃O₈ in HEAq over H₂SO₂ and CaO until the weight was constant, Smithells (l.c. p. 131) obtained a substance which gave results on analyses agreeing fairly with the formula UO₂F₂.HF.H₂O.

A solution in water of either form of UO,F, mixed with KFAq and KHF Aq, and evaporated, gives the quadratic fluoxy-uranate K₂UO₂F₃ (S., l.o. p. 130-1). For the compounds of UO₂F₂ with MF v. Uranoxy-Luorides (p. 824).

Ditte (C. R. 91, 115) gave the formula UOF₄ to the abbligate abblight of the second of the compounds of UOF₄.

to the sublimate obtained by heating, in a closed Pt crucible, the solid that remained when U2O, was treated with boiling HFAq. Ditte said that this solid was UO_F₂; Smithells (l.c.) has, how, ever, shown that the solid obtained by the method used by Ditte is UF₄, and that the sublimate formed by heating this is a-UO₂F₂.

Uranium, oxysulphides of. Two compounds

probably exist.

probably exist.

URANIUM OXYSULPHIDE U₄O₂S₄. This composition was given by Hermann (J. 1861, 258) to a dark, greyish-black solid, obtained by heating UO₂, U₄O₄, or NH₄, uranstego redness in vapour of CS₄. Dissolves in conc. HClAq; burnp when heated in air (cf. M. Rose, G. A. 73, 139).

URANYL SULPHIDE (UO₂)S. A brown solid, the land the pure a proposition of sultiments.

obtained by ppg an ammoniacal solution of a uranyl salt by cold (NH₄)₂SAq, and quickly washing with cone, alcohol. Probably not obtained ours, as it quickly denomposes; water produces UO.xH.O; at 40°-50° it is changed to UO. and B (Remelé, P. 124, 114; Zimmermann, A. 204, 204). (UO.)S is somewhat sol. water or dilute alcohol; dissolved by conc. HClAq, giving UCl.

and S; dissolved by (NH₄)₂SAq, only in presence of (NH₄)₂CO₂Aq (Zimmermann, l.c.), forming a brown liquid.

Uranium black. By allowing (UO,)S to stand in contact with freshly prepared (NH₄)₂SAq, in absence of air, a dull black amorphous powder is obtained. This solid dissolves in mineral as obtained. This sound dissolves in inherat acids, giving off traces o'H₂S; it dissolves partly in warm (NH₄)₂CO₂Aq, but not in warm (NH₄)₂SAq, nor in caustic alkali solutions; heated in a tube to c. 270° it gives off a very little NH, and H₂O. Zimmermann (A. 204, 204) gives the formula U,O₁₀ to uranium black, neglecting (as impurities) the traces of NH, and S which the substance contains.

. Uranium red. By allowing (UO2)S to stand for 24-48 hours in contact with cold (NH1)2SAq, exposed to air, a deep-red solid is obtained; soluble in dilute mineral acids, with separation of S and evolution of H₂S; gives off NH₃, S, and H₂O when heated to 150° and, at above 200°, leaves U3O, (Zimmermann, L.c.). According to Z., the formation of this red substance takes place only when (NH),2,30, is present in the (NH),2,30 used; (NH),2,30 is formed by the action of the air. Z. gives to Z. gives to uranium red the composition $U_sS(NH_s)_2O_s=UO_xONH_sSNH_s2U_2O_s$ (cf. Patera, J. pr. 51, 122; Remelé, P. 124, 158; Hermann, J. 1861.

Uranium, salts of. Two classes of salts are formed by treating oxides of U with acids; UO₂ forms corresponding salts, UX₂ when X = the radicle of a dibasic acid, and UX₄ when X = the radicle of a monobasic acid; UO₂ forms salts (UO2)X when X = the radicle of a dibasic acid. and (UO₂)X₂ when X = the radicle of a mono-basic acid. The salts UX₁ and UX₁₂ are called uranous salts; and (UO₂)X₁₂ and (UO₂)X¹¹ are called uranyl salts. (For reactions of the two classes of salts v. URANIUM, Detection and estimation of, p. 822.) Besides the normal salts, a large number of basic salts of both classes is known, and also many double salts.

The chief uranous salts are arsenates, phosphates, and sulphites. The chief uranyl salts are arsenates, bromate, double carbonates, chromates, hypophosphite, iodate, nitrates, oxalate, phosphates, phosphite, selenates, selenites, sulphates, and sulphates (v. Nitrates, Sul-PHATES, &c.).

Ursnium, sulphides of. When U is burnt in vapour of S, the disulphide US, is formed; by passing H.S over heated UBr, the sesquisulphide U₂S₃ is produced; and by heating U₂S₃ in H the monosulphide US is obtained. The

mol. w. of none of these is known.

URANIUM DISULPHIDE US₂. Prepared by heating U in vapour of S (Péligot, P. 54, \$22; c), Zimmermann, A. 216, 18); also by heating UCL 40 reduces in H₂S (Hermann, J. 1861. 258). A dark greyish-black powder; becomes crystal-line when fused with borax; oxidises slowly in air, rapidly on heating. Easily soluble in conc. HClAq (Hermann, l.c.).

HULAQ (Hermann, Lc.). Or Unawum sesquisulphine U₃S₃. A stream of dry H₃S, perfectly free from air is passed over heated UBr, as long as HBr is given off. Grey-black all at the stream of the st black solid, forming pseudomorphs of UBra; decomposes in air, giving off HaSt burns when heated in air; scarcely acted an by HClAq or

dilute HNO, Aq; decomposed violently by conc. HNO, (Alibegoff, A. 283, 117).

UBANIUM MONOSULPHIDE US. A black, amorphous powder; obtained by passing dry H over bhous power, obtained by passing dry 11 over U_1S_1 , kept at a red heat, for c. 40 hours, until H_1S is no longer given off. Similar in properties to U_4S_1 (Mibegoff, A. 233, 135).

Uranium thio-acids, salts of. No thio-acid, nor salt of a thio-acid, of U has been definitely isolated. Uranium red (v. supra, p. 828) may perhaps be an ammonium oxythionate of

M. M. P. M. URANOXYBROMIDES v. p. 822, under UBANIUM TETRABROMIDE.

URANOXYCHLORIDES v. p. 823, under URANIUM TETRACHLORIDE.

URANOXYFLUORIDES v. p. 824, under

URANIUM TETRAFLUORIDE.

URANYL COMPOUNDS, compounds of the radicle UO₂; v. Uranyl ammonium chlorides (p. 827), Uranyl bromide (p. 827), Uranyl chloride (p. 827), Uranyl fluoride (p. 828), URANYL SALTS (p. 828), URANYL SULPHIDE (p.

URAZOLE. A name given by Pinner (B. 20, and the property of th 2358) to di-oxy-triazole, which may be repre-

sented as NH.C(OH) N of NH.CO NH.

UREA CH, N₂O, i.e. CO(NH₂)₂. Carbamide.

Mol. w. 60. [132°] (Lubavin B. 3, 205). S.G.
1323 (Schröder, B. 12, 562). S. (alcohol) 20 in the cold; 100 at 78°. H.C.v. 152,500. H.C.p. 152,200 (Stohmann s. Langbein, J. pr. [2] 44, 387); 160,900 (Berthelot a. Petit, C. R. 109,

759; 110, 887). H.F. 80,800.

Occurrence.—In the urine of mammalia, especially in that of flesh-eaters (Fourcroy a. Vauquelin, A. D. 1799). Occurs in small quantity in blood, muscle, chyle, and lymph of mammalia (Wurtz, C. R. 49, 52; Poisseuille a. Gobley, J. 1869, 612; Verdeil a. Dollfus, A. 74, 214; Munk, Pf. 11, 100; Pickard, C. R. 83, 1179; 87, 533; Gréhant a. Quinquand, C. R. 108, 1092; Garrod, Pr. 53, 478). Constitutes about 30 p.c. of the solid substance of the vitreous humour of the eye (Millon, C. R. 26, 119; A. 66, 128). Occurs also in saliva (Rabuteau, J. 1873, 877), in cow's milk (Lefort, Z. 1866, 190; Vogel, J. 1867, 932), and in other animal secretions.

Formation.-1. By evaporating a solution of ammonium cyanate (Liebig a. Wöhler [1828], B. J. 12, 266; P. 12, 253; 15, 619; A. 38, 108).

2. By adding a little NHO, to an ethercal solution of cyanamide (Cannizzaro a. Cloëz, A.78. 230) or by the action of dilute (50 p.c.) H.SO. on cyanamide (Baumann, B. 6, 1373).—3. From COCl₂ and dry NH, (Regnault, A. Ch. [2] 69. Natanson, A. 98, 287), gaanidine and 180; Natanson, A. 98, 287), granidine and NH Cl being formed at the same time (Fenton, NH. Ci being formed as the same carbonic ether, C. J. 385, 793).—4. By heating carbonic ether, with NH, Aq at 180°.—5. By heating ammonium carbamate at 140° (Basaroff, J. pr. [2] 1, 283). 6. By passing an alternating electric current through a solution of ammonium carbamate (Drechsel, J. pr. [2] 22, 481).—7? By electrolysis of ammonia solution using carbon electrodes (Millot, Bl. [2] 46, 248).—8. By passing a mixture of NH, and CO, through a red-hot tube (Dexter, Am. 4, 85).—9. Formed by passing air charged with NH, and vapour of benzene over a red-hot helix of platinum wire (Herroun, C. J.

89, 471). Acetylene, but not ethylene, may be substituted for benzene.—10. By heating ammonium thiocarbamate NH_xCO.SNH_p or by shaking it with water and PbCO₂.—11. By the action of aqueous KMnO₄ on thio-urea (Alaly, M. 11, 277).—12. By the action of KMnO, on KCy in acid solution (Baudrimont, J. 1880, 393).— 13. By the action of NH Aq and H,S on copper fulminate (Gladstone, A. 66, 2) .-- 14. By heating oxamide with HgO (Williamson, Memoires du Congres scientif. deel enise, a.n. 1847). - 15. By oxidation of uric acid.—16. By the action of KGlO₃ and HCl on guantine (Strecker, A. 118, 159).—17. By boiling guandine with baryta (Baumann, B. 6, 1376).—18. By boiling biguanide sulphate or phenyl-biguanide sulphate with baryta (Emich, M. 12, 11). - 19. By the action of baryta on arginin (Schulze a. Likiernik, B. 24, 2701).-20. By boiling creatin with baryta.-2101.—20. By boining creatin with baryta.—21. A product of exidation of froteids by KMnO, (Béchamp, A. Ch. [3] 48, 348; C. R. 70, 866; Ritter, Bl. [2] 16, 323. Stacedeler (J. pr. 72, 251) and Loew (J. pr. [2] 2, 289) failed to obtain urea in this manner. Dreschel (B. 23, 3097) obtained urea from albumen by electrolysis, but not by oxidation.

Preparation. -- 1. Urine, concentrated by evaporation, is treated with nitrig or oxalic acid, and the ppd. nitrate or oxalite of urea is decomposed by CaCO₃, 2. A solution of potassium cyanate mixed with annuonium sulphate is evaporated on a water-bath to dryness, and the residue extracted with alcohol .- 3. A mixture of dry K₁FeCy₆ (28 pts.) and MnO. (14 pts.) is heated still sticky on an iron plate. A cold aqueous extract of the mass is mixed with aqueous extract of the mass is mixed with aqueous extract of the mass is mixed with alcohol (Liebig).—4. Dry K.FeCy. (8 pts.) is fused with K.CO₄ (8 pts.) and PbQ. (19 pts.) and PbQ. mixture is dissolved in water, mixed with (NH₁)₂SO₄ (8 pts.) evaporated, and extracted with alcohol (Clemin, A. 66, 382). Any K₁FeCy left can be removed by FeSO, -5. Lead cyanate is digested with (NII), SO, (J. Williams, C. J. 21, 64), -6. From NH, Aq. COS, and lead carbonate (Schmidt, B. 10, 193), -7. By the action of (NH), SO, on KCyO obtained by heating dry KF-Cy₈ with K-Cr₂O; the yield being 25 p.c. of the weight of ferrocyanide (C. A. Bell, C. N. 32, 99).-8. A stream of dry NII, gas is passed through phenyl-carbonate (from phenol-sodium and COCL), melted in a water-bath, and the mele is then poured into hot water; the aqueous solution after separation from the phenol is evaporated to crystallisation (Hentschel, B. 17, £286).

1'roperties. — Dimetric crystals, v. e. sol. water, m. sol. cold alcohol, insol. CHCl₂, nearly insol. ether. Sublimes at 130°. In vacuo it distils at 135° (Bourgeois, Bl. [3] 7, 45). Urea is not attacked by pure HNO, (Franchimont,

R: T. C. 6, 217).

Reactions .- 1. When heated alone at 1500-170° it yields NH, cyanuric and and biuret; at 140° it yields ammelide.—2. Decomposed into CO₂ and NH, by heating with water in sealed tubes above 100°, by boiling with potash, lime, or magnesia, by warning with cone. H₂SO₄, by evaporating with lead acetate, and by the action of ozone (Gorup-Besanez, A. 125, 207)

UREA. 830

in presence of free alkali. CaO produces cyanamide (Emich, M. 10, 330). A 8 p.c. HCl solution decomposes 4 p.c. of the urea in 24 hours. NaOHAq of the same strength has less effect. Cold water does not decompose urea (Berthelot a. André, Bl. [2] 47, 840).—3. Alcoholic potash forms, on heating in sealed tubes, cyanic acid, NH, and water (Haller, Bl. [2] 45, 705).— 4. Urea hydrochloride at 145° yields NH,Cl and cyanuric acid (De Vry, A. 61, 249):-5, Chlorine passed over melted urea ferms HCl, nitrogen, NH.Cl, and evanuric acid (Wurtz, A. 64, 307).— 6. Hypochlorous acid, hypochlorites, chlorine-water, and hypobromites, set free nitrogen, e.g. $CON_{a}H_{4} + 3HOCl = CO_{2} + 3HCl + 2H_{2}O + N_{2}$ 7. Nitrous acid added to a hot solution forms CO, and nitrogen: CO, II, + N,O, = CO, + 2H,O + 2N, Nitrous acid (2 mols) when added to a cold solution of urea (1 mol.) reacts as follows: 2CON₂H₄ + N₂O₃ = (NH₁)₂CO₃ + 2N₂ + CO₂ (Claus, B. 4, 140)₂ - 8. Neutral KMnO₄ has no action in the cold, and acts but slowly at 100°. In acid solutions KMnO, gives off nitrogen (1 vol.) and CO₂ (2 vols.) (Béchafip, J. 1856, 696; cf. Wanklyn a. Gamgee, C. J. 21, 25).—9. Bromine added gradually to an alcoholic solution of urea forms NH Br, cyanuric acid, and nitrogen. In sealed tubes Br gives NH Br and cyamelide (Smolka, M. 8, 64).—10. Heating with P.O. forms (Smolka, M. 8, 54).— 10. Heating with P.O. Johns oyanic and cyanuric acids, animelide, cyamelide, and NH₃ (Weltzien, A. 107, 219).—11. Yields eyanamide on warming with Na (Fenton, C. J. 41, 262).—12. Conc. HNO₃ reacts thus: CON₂H₁ + 21INO₃ = CO₃ + N₂O + NII, NO₃ + H₂O (Franchimont, R. T. C. 2, 96; 3, 219).—13. P₂S₃ forms crystalline C₂H,N₃PS₂O₂, which yields C₂H,AgN₃PS₂O₂ and C₂H,Ag,N₃PS₂O₂, andegives off PH₃ on warming (Kutschig, M. 9, 406).— 14. Zinc-dust at a red heat forms ZnCy, ammonia, and hydrogen (Aufschläger, M. 13, 272). 15. CS₂ at 100 forms COS and ammonium sulphocyanide. With alcohol and CS, the products ** age meraptan, CO₂, and ammonium's sulphocyanide (Ladenburg, %. [2] 5, 253; B. 1, 273;
2, 271; Fleury, A. 123, 144).—16. Alcohols in sealed tubes form carbamic ethers and alkyl allophanates (Cahours, C. R. 76, 1387).-17. Boiling Ac,O forms acctamide and diacetamide (Hofmann, B.14, 2733). -18. ZnEt, forms CON, H, Zn, which is reconverted into urea by water (Gal, Bl. [2] 39, 648),—19. Oxalic ether at 135-170° forms oxamide, allophanic ether, and alcohol (Grabowski, & 134, 115). Oxamic ether forms, on fusion, oxaluramide (Carstanjen, J. pr. [2] 9, 143) .- 20. Methylamido-acetic acid (sarcosine) forms methyl-hydantoin on fusion (Ruppert, B. 6, 1278).-21. Aniline at 150°-170° gives NH. o, 1210).—21. Amune su, 130.—110. gives NH₂ and di-phenyl-urea (Baeyer, A. 131, 251).—22. Antitine sulphonic acid at 120? gives NH₂CO.NH.C.H., SO₃H (Ville, Bl. [3] 6, 6).—
23. Biguanide sulphate terms, on heating, amulion, NH, SO₃CO. Society of Society and Society of zo. Signature suprate terms, on nearing, ammeline, M. 10, 95). 24. Heated with acctone and ZnCl or P.O. at 110°-140° it gives strimethylpyridine and a base C.H., N [112°]; (320°). (Riehre, A. 238, 22). This base forms hard monoclinic crystals, with metallic ring; its solutions fluoresce. It gives B'2H2PtCle: [225°].-25. Heated with acetyl-acetome (1 mol.), urea: into ammonism carbonate. A conc. aqueous (2 mols.) forms CH₂(CMe:N.CO.NH₂), which solution of furfuraldehyde followed by a drop of crystallises from alcohol [200°] (Combes, Bl. [3] HClAq (S.G. 1·10) colours a crystal of urea

The same body is formed, together **7**, 790). with CH. CMe:N CO [198], by adding HClAq or H.SO, to an alcoholic solution of urea and acetyl-acetone (Evans, J. pr. [2] 46, 852; 48, 499). — 26. Benzoyl-acetone forms, in like Bz.CH, CMe:N.CO.NH, [1919] and CH₂<CMe:N>CO [227°] (Evans, J. pr. [2] 46, 352- 48, 509) .- 27. Acctoacetic ether (2 mols.) and NaOEt (2 mols.) form in the cold C13H22N2O7Na2 [c. 165°] (Ernert, A. 258, 361). Acctoacetic ether in alcoholic solution forms uramido-crotonic acid (q, v_*) , -28. Urca reacts with aldehydes in the cold. In aqueous solution a diureïde R.CH(NII.CO.NH₂)₂ is usually formed, while solid urea forms triureides. On warming with excess of aldehyde, Wi- and tri-ureïdes yield tetraand hexa-ureides (H. Schiff, A. 151, 186). These ureides are sparingly soluble neutral solids, and are split up by warming with acids into the parent substances. Benzoic aldehyde forms benzylidene-di-urea (q. v.), while o-oxy-benzoic aldehyde forms C₀H₁(OH).CH(NH.CO.NH₂)₂aq, which is converted by acctoacetic ether in alcohol into C_aH₄(OH).CH:N.CO.N:CMe.CH_a.CO₂Et [200°], C₀H₄(OH).CH:N.CO.NH.CMe:CH.CO₂Et [204°], and C₆H₄CH:N.CO NH, which decomposes between 260° and 270° (Biginelli, B. composes between 2:00° and 2:70° (Bighield, B. 24, 2963). Acrolein fofms (CON₂H_{1),2}SC₃H₄O, which chars at 2:50° (Liūdy, M. 10, 2:95). o-Nitrobenzoic aldehyde forms nitro-benzylidene-diurea C.H.(NO.).CH(NH.CO.NH.), aq [1900]. In like manner cuminic aldehyde in alcohol forms the di-ureïde C₃H₁,C₃H₂,CH(NH.CO.NH.)₂ [176°] (Biginelli, B. 24, 2964), and cinnamic aldehyde forms Ph.CH:CH.CH(NH.CO.NH.)₂ [172°], and compounds melting at 116° and 212° .-29. Chloral added to conc. aqueous solutions of urea forms (C.HCl,O)CON_H, [150°], v. e. sol. hot water, and (C.HCl,O)CON_H, [190°] nearly insol. hot water, both compounds being crystalline (Jacobsen, A. 157, 246). Chloral cyanhydrin at 105° forms the very stable crystalline C.H. Cl. N.O (Pinner a. Fuchs, B. 10, 1069).-30. Benzene sulphonic chloride at 100° forms 50. Benzene suphonic chloride at 100 forms colourless crystals of C₈H₈SON₄H₅C_{.0}2 aq (Elander, Bl. [2] 34, 207). Naphthalene (a)-sulphonic chloride acts similarly.—31. Cinnamoyl chloride forms C. H₆(N. H. CO. N.I. C. H₆, N. H. CO. N. H. J. [184°] (Biginelli, B. 24, 2965).—32. ClCH₂.OH forms methylene-urea, which is split up by hot dilute H.SO, into formic aldehyde and urea (Von Hemmelmayr, M. 12, 89) .- 33. Trichlorolactic acid and a little water form, on heating, acetyleneurea C₁H_sN₄O₂ (Pinner, B. 17, 1997).—34. Hexachloro-acctons (2 mols.) heated with urea (1 mol.) at 150° forms CO:N₂H₂(C₂Cl₂O)₂, crystallising from alcohol in hexagonal plates (Cloez, \$\textit{L}\$. Ch. [6] 9, 145). Detection.-Urea gives, in conc. solution,

orystalline pps. with nitric and oxalic acids. Urea dissolved in amyl alcohol is completely ppd. by an ethereal solution of oxalic acid (Brücke, M. 8, 195). Mug-lus (C. R. 78, 182) filters cutrid urine, dries the filter at 35°, and employs it as a test for urea, which it converts into ammonism carbonate. A conc. aqueous solution of furfuraldehyde followed by a drop of violet (Schiff, B. 10, 774). o-Nitro-benzoie aldehyde added to an alcoholie solution of urea forms, on warming, a white pp. of o-nitro-benzylidene-di-urea [200°]. When present in small quantities this compound may be detected by resolving into the parent substances by boiling with very dilute H₂SO₄, and then adding a little phenylhydrazine solution, which produces a red colour (Liudy, M. 10, 295). Mercuric nitrate gives a white pp. with solutions of uses. The various methods of estimating urea may also be employed for its detection.

Estimation. - Hypobromite Urea is mixed with NaOH (100g. in 250 c.c. water) to which bromine (25 g.) has been added, and the nitrogen collected and measured (Knop, Art. and margen confected and intensaried (Mop. Fr. 9, 226; Hüfner, J. pr. [2] 3, 1; Dupró, C. J. 31, 534; Simpson a. V'Kecfe, C. J. 31, 838; Russell a. West, C. J. 27, 749; Eykman, R. T. C. 3, 125; Schleich, J. pr. [2] 10, 263; Colquhoun, C. N. 67, 123; Camerer, Zeit. Biol. 29, 239). When this method is applied to urine it must be remembered that uric acid gives off 48 p.c. and creatinin 37 p.c. of its nitrogen in this way (Falck, Fr. 21, 300). Nevertheless, the quantity of nitrogen evolved is 8 p.c. less than the calculated amount (R. a. W.). Using Knop's solution, ammonia, urea, and oxamide give off 93, 923, and 75 p.c. of their nitrogen as gas (Foster, C. J. 33, 470; 35, 170). In the case of urea and oxamide the suppressed 'nitrogen is present as cyanate and as nitrate (Fauconier; Luther, H. 13, 500). The amount of suppressed nitrogen is less in dilute than in concentrated solutions (Hüfner, H. 1, 350; cf. Pflüger a. Bohland, Pf. 38, 325; 39, 1, 143), and is greatly diminished by the addition of 1 to 5 p.c. acetoacetic ether (Jacoby, Fr. 24, 318). According to Duggan (Am. 4, 47), if bromine is added to a solution of urea in NaOHAq the yield of nitrogen is 99.4 p.c. of the theoretical amount. In estimating urea in urine Pflüger (Fr. 26, 117) adds HClAq (1 c.c.) to urine (10 c.c.), ppts. various nitrogenous bodies by phosphotungstic acid, neutralises the filtrate with lime and then adds an equal volume of conc. NaOHAq and, after allowing to stand for some time, decomposes with Knop's hypobromite. Frothing of albuminous urine can be avoided by first shaking with a pilule of fat (Méhu, J. Ph. [5] 15, 607). Hamburger (R. T. C. 2, 181) introduced a volumetric method of employing hypobromite, but Pflüger a. Schwenck (Pf. 37, 399) consider the method to be untrastworthy. E. Salkowski adds two drops of HCl to urine (2.5 c.c.) diluted with 5 or 10 volumes of water until the air is expelled from the flask, then adds the hypobromite, continues boiling, and collects the nitrogen. Fenton (C. J. 33, and contects the introgen. Fenton (C. J. 53, 300) Accommends the use of sodium hypo-chlorite, which was first proposed by E. W. Davy (A.D. 1854). In this case free Nacili must not be present, though excess of Na.CO. may be present.

Mercuric nitrate method. Urea is completely ppd. by a solution of $Hg(NO_s)_2$. The white pp. is not decomposed, and therefore not turned yellow by Na₂CO₂. Urine (2 vols.) als mixed with a solution (1 vol.) frepared from saturated solutions of baryta (2 vols.) and $Ba(NO_s)_2$ (1 vol.); filtered through a dry filter

from the ppd. sulphate and phosphate and 15 c.c. (equivalent to 10 c.c. urine) of the filtrate are titrated with standard mercuric nitrate till a drop taken out gives a yollow pp. with Na,CO_a (Liebig, A. 85, 370). Assuming the compound CON.H.2HgO to be formed, 1 pt. urea should ppt. 7.2 pts. HgO, but in practice 7.72 pts. of the latter are required. A solution of 71:48 g. mercury in HNO, diluted to 1 litre is equivalent to 01 g. area per c.c. If the urine contains more than 2 p.c. urce the titration gives too_low results; in this case the urine must be diluted. When inercuric nitrate is added to a solution of urea nitric acid is set free. Labig recommended the addition of M.CO, from time to time to keep the liquid neutral. Pflüger (Fr. 19, 375) proceeds as follows: During the titration, after each addition of $Hg(NO_3)$ a drop is placed in contact with a little pasty NaHCO₂. Long before the titration is ended, a yellow colour is seen between the two drops, but disappears on mixing them together. When the yellow colour is permanent, the titration is near its end; at this point the solution is neutralised by Na₂CO₂, and the tilration continued till a permanent yellow colour is got on mixing the drops. Should the entire liquid become yellow on adding Na,CO, a fresh quantity of urea solution must be taken and the operation be repeated with greater speed. The presence of over 1 p.c. NaCl in urine inter-feres with the titration when Na₂CO₄ is used as indicator, the final reaction not being sharp. Since NaHCO, does not ppt. HgCl,, when the bi-carbonate is used as indicator the titration may proceed as if NaCl were absent, subtracting the amount of Hg(NO₃), that is converted into HgCl₂ by the chloride (Rautenburg, A. 133, 55; Pfeiffer, Pr. 24, 475; Pflüger, Fr. 27, 120). It is, however, better to ppt. the chlorides by AgNO, and titrate in the usual way.

Barium carbonate method. The solution is heated with BaCl, and NI,Aqin scaled tubes at \$20°-240° and the ppd. BaCO, weight (Bunsen, A. 65, 575). Before applying this method to urine other substances which might form BaCO, must be ppd. by phosphotungstic acid (Pflüger a. Bleibtreu, Fr. 28, 377).

acid (Pflüger a. Bleibtreu, Fr. 28, 377).

Kjeldahl's method. Nitrogen in urea may be estimated by Kjeldahl's method. 5 c.c. urine gre heated with H.SO, (10 c.c.), and Nordhausen H.SO, (10 c.c.) until no more water or gre comes off, and the liquid is clear yellow. After cooling, water (200 c.c.) and N.OH areadded and NH, distilled off. In the case of urine it must be remembered that about 13 p.c. of the nitrogen is, on an average, combined in substances other than urea (Pflüger, Pr. 35, 464, 40, 533; Camerer, Z. B. 24, 306).

Other methods. Urea may also be estimated by fermentation and determination of aminonia set free (Miquel, C. R. 111, 501).

Campani (G. 17, 187) proposes to decompose urea by nitrous acid, and pass the CO, into a solution of lime-water of known strength, and titrate with oxalic acid.

Cazeneuve and Hugouneng (Bl. [2] 48, 82) Pheat urea with a large excess of water and titrate the resulting ammonium carbonate.

Riegler (F. 83, 49) decomposes ures with Millon's reagent and measures the mixture of N and CO₂ evolved.

Möiner a. Sjögvist (Fr. 80, 888) add 5 c.c. Moiner a. Bjöqvist (Br. 30, 588) and 5 c.c. of a saturated solution of BaCl, containing 5 p.c. baryta to 5 c.c. urine and then add 100 c.c. of a mixture of 97 p.c. alcohol (2 pts.) and ether (1 pt.). After 24 hours the liquid is filtered, the pp. washed with 50 c.c. alcoholether, and the filtrate and washings evaporated at 50° to 25 c.c., MgO and some water added. and the evaporation continued as long as NH, comes off. The urea is then determined by Bunsen or Kjeldahl's method (Bödtker, H. 17, 140).

Salts .- B'HCl. Very deliquescent crystalline mass, formed com urea and dry HCl. De-At 140° composed by water into urea and HCl. it yields NH₄Cl and cyanurio acid.—B'HNO₄. Small plates, sl. sol. water and alcohol, v. sl. sol. HNO₄.—B'₂H₄Co₄. S. 4.4 at 15°. S. (alcohol of S.G. 833) 1-65. Monoolinic tables; (alcohol of S.G. 833) 1°05. Monooning tables, a:b:c=1::04::491; $a=82^\circ$ 10' (Loschmidt, Sitz. W. 51, ii. 7, 384). V. sol. hot water. Ppd. from its aqueous solution by oxalic acid.— -B'H₂CO₄aq (Lubavin, A. Suppl. 8, 83). -B'HAuCl₄aq: orange-red prisms or needles, v. sol. water, alcohol, and ether. B', HAuCl, : yellow needles, v. sol. hot water (Heintz, A. 202, 264).—B',H_PtCl_s2aq. Yellow, deliquescent tables, v. sol. water and alcohol, insol. ether (Heintz, A. 198, 91).—B'H,PO,. Large crystals, v. sol. water and alcohol, sl. sol. ether (Lehmann, Buchn. Rep. 15, 224; Schmeltzer a. Birnbaum, Z. [2] 5, 200). Its solution does not ppt. MgSO,

-B', 2H, PO, Its aqueous solution gives a crystalline pp. of cyanuric acid on heating.

Tri-chloro-acetate B'C, HCl, O, Plates (from gloohol) (De Clermont, J. 1873, 536) .trom siconoj (De Ciernont, J. 1873, 536).— The fumaratte B'.C.H.O., maleates B'C.H.O., and B.O.H.O., malate B'.C.H.O., gallate B'C.H.O., and succinate B'.C.H.O., [145°], all crystallise in monoclinic forms (Loschmidt, M. 1871). all crystallise in monoclinic forms (Loschmidt, Sitz. W. 52, ii. 238). The parabanate B'C,H,M,O, and tartrate B',C,H,O, are trimetric.—The citrate B',C,H,O, is 'triclinic (L.). An acid tartrate B',C,H,O, and an acid citrate B',C,H,O, have been prepared (Hlasiwetz, J. 1856, 698).—Cyanurate B',C,N,H,O, Monoclinic crystals.—Picrate B',C,N,H,O, (Smalle, H, 5,990). S. 1.9 B'C,H,N,O, [142°] (Smolka, M. 6, 920). S. 1'9 at 18:5°. S. (95 p.c. alcohol) 3 at 18°. Slender yellow needles (from alcohol). Tri-chloromethanu sulphinate B'CCl,SO,H. [96°– 100°]. Thin prisms (McGowan, J. pr. [2] 34,

Compounds with metallic oxides.— B'.8Ag.O. (Liebig). Formed by adding moist Ag.O to a solution of urea. Grey plwder com-Ag₂O to a solution of urea. Grey pluwder composed of slender needles. According to Mülder (B. 6, 1019), the yellow pp. got by adding NaOH to a solution of urea mixed with AgNO, is GON,H,Ag., It combines with iodine, forming CON,H,Ag.I., a greenish mass, darkened by light (Tafel a. Enoch, B. 23, 1554).—3°,HgO. Got by adding Hg(NO₂), to a solution of urea mixed with KOH. White pp.—B',3HgO. White mixed with KOH. White pp.—B',3HgO. White pp. formed by adding HgOl, to a solution of urea and HgOl, changes to a yellow granular powder on boiling with water.—B'HgO. Formed' by adding Hg(NO₂), to a warm solution of urea by adding Hg(NO₂), to a warm solution of urea (Dessaignes, A. 82, 232; Liebig, A. 85, 289).

Compounds with metallic salts.—B'AgNO₂ Prisms. Yields silver cyanate on acctamide at 50° (Schmidt, J. Or. [2] 5, 68).

NaCl. Deliquescent prisms. Alcohol extracts urea from the compound.—B'NaNO, aq. Prisms (from water).—B'NH,Cl. Deliquescent crystals. -B'₃(NH₄Cl)₂HCl. Formed by dissolving urea in bleaching-powder solution (Beckmann, A. 91, 367. Large plates, sol. alcohol mixed with ether.—B',Mg(NO,), (Werther, J. pr. 35, 5).—B',Ca(NO,),—B',ZnCl,—Very deliquescent crystals (Neubauer a. Kerner, A. 101, 337).—B'CaCl, Needles.—B',Hg(NO,),2HgO. Granu^a lar powder formed by mixing warm dilute solutions of urea and mercuric nitrate. At the moment of formation the pp. is flocculent.— B',Hg(NO₃),2HgO. • Formed by pouring mercuric nitrate into a solution of urea as long as a pp. is produced, and keeping the whole at 40° pp. is produced, and keeping the whole at 40° pp. is for some time (Liebig). Six-sided lamins.

—B'₂Hg(NO₃)₂HgO. Formed by adding an acid solution of mercuric nitrate to a solution of trea nitrate. Crusts of small tabular crystals (Liebig, A. 85, 296).—B'HgCl₂. Flat crystals, v. sl. sol. cold water (W.).—B'₁₂Cr₈O₂₁ 3aq. Formed by the action of water on the product of the action of CrO₂Cl₂ on urea (W. J. Sell, Pr. 33, 267; 45, 321). Olive-green needles (from hot water). PtCl, added to its solution in not water ppts. silky green needles of B', Cr, Cl, (PtOl,), 2aq. The chromate treated with PbCl, forms lead chromate and a liquid from which gaseous HCl ppts. green prisms of B'12Cr2O, 6aq, the aqueous solution of which heated with Ag₂SO₄ gives dark-green prisms of B'₁₂Cr₂(SO₄), 10aq. In a similar way green prisms of B'₁₂Cr₂(NO₄)₆ may be got.—B'₁₂Cr₆Cl₂O₁, 2aq. Green monoclinic crystals, got from the product of the action of Cro.Cl. on urea by crystallising from conc. HClAq (1 vol.) diluted with water (9 vols.). By treatment with water it is split up into B'₁₂Cr₂O₂₁ and B'₁₂Cr₂O₃. By treatment with conc. HClAq and B',Cr,Cl,s. By treatment with conc. HClAq (1 vol.) and water (6 vols.) it is converted into the salts B',Cr,Cl,Ql,1 3aq. — B',Cr,Ol,2 4aq. — B',2Cr,Cl,6 Gaq. — B',2Cr,Cl,6 GlgCl, — B',2Cr,(CO,),4 aq. — B',2Cr,Cl,1,a. — B',2Cr,(SO,),I, — B',2Cr,(CO,),I, — B',2Cr,(CO,),I, — B',2Cr,(CO,),I, — B',2Cr,(CO,),I, — B',2Cr,Cl, — B',2Cr,(CO,),I, — B',2Cr,Cl, — B',2Cr,Cl, — B',2Cr,Cl, — B',2Cr,Cl,1, — B',2Cr,Cl,2, & B',2Cr,Cl,2,

v. sol. water, being decomposed into urea and formic acid.

Attyl derivative C,H,N,O₂ i.e.

Altayl derivative C,H,N,O₂ i.e.

NH,CO.NHAc. Acetweide. Mol. w. 102.

[214]. H.F. -200 (M.). S. (alcohol) 1 in
the cold; 10 at 78°. Formed by boiling urea
with Accl or Ac₂O (Zinin, A. 92, 405'; G.;

Leftde, R. T. C. 8, 235). Got also by the action of KMnO, on methyl-uracil (Behrend, A. 229, 29). Four-sided needles (from alcohol). Slowly but completely usecomposed by pure HNO, with evolution of CO. (1 volward N.O (2 vols.) (Franchimout, R. T. C. 6, 215). It is not ppd. bas Ho(NO).

Formed also from mercuric fulminate and AcCl (Scholl, B. 23, 8515). Needles (from alcohol). sl. sol. cold water.

Chloro-acetyl derivative
NH_CO.NH.CO.CH.Cl. Formed from chloro-acetyl chloride and urea (Jazukovitch, Z. 1868, 284; Tomfnasi, C. R. 76, 640). Thin needles (from alcohol). Begins to melt at 160°.

Tri-chloro-acety derivative
NH_CO.NH.CO.CCI, [150]. Crystals (from alcohol) (De Clermont, J. 1874, 798; Meldola a. Tommasi, C. J. 1874, 404; Cloez, A. Ch. [6] 9, 219). Nearly insol. hot water.

Bromo-acetyl derivative
NH_CO.NH.CO.CH.Br. Needles (from dilute alcohol) (Baeyer, A. 130, 156). Pure HNO gives off CO, (1 vol.) and N₂O (2 vols.) (Franchismont, R. T. O. 6, 218).

Tri-bromo-acetyl derivative NH, CO.NH.CO.CBr, [148°]. Formed by the action of Bron an aqueous solution of di-bromobarbituric acid (Baeyer). Crystals, v. sol. hot alcohol. Yields crystalline B'₂Ba(OH), xaq, v. e. sol, water.

Cyano-acetyl derivative NH, CO.NH.CO.CH, Cy. [200°-210°] (Mulder,

B. 12, 466). Crystalline.
Butyryl derivative NH_CO.NHC,II,O.
[176°]. Formed from urea and butyryl chloride (Moldenhauer, A. 94, 101). Plates.

Isovaleryl . derivative $C_6H_{12}N_2O_2$

[1912]. Minute prisms, v. sl. sol. water.

Carbonyl derivative CO(NH.CO.NH.)₂,

Formed by heating urea with COCl₂ at 100°
(E. Schmidt, J. pr. [2] 5, 39; Emich, M. 10,

347). Powder composed of minute crystals, v.

sl. sol. cold water and alcohol. Decomposed by heat into NH, and cyanuric acid. Boiling KOH also produces cyanuric acid.—B'HgO; crystalline powder, insol. water.

Succinyl derivative
C.H.O.(NH.CO.NH.). Formed by heating urea
(2 mols.) with succinyl chloride (1 mol.) at 65°
(Conrad, J. pr. [2] 9, 301). Colourless powder,
v. sl. sol. hot water.

Vol. IV.

Methyl-malonyl derivative CHMe:C.O.:N.H.CO. [192°]. Formed by heating methyl-malonic acid with urea and POOl. (Franchimont a. Klobbie, R. T. C. 7, 22). Pointed plates, v. sol. water and alcohol.

Bensoyl derivative NH₂CO.NHBz.

200°]. S. (alcohol) 1 in the cold; 4 at 78°. Formed by heating urea with BzCl or Bz₂O at 150° (Zinin, A. 92, 404; Geuther, Z. [2]=4, 299). Four-sided plates (from alcohol), insol.

CO(NEBz)z Di-bensoyl derivative CO(NEB2)₂. [210°] (S.); [197°] (H.). A product of the action of COCl₂ on benzamide at 165° (E. Schmidt, J. prac[2] 5, 58). Formed also by heating guanidine carbonate with B2,0 at 100° (Creath, B. 7, 1739), and by treating mercuric fulminate with B2Cl (Hollemann, R. T. C. 10, 72; B. 23, 2998, 3742). Needles (from alcohol), al. sol. water. Aniline at 180° gives NT₁₂ benzamide, hearsanilide and adjumble vives. Di-bensoyl derivative

benzanilde, and s-dreahenyl-ures.

2.Di-benzoyl derivative NH_CO.NBz_

[c. 197°]. Formed by heating sodium benzoyl
eyanamide NaBzN.CN with BzCl, followed by boiling alcohol (Buddéus; J. pr. [2] 42, 97). White needles.

m-Nitro-bensoyl derivative NH₂CO.NH.CO.C₂H₄.NO; [1:3]. Plates (Griess. B. 8, 222).

m-Amido-bensoylderivative C₂H₂N₃O₂.

Formed by boiling the preceding body with aqueous aumonium sulphide (G₂). Needles (from water), decomposing at 200°. — B'HOl aq: needles.—B',H,PtCl₂.

(8)-Naphthoylderivative

NH.CO.NH.CO.C_{1e}H., [215°]. Formed from naphthoyl chloride and urea (Vieth, A. 180, 319). Minute needles, m. sol. alcohol, v. sl. sol.

benzene.

Di-(Brnaphthoyl urea [286] (Ekstrand, B. 20, 1853). Needles.

Lactyl derivg tive v. Lactyl-urka.

Glycollyl derivative v. Hydantoïn.

Reference. - Oxy-urea.

UREA CARBOXYLIC ACID v. ALLOPHANIC

UREA CHLORIDES. A name sometimes ed to denote alkyl-carbamic chlorides nsed X.NH.CO.CI.

URECAITIN C28 II 42O8. Occurs, together with urechitoxin, in the leaves of Urechites subcrecta, growing in Jamaica (Bowrey, C. J. 33, 252). Crystallises from alcohol in needles (containing xaq), tastes bitter. It is very poisonous (Pr. 27, 309). Nearly insol. water, m. sol. ether. Appears to be a glucoside. Conc. H.SO, forms a yellow liquid, turning red, and . finally purple, especially in presence of an oxidising agent.

• Urechitoxin C₁₃H₂₀O₃. Bitter poison, split up by acids into sugar and urechitoxetin.

UREIDES. Compounds obtained by climination of water between urea and an acid or an aldehyde. Many of them may be represented as amides in which NII2 is replaced by NH.CO.NH2.

BIURET v. vol. i. p. 517. URETHANE v. CARBAMIO ETHER. ISURETINE v. FORMAMIDOXIM. URIC'ACID C,H,N,O, i.e.

CO NH.CO.C.NH CO (Medicus, A. 175, 243; Fischer, B. 17, 329, 1776). Mol. w. 168. S.G. 187. H.C.p. 461,400 (Berthelot, G. R. 110, 887; Matignoff, C. R. 110, 1267); 462,500 (Stohmann, J. pr. [2] 44, 590). H.C.v. 462,700 (M.). H.F. 148,100 (M.). S. 002 at 0°; 006 at 20°; 062 at 100° (Blarez a. Denigès, C. R. 104, 1847; cf. Gerrod, Pr. 35, 63).

Occurrence.-In urine and in ufinary calculi (Schoele, a.D. 1776; Liebig a. Wöhler, A. 26; 241; Horbaczowski, M. 12, 221). About 5g. is daily excreted in human urine. Uric acid occurs in urine of carrivora, herbivora (Mittelbach, H. 12, 463), and of birds. Serpent's urine is chiefly composed of acid ammonium urate. A considerable quantity occurs in the blood of A considerable quantity occurs in the blood or gouty subjects, and solidin urate is deposited as 'chalk-stones.' Very small quantities are normally present in the liver, lungs, brain, and blood. It occurs in the green gland of the fresh-water crayfish (Griffiths, Pr. 38, 187). Urea, glycocoll, leucine, and aspartic acid given to lowls appear in the urine as uric acid (Jane a.

Meyer, B. 10, 1930; Knierim, B. 10, 1930).

Synthesis.—1. By rapidly heating glycocoll (1 pt.) with urea (10 pts.) to 230° (Horbaczewski, B. 15, 2678; M. 3, 796; 6, 356).—2. By heating

ures with tri-chloro-lactic acid or its amide (Horbaczewski, M. 8, 201, 584).—3. By preparing methyl-uracil from acetoacetic ether and urea; converting methyl-uracil into nitro-uracil carboxylic acid by treatment with fuming HNO;; boiling the carboxylic acid with water, and reducing the resulting nitro-uracil to amido-uracil, and finally to isobarbituric acid by means of tin and HClAq; oxidising the isobarbituric acid to isodialuric acid; and heating the isodialuric acid 1801 acid (1 pt.) with urea (1 pt.) and H₂SO₄ (6 pts.) (Behrend a. Roosen, A. 251, 235).—4. By fusing urea (4 g.) with cyano acetic acid (1 g.) (Formánek, B. 24, 3419).

Preparation .- 1. Serpent urine is dissolved in boiling KOHAq, filtered, and the uric acid and by HCl or dilute H₂SO₄. If the uric acid is much coloured a little KMnO, or K,Cr,O, (Gibbs, Am. S. [2] 48, 215) should be added to the boiling alkaline solution before ppn.—2. Guano is boiled with borax (1 pt.) and water (120 pts.), and the solution of sodium urate thus obtained pd. by HCl.--3. Guano is extracted with dilute HClAq, and the residue dissolved in conc. H2SO4

and ppd. by water.

Properties .- White anhydrous scales When slowly deposited from dilute solutions (e.g. urine) it separates as large crystals (containing 2aq). Nearly insol. water, insol. alcohol and ether. Sol. conc. H.SO, and reppd. by water. Its solution in hot H.SO, deposits on cooling a deliquescent compound of uric acid with H₂SO₄. Uric acid is m. sol. glycerin, hot NaOAc, and sodium phosphate. Lithium carbonate (1 pt.) dissolved in water (90 pts.) can dissolve uric acid (4 pts.). Aqueous

K.CO, also dissolves uric acid.

Reactions .- 1. Decomposed by heat, without fusion, yielding HCy and a sublimate of evanuric acid, ammonium cyanate, urea, and ammonium carbonate, and leaving a carbonaceous residue. 2. Water at 180° forms mycomelic acid (Hlasigetz, A. 103, 211).—3. Potash-fusien yields NH, and potassium oxalate, carbonate, and cyanate. - 4. Chlorine and bromine in presence of water yield alloxan, urea, and parabanic acid (Hardy, A. Ch. [4] 2, 372). Alloxan is also produced by iodine, by HNO, and by MnO, and H.SO,.—5. Boiling with water and PbO, yields allantoin. Allantoin is also produced by ozone (Gorup-Besanez, A. 110, 94), alkaline K,FeCy, KMnO, (Claus, B. 7, 226), and MnO, and water. 6. Pure HNO, decomposes uric acid in the cold, with evolution of CO₂(14 vols.), N₂O (24 vols.), and nitrogen (4 vals.) (Franchimont, R. T. C. 6, 222). 7. KNO; and HOAc yield urinilio acid (Sokoloff, Z. [2] 5, 78) and stryphnic acid (Gibbs, Am. 3. [2] 48, 215).—8. HIAq at 165° forms glycocoll, MH,I, and CO; (Strecker, Z. [2] 4, 215).—9. Exposed to the air in alkaline solutionary yields exonic and uroxanic acids.—10. A dilute solution of sodic trate absorbs oxygen from the sir at 85° or some trate absorbs oxygen from the six at \$5^{\circ} according to the equation $O_1HN_0O_2^*+O_1+O_2H_2O_3$ (uroxanicacid). Usic acid in dilutional matches acid in completely decomposed by 35 days, digestion at \$5^{\circ} (Nenoki a. Sleber, J. pr. [3] \cdot 5, 18). 5 g. uric acid dissolved in 200 c.a. water and 20 g. potash disappeared in 5 days. However, if no oxygen be present the uric acid is not affected.—11. In fermenting urine uric

acid is completely split up into CO, and NH.

(Sestini, G. 20, 188).

Detection.—Uric acid may be recognised by its insolubility in water and HClAq, by its crystalline character under the microscope, and especially by the murexide reaction. When evaporated with HNO, on a water-bath it leaves an orange residue, which is coloured violet-red by ammonia and violet blue by potash. A solu-tion of uric acid in aqueous Na₂CO₂ produces a dark-brown spot of reduced silver when added to paper moistened with AgNO, (Schiff, A. 109, 65). Uric acid (1 mol.) reduces boiling Fehling's solution, ferming a pp. of Cu₂O (1 mol.) (W: Müller, J. Th. 1881, 73). In presence of KOH uric acid dissolves CuO, forming a blue solution, which slowly deposits white cuprous urate. The compound $C_5H_4N_4G_5Cu_2O$ is ppd. when an alkaline solution of uric acid is treated with Fehling's line solution of uric acid is treated with remning solution and hydroxylamine hydrochloride (Balke, J. pr. [2] 47,546). Uric acid evaporated with a little dilute HNO₂ gives a blue colour on shaking with H₂SO₄ and benzene containing thiophene (Denigès, J. Ph. [5] 18, 161).

Estimation in urine.—1. Urine (500 c.c.) is

concentrated, HCl is added, and after twenty-four hours the pp. is collected and weighed. Uric acid may be separated from xanthine by ppn. with cone. H.SO₄ (Horbaczewski, H. 18, 341; cf. Wulff, H. 17, 934).—2. Uwne (200 c.e.) is mixed with cone. Na₂CO₃Aq (10 v.e.), and after an hour cone. NH₂ClAq (20 c.e.) added. After forty sight hours than vir sullected washed forty-eight hours the pp. is collected, washed with HCl (1 pt. of S.G. 1-123), diluted with water (10 pts.), the washings allowed six hours to deposit any dissolved uric acid, the combined pps. washed with alcohol and dried at 110° (Salkowski, Fr. 16, 373). Uric acid may also be ppd. as ammonium urate by saturating urine with solid NH₄Cl (30 g. to 100 c.c.) (Hopkins, Pr. 52, 93).—3. Fresh urine is mixed with very dilute (15 p.c.) NaOHAq, filtered from phosphates, and diluted to S.G. 1.010. To 300 c.c. of this solution is added 50 c.c. of magnesia mixture [MgSO, 7aq (1 pt.), NH Ol (2 pts.), NH,Aq (4 pts. of S.G. 924), and water (8 pts.)]. The pp. is filtered off, and 175 c.c. of the filtrate hixed with 5 g. CaCO, and 5 c.c. of a 8 p.c. solution of AgNO. The pp. is washed and dried, and a nitrogen estimation made by Kjeland a mittogen estimation made by Mjedahl's method (Camerer, Z. B. 26, 84; cf. Salkowski, Pf. 5, 319).—4. Urine (25 c.c.) is mixed with NaHOO₂(1g.), and NH₂Aq (2 to 3 c.c.), and ammoniacal AgNo₂ (1 to 2 c.c. of a solution of 5 g. AgNO₂ in 100 c.c. water, to which NH₂Aq is added till the ppd. Ag₂O is just re-dissolved.

The UP. is collected washed discolved in HNO. The (pp. is collected, washed, dissolved in HNO, and the silver determined volumetrically by the sulphocyanide method (Haycraft, Fr. 25, 167; 80, 648). This method is liable, according to Salkowski (H. 14, 31) and Gossage (Pr. 44, 884), to appear on the property of the same of the s is partly due to variations in composition of the silver urate, and partly to presence of bodies of the xanthine group (Deroide, Bl. [8] 7, 863)

V. also Herrmann, H. 12,496; Ozapek, H. 12

502), 7-5. In a solution containing not more than 0125 p.c. of uric acid 1 c.c. of decinorfia permanganate is reduced by 0074 g. uric acid (Blarez a. Denigès, C.-R. 104, 789).—6. By treat

ment with a standard iodine solution in presence

ment with a standard iodine solution in presence of alkali (Kreidl, M. 14, 109).

Salts.—(NH₀)HA". S. 06 at 15°. Slender needles.—(NH₀)₁HA".—(NH₀)₂H₂A". (Maly, J. 1865, 621).—K₁A". S. 8 at 16°. Small needles.—KHA". S. 18 at 20°. Amorphous.—Na,A" aq. S. 15. Nodules.—NaHA" ½aq (dried at 100°). Crystalline powder. S. 09 at 15°; 8 at 100°. Crystalline powder. S. 09 at 15°; 8 at 100°. Crystalline powder. S. '09 at 16°; '8 at 100°. Occurs as an amorphrus urinary deposit—LiHA". S. '27 at 20; '9 at 40°; 2·5 at 100°. (Schilling, A. 122, 241).—BaA"aq (dried at 100°). Granular pp. S. '013 in the cold.—BaH,A", 2aq (dried at 100°). Amorphous, insoluble powder (Behrend a. Roosen, A. 251, 250).—CaA". S. '066 in the cold; '07 at 100°.—CaH,A", 2aq. S. '15 in the cold; '37 at 100°.—CaH,A", 2aq. S. '15 in the cold; '37 at 100°.—StA'' 25 at 100°.—Readles. S. '023 in the cold; '0.55 at 100°. KClAq.—STA 22q. Minute stemate groups an needles. S. 023 in the ccdd; 055 at 100°.—SrH_A", 2aq.—MgH_A", 2aq. S. 03 in the cold; 6 at 100°.—PbH_AM', 2 (dried at 100°). Insol. water.—PbA" (dried at 100°).—Cu_A" aq.— Cu,A";(OH); 4aq: green pp.

Reference.—METHYL-URIC ACID.

Iso-urio acid C.H.N.O. Formed by boiling cyanamide (1 pt.) with an aqueous solution of alloxantin (2 pts.) (Mulder, B. 6, 1236; 7, 1633). Powder, almost insol. water. Oxidised by boiling with I and water. Its solution in K2COs reduces

Pseudo-uric acid C.H.N.9, i.e.

CO NH.CO CH.NH.CO.NH2. Formed by the groups of slender needles.

URINILIC ACID C₈H,N,O₈. Formed by the action of KNO₂ and HOAc on uric acid (Sokoloff, Z. 1869, 78). Prisms (from water).—K₂HA'''. Z. 1803, (8). Frisms (1rom weer).—A₂nA...
Prisms, v. e. sol. water. Ca₄A''₂. Crystalline
pp.insol. water and HOAc.—Sr₃A'''₂.—Ba₃A'''₂.—
CdHA''' 8aq —CuHA''' 4aq. Slonder red needles.
—Ag₂HA'''. Pp.—Ag₂A'''. Gelatinous pp. quickly
blackening in light.

UROBILIN.

Occurrence.--Often in urine (Jaffé; Disqué,

ppd. by lead acetate and sub-acetate until the absorption band at F is removed. The yp. is extracted with alcohol, acidified with HCl or H₂SO₄, filtered, diluted with water, and extracted with chloroform.

Properties.-A red amorphous, shiny substance. Prepared as above it contains HCl or H.SO., as the case may be. Its spectrum exhibits a dark band at F, destroyed by NH, but on adding NaOH another band near the red is formed (MaoMunn, Pr. 80, 250; 81, 26, 206; v. also Hydrobhithuric, this vol. p. 278.

e. also hypeoblimusis, this vol. p. 273.

e Detection and estimation in urine: Jolles, H. 18, 545; Studensky, C. C. 1892, ii. 668.

UROCANIMIC ACID C₁₂H₁₂N₄O₄. [213°]. Occurs in dog's urine (Jaffé, B. 7, 1669; 8, 811).

Prisms (containing 4aq), v. sol. hot water, insol. alcohol and ether. Decomposed by fusion into CO₂ and urocanine C₁H₁,N₂O, an amorphous base yielding B'H₂PtCl₂.—HA'2HCl: needles, v. e. sol. water.—HA'2HNO₂: crystalline pp. insol. dilute HNO₂, v. sol. water.—HA'H₂SO₂. Minute needles and plates.

UROCHLORALIC ACID C.H., Cl.O. (?) [142°]. S. (ether) 4. Found in the urine after administration of childral (Von Mering a. Musculus, B. 8, 662; H. 6, 483; Külz, C. C. 1881, 486). Silky needles, v. c. sol. water and alcohol. Decomposed by boiling dilute II.SO, into tri-chloro-ethyl alcohol and glycuronto acid C.H., O, — NaA'.—RA'.—Bah',: satiny plates (from etheralcohol).

UROFUSCOHÆMATIN v. this vol. p. 274.

UROLEUCIC ACID CuH, Os. [133.5°]. An acid occurring in human urine which darkens on addition of alkalis (Kirk, Brit. Med. Journ. [1888] 2, 232) Crystals. Its solution is ppd. by Pb(OAc), and gives a transient green colour with very dilute FeCl. FeCl, colours the crystals relayed. tals rod.

UROMELANIN C18H19N,O16. A black substance which separates on treating urine with 11_SO, or HClAq in presence in air (Thudichum, $J.\ pr.\ 104,\ 257;\ C.\ R.\ 106,\ 1803;\ Plosz,\ H.\ 8, 89;\ Udranski,\ H.\ 11,\ 537;\ 12,\ 32;\ this vol.\ p. 274). It yields <math>C_{18}H_{46}AgN_{1}O_{6}$ (Thudwiffum).

URONITROTOLUOLIC ACID C, H15NO,. Oc. curs in urine of dogs after a dose of o-nitro-toluene (Jaffé, H. 2, 47). Very deliquescent. Asbestos like mass, v. e. sol. water and alcohol. Decomposed by dilute H₂SO, into o-nitro-benzyl alcohol and a syrupy acid. Salts. — BaA'z: crystalline powder, v. e. sol. water, insol. alcohol. -CO(NH₂)₂HA' 2 aq. [149°]. Needles, v. e. sol.

water, sl. sol. cold alcohol.
UROROSEIN v. this vol. p. 274.
UROSULPHINIC ACID C.H.N.SO...* Formed by heating thio-uramido-barbituric acid (1 pt.) with H.SO. (2 pts.) at 160° (Nencki, B. 4, 724;

to stand for most HClAq). Its K sait crystallises in needles, m. sol. cold water.

UROXANIC ACID C.H.,N.O... Formed by leaving a solution of uric acid (5 g.) in water (200 c.c.) containing KOH (20 g.) to stand for 5 days at 35°, neutralising by HOAc, filtering, and evaporating (Nencki a. Sieher, J. pr. [2] 24, 504; cf. Städeler, A. 78, 286; 80, 119; Streeker, A. 155, 177; Mulder, B. 8, 1291). Tetrahedra, sl. sel. cold water, insol. alcohol. Decomposed st. sol. cold water, insol. alcohol. Decomposed by boiling water into CO₂, urea, and allanturic acid.—K,A'\$3aq. Four-sided pearly plates, v. spl. hot water.—CaA'' 4aq.—BaA'' 5aq.—PbA'' 4aq. Insol. water.—Ag,A'': flocculent pp., turned red by light.

turned red by light.

URSONEO._{3.H.4.O.} 2aq. [265°] (Gintl, M. 14.

255). Occurs in the leaves of the red bear-berry
(Arctostsphylos Uva-ursi) (Trommsdorff, Ar. Ph.

[2]:80, 273; Hlasiwetz, J. pr. 68, 123). Needles,
hsol. water, acids, and alkalis, sl. sol. alcohol
and ether. Conc. H.SO, added to its solution
in Ac,O gives a red colour, changing through
hlus to green. Does not react with hydroxylshine. blue to green. Does not react with hydroxylamine or phenyl-hydrazine. Reduced by HI and P at 860° to O₁₂H₂₁ (256°-267°).

**Acetyl derivative [264°].

Bensoyl derivative [2149].

URUSHIO ACID C14H18O2. S.G. 25 985. Occurs in urushi or Japanese lacquer (Yoshida, S.G. 25 -985. 1 C. J. 43, 472). Dark, pasty mass, v. sol. benzene and ether, insol. water. Br in CS, forms C₁,H₁₂Br₂O₂. HNO₂ forms C₁,H₁₆(NO₂)₂O₂, which forms FeA'₂. Chromic acid mixture forms oxyurushio acid C₁₄H₁₈O₂.—PbA', (dried at 100°). [110°-115°]. Flocculent pp.—FeH₂A'₁₂ 2aq.—

FeH, A', Deep-black pp.

USNETIC ACID C, H₁₀O₂. [172°]. Occurs in small quantity, together with usene acid, in the lichen Usnea barbata (Hesse, B. 10, 1326). Flat prisms (from alcohol), v. sol. ether. FeCl. colours its alcoholic solution bluish-violet. Bleaching-powder does not colour its alkaline solution. Is perhaps identical with decarb-

USNIC ACID C₁₈H₁₆O, (Salkowski; Paterno) or C₁₈H₁₆O₆ (Hesse), or C₁₆H₁₆O, (Stenhouse a. Groves, C.J. 39, 234). Carbusnic acid. [195·4° cor.]. S. (ether) 3 at 20°. Occurs in the lichens Usnea barbata, Usnea florida, Leora sordida (Knop, A. 49, 103; Rochleder a. Heldt, A. 48, 12; Thomson, A. 53, 252; Stenhouse, Pr. 18, 222; A. 68, 97, 114; 155, 51; Hesse, A. 117, 843; Paterno, G. 8, 225; Salkowski, B. 8, 1459). Sulphur-yellow monoclinic crystals, sl. sol. alcohol, v. sol. hot ether and benzene. Does not yield betorcin when heated. Conc. H2SO, forms usnolic acid C_2 , $H_{21}O_{10}$ [213°] crystallising in small \sqrt{c} wish prisms (Stenhouse a. Groves, °C. J. 39, 236). When it is heated with an alcoholic solution of aniline it yields the anilide C₁₈H₁₈O₄(NHPh), crystallising from alcohol in pale-yellow plates [171°], and forming in KOHAq a yellow solution from which HCl ppts. C2H23NO. [171°].

Salts.—NaC₁₈H₁₇O₈ 2aq (Spica, G. 12, 432). Pale-yellow, silky needles.— KC₁₈H₁₈O₈ 3aq or KC18H17O 3aq. Pale-yellow plates (from 50 p.c. KC₁₈H₁₇O₅ oaq. Pale-yellow plates (from 50 p.c. alcohol) (Hesse, B. 10, 1325).—KC₁₈H₁₇O₅ aq or KC₁₈H₁₇O₄ aq. Yellow prisms (from 93 p.c. alcohol).—CuA'₂: green pp.

*Decarbusnein C₁₇H₁₈O₄. [175]. Formed by heating usnic acid (1 pt.) with alcohol (3½ pts.) at 150° (Paterno, G. 12, 234). Yellow, silky

needles, sol. hot alcohol, sl. sol. water and ether. Not coloured by FeCl. Not attacked by AcCl. Reduces warm ammoniacal AgNO. Boiling KOHAq in absence of air splits it up into HOAc and decarbusnic acid $C_{ls}H_{ls}O_{s}$, which crystallises from alcohol in lemon-yellow prisms [199] and yields, when boiled with Ac,0, two acetyl derivatives $C_{15}H_{15}ACO_{5}$ [148°] (isomeric with decarbuspein) and $C_{15}H_{15}ACO_{5}$ [181°].

Pyrouanic seid $C_{12}H_{10}O_{5}$ (P.); $C_{2}H_{2}O_{4}$ (Salkowski, B. 8, 1461). [197°]. Formed, together with pyrousnetic acid, by boiling usnic acid (2, the bound water (5 th

pts.) with KOH (5 pts.) and water (5 pts.) in an atmosphere of hydrogen (Paterno, G.S., \$13; 12; OXYLIC ACID.

242). Shining scales (from ether), v. sol. alcohol, sl. sol. ether. Its alkaline solution absorbs oxygen from the air, turning green and ultimately brown. Reduces ammoniacal AgNO, readily. Ac O yields an acetyl derivative [205°]. Alcohol and HCl form an ether [147°]. Pyrousnic acid is split up on dry distillation in a current of H into CO₂ and usneels C₁₁H₁₂O₃, which crystallises from alcohol in yellow pris-matic tablets [176°] and is converted by AcCl into a di-acetyl derivative [142°].

Pyrousnetic acid C_{1,}H_{1,}O₄ i.e. C_{1,}H_{1,1}O₄ (CO,H). [186°]. Formed by boiling usnic acid, (10 pts.) with KOH (25 pts.) and water (25 pts.) for 15 minutes (Paterno, G. 12, 238). Colourless plates or needles (from alcohol). Ac₂O yields C₁₄H₁₃AcO₂ [168°]. When heated in a current of H, pyrousnetic acid is split up into CO₂ and us netole C₁₅H₁₄O₄, which crystallises from dilute alcohol in yellowish needles [179°].

(β)-Usnic acid v. Cladonic acid.
UVIC ACID v. Pyrotritaric acid.

UVINONE $C_{1i}H_{12}O_{4}$ i.e., O < CMe: C.CO.C:CMe > O (?) [247°]. to the extent of 2 p.c., by distilling pyrotritaric acid (Dietrich a. Paal, B. 20, 1086). Yellow needles (by sublimation), sol. HOAq, v. sl. sol. alcohol. Conc. Haso, forms a solution with green fluorescence. Br at 100° Yorms crystal-

green fluorescence. Br 2t 100° forms crystal-line C.H.Br.,O...
UVITIC AICD C.H.,O., i.e.
C.H.Me(CO.H.),[1:3:5]. Mesidic acid. Mol. w.
180. [288°]. H.C.v. and p. 928,900. H.F.
193,100 (Stohmann, J. pr. [2] 40, 128). Formed,
together with uvitonic acid, by boiling pyruvic
acid with baryta-water (Finck, A. 122, 184).
Formed also by oxidation of mesitylene or mesitylenic acid (Fittig a. Von Furtenbach, Z. [2]
4, 1; A. 147, 295), by oxidation of di-methylcthyl-bengen (Wroblewsky, A. 192, 217), and thyl-benzene (Wroblewsky, A. 192, 217), and by heating L.H.Me(SO,NH.)(CO,H), with conc. HClAq at 230° (Hall a. Remsen, Am. 2, 136). Slender needles (from water), v. sl. sol. hot water, m. sol. alcohol and ether. Yields toluene on heating with soda-lime (Baeyer, Z. [2] 4, 119). The Ca salt heated with lime yields mtoluic acid (Böttinger a. Ramsay, A. 168, 255). Chromic acid mixture oxidises it to trimesic acid.

Salts.—K.A": plates (from alcohol), v. sol. water.—BaA" aq.—CaA" aq.—Ag₂A". Nearly insel. cold water.

Ethyl ether Et.A". [35°]. 'Crystakine. References.—Amido-, Bromo-, Nitro-, and OXY-INVITIO ACID.

Isouvitic acid v. CARBOXY-PHENYL-ACETIC ACID. Uvitonic acid v. Methyl-pyridine-dicarb-

idene di-ACETONAMINE.

WELERAL v. Valeric aldehyde.

VALERAL-DI-ACETONAMINE

v. Pentyl
Mktz, A. 90, 109; Parkinson, A. 90, 119). Formed also from thiorisovaleric aldehyde and VALERALDINE C14HaNS, Thiovaleraldine. dry NH, (Schröder, B. 4, 468), Plates (from ether), with powerful smell, sol. alcohol, insol. water. B'HCl. Needles, sol. water.

VALERCREATININ v. METHYL-GUANIDO-VALERIC ACID.

VALERIAN OIL. An essential oil obtained from the root of Valeriana officinalis. It contains a terpene $C_{10}H_{10}$ (156°) $[\alpha]_{D} = -21^{\circ}$, a camphene, borneol $C_{10}H_{10}$, O, di-bornyl oxide $(C_{10}H_{11})_{0}O$ (285°-290°), formyl-, acetyl-, and valeryl-borneol, and a little valeric acid (fierhardt, A. Ch. [3] 7, 275; Pierlot, A. Ch. [3] 56, 291; Bruylants, J. Ph. [4] 27, 349; B. 11, 452; Haller, C. R. 103, 151; Oliviero, C. R. 117, 1096).

1090).

n-VALERIC ACID $C_3H_{10}O_2$ i.e. $CH_{2}.CH_{2}.CH_{2}.CH_{2}.CO_2H$. Mpl. w. 102. (186° cor.). S.G. $\frac{9}{6}$ 9562 (Zander, A. 224, 65); $\frac{15}{6}$ 9446; $\frac{25}{6}$ 9375 (Perkin); $\frac{20}{6}$ 9298 (Brühl). C.E. (0°-10°) 00098 (Z.). S. 3·5 at 16°. S.V. 130·0 (Z.). M.M. 5·513 at 13·6°. $\mu_{\theta} = 1$ ·4093. $R_{\infty} = 43\cdot16$ (Brühl). H.F. 137,800 (Stohmann, $\frac{1}{2}$ ar [2] 49. 99). Occurs in early a word virous control of the second virous co J. pr. [2] 49, 99). Occurs in crude wood vinegar (Grodzki a. Krämer, B. 11, 1358).

Formation.—1. By saponifying its nitrile (nbutyl cyanide) (Lieben a. Rossi, A. 159, 58; G. 1, 239).—2. By oxidation of n-amyl alcohol (L. a. R.).-8. By the action of metallic silver on a mixture of E41 and 3-iodopropionic acid (W. von Schneider, Z., 2] 5, 343).—4. By oxidising a-oxy-n-caproic acid (Erlenmeyer, B. 9, 1840).—5. By heating \$\beta\$-acetyl-propionic acid with HI and P at 200° (Kehrer a. Tollens, A. 206, 233).—6. By reducing Bacetyl-propionic acid with sodium-amalgam (Wolff, A. 208, 110).—7. By heating an-propyl-malonic acid at 180° (Juslin, B. 17, 2504; Furth, M. 9, 308).—8. By fernentation of calcium lactate (Fitz, B. 13, 1309; 14, 1094). 9. By heating the lactone of γ -oxy-n-valeric acid with HIAq and P at 240° (Fittig, A. 226, 346).—10. A product of exidation of easter oil by dilute HNO, (Wahlforss, B. 22 Ref., 438).

Properties .- Liquid, smelling like butyric acid.

Salts.-KA'. Plates (from alcohol). Salts.—KA: rintes (from account).—
CaA'₂aq. S. 10·267 at 0°; 8·144 at 60°. Least
soluble at 60°-70° (F.);—CaA'₁1₃aq (Schottlemmer, A. 161, 270).—BaA'₂. S. 21·693 at 0°;
23·076 at 80°.—MaA'₂ aq.—GuA'₂: minute green

Accounts More sol cold than hot water.—ZnA'₂. needles. More sol. cold than hot water.—ZnA'₂. S. 2·6 at 25°.—AgA'. S. 229 at 3°; 641 at 70·5°

Methyl ether MeA'. (127.3°). S.G. $\frac{3}{2}$. 9097 (G.); $\frac{2}{2}$. 9795. C.E. (0°-10°) 00106. S.V. 149·1 (Gartenmeister, A. 233, 273). $\mu_{\rho} = 1.3997$.

Tayl (distributions of the property of the pr

eous (B.).

n-Propyl ether PrA'. (167.5°). S.G. §
*8888. C.E. (0°-10°) *00106 (G.). S.V. 197.8.

n-Butyl ether C.H.A'. (185.8°). S.G. §
*8847. C.E. (0°-10°) *00101. S.V. 222·1.

n-Amyl ether *C.H.₁₁A'. Mol. W. 172.
(908.7°). S.G. § *812 (G.). *2° *8568 (Brahl)*
C.E. (0°-10°) *00097. S.V. 245-8. μ_g 1.417.

R_Φ 80·48.

n-Hexyl other O.H.A'. (223.8°). (8797. C.E. (0°-10°) 00096. S.V. 272.0.

n-Heptyl ether C,H,,A'. (248.6°). S.G. § 8786. C.E. (0°-10°) 00090. S.V. 297.4. n-Octyl ether C,H,A'. (260.2°). SeG. § 8784. C.E. (0°-10°) 00088. S.V. 322.6. Amide C.H., CO.NH. Mol. w. 101. •[116°]. Pearly plates (Weidel a. Ciamician, B. 13, 69).

V. sol. water, alcohol, and ether.

Nitrile C.H. CN. n-Butyl cyanide. (140°). S.G. ² 816 (Lieben a. Rossi, A. 158, 171). Formed, together with amylamine, by allowing a mixture of hexoic amide (1 mol.) and bromine (2 mors.) to run into a 10 p.c. solution of NaOH

(Hofmann, B. 17, 1410).

Isovaleric acid. (CH₂), CH.CH₂, CO₂H. Isopropyl-acetic acid. (176° cor.). S.G. § 9386; § 93261 (Perkin); § 931 (E. a. H.). M.M. 5-635 at 16°. S. 4.24 at 20°.

Vapour tension: Richardson, C. J. 49, 767. Heat of neutralisation : Gal a. Werner, Bl. [2] 46, 801.

Occurs in the fat of Delphinum Phocana (Chevroul [1817], Corps gras, pp. 99, 209), in valerian cot (Grote B. J. 11, 225; Trommedorff a. Ettling, A. 4, 229; 6, 176), in the root of Angelica Archangelica (Moyer a. Zenner, A. 55, 828), in the root of Athamanta Oreoselinum, in the bark of the alder tree, in the herries and bark of the Guelder rose (Viburnum Opulus) (Moro, A.

55, 330), in the root of Viburnum prunifolium (Allen, Ph. [3] 11, 413), and in oil of geranium (O. Jacobsen, A. 157, 232). A valeric acid occurs in rosin cil (Lwoff, B. 20, 1017) and in yolk

of wool (suint) (Buisine, Bl. [2] 48, 639). Formation. -1. By exidation of inactive fermentation amyl alcohol (Dumas a. Stas, A. 38, 156; 35, 143; Erlenmeyer a. Helf, A. 100, 257; Pedler, C. J. 21, 74).—2. By boiling its nitrile with alcoholic potash (E. a. H.; Schmidt a. Sachtleben, A. 193, 87).—3. Together with the active acid by oxidation of leucine (amido-hexolo acid) (E. a. H., cf. Neubauer, A. 106, 50).—4. By heating sisopropyl-malonic acid at 180° (B. 11, 596).-5. By oxidising di-methyl-allyl-carbinol, treating the resulting CMe2(OH).CH2CO2H with HI, and reducing the β-iodo-valeric acid so formed by means of 3 p.c. sodium-amalgam applied in an acid solution (Schirokoff, J. pr. [2] 23, 286).—6. By the action of KOH or HClAq on Athamantin (Schnedermann a. Winckler, A. 51, 324) 47. By putrefactive fermentation of pro-terids (Hjenko, A. 63, 269).—8. By the action of CrO, on gelatin and albumen (Schlieper, A. 59, 7; Guckelberger, A. 64, 71). - 9. From isopropylaceto-acetic ether (Frankland a. Duppa, A. 145. 84).—10. By distilling isopropyl-malonic acid Conrad a. Bischoff, A. 204, 151).—11. A product of distillation of colophony (Renard, A. Ch.

[6] 1, 253). Preparation.-1. Isoamyl alcohol is oxidised by less than the calculated quantity of KMnO, in the cold. Some acetic acid is formed, but this can be got rid of by distribing a dilute solu-tion of the acids, for valeric acid passes over in the first quarter of the distillate, the acetic acid remaining behind (Duclaux, C. R. 105, 171).—2. By oxidising isoamyl alcohol (1,000 c.c.) with K₂Cr₂O₂ (1000 g.) dissolved in water (8,500 c.c.) by adding in the cold H₂SO₄ (1,400 g.) mixed with water (800 g.). The resulting isoamyl isovalerate is saponified by potash (Pierre a. Puchot, A. Ch. [4] 29, 229).—8. By

distilling valerian root with dilute phosphoric acid, neutralising the distillate with Na₂CO₂, and, decomposing the resulting Na salt by H₂SO₂. In purifying valeric acid use may be made of the fact that the acid forms crystalline acid salts with K and Na (Lesceut, Bl. [2] 27,

Properties .- Liquid, inactive to light. Its smell is powerful and unpleasant. «Sl. sol. water. Separated from aqueous solution by CaCl... Volatile with steam. Mixes with alcohol and ether. It is set free from its salts by mineral soids, by HOAc, by oxalic, tartaric, citric, and malic acids, but not by buttric acid. conc. valeric acid is added to a solution of cupric acetate, anhydrous cupric val rate separates in oily drops, which soon change to a greenish-blue crystalline powder of the hydrated salt; butyric scid would at once give a crystalline pp. (Larocque a. Huraut, J. Ph. [3] 9, 430).

Reactions.—1. Oxidised by thromic acid mixture at 20° to acetic acid and CO.—2. Boiling dilute HNO, forms nitro-valence acid, methyl-malic acid, and a little di-nitro-propane methyl-malic acid, and a little di-nitro-propane (when prepared from valerian) or di-nitro-butane (when prepared from isoamyl alcohol) (Bredt, B. 14, 1782; 15, 2319; cf. Dessaignes, A. 79, 874).—\$. Dilute alkaline KMnO, forms CMe₂(OH).CH₂.CO₂H.—4. Electrolysis of the K salt in 50nc. solution yields octane C₂H₄Pr₂ (Kolbe, A. 69, 259).—5. Passed through a red-hot tube it yields ethylene, propylene, butylene, and other hydrocarbons (Hofmann. C. J. 3. 121). and other hydrocarbons (Hofmann, C. J. 3, 121). 6. The Ca salt yields di-isobutyl ketone on distillation by itself, valeric aldehyde on distillation with calcium formate, and methyl isobutyl ketone on distillation with calcium acotate.

ketone on distillation with calcium acctate.

Salta.—NH,A'. V. sol. water and alcohol.

(NH₄)H₄A'₂.—KA'. Deliquescent crystalline mass. S. (alcohol) 26 at 20°. [140°].—LiA'₂aq. Nodules.—TlA'. V. sol. water.—CaA'₂8aq: needles (Barone, A. 165, 120; Schmidt a. Sachtleben, A. 193, 87; Schirokoff, J. pr. [2] 23, 286). S. 18 4 at 0° (Sedlitzky, M. 8, 563).—CaA'₂4aq.—CaA'₂5aq.—BaA'₂. Triclinic plates. S. 94 at 18°. S. (alcohol) 3'3 at 20°.—BaA'₂aq.—BaA'₂ 2aq.—SrA'₂—MnA'₂2aq.—ZnA'₂2aq.—ZnA'₂2aq.—ZnA'₂2aq. Crystalline.—ZnA'₂, S. 1 in the cold. S. (80 p.c. alcohol) 1'7 in the cold; S. (40 cold; S. (40 cold; S. (40 cold); S. (40 co sold. S. (80 p.c. alcohol) 1.7 in the cold; S. (ether) '2 in the cold; 5 at 35° (Wit.stein, J. 1847, 557). — ZnA'₂12aq. — ZnA'₂2NH₂ (Jutschak, B. 5, 30). — CuA'₂, Green crystalline pp. — CuA'₂aq. — Bi₂A'₁(OH)₂O₂ (Schucht, Ar. Ph. [8] 2, 97). — FeA'₁. — FeA'₂(OH)₂. — FeA'₂(OH)₂. — FeA'₃(OH)₂. — FeA'₃(OH)₂. — Groups of needles, sl. sol. water. — AgA'. S. — 177 at 0° (Sédlitzky); ·185 at 20° (Erlenmeyer). (Erlenmeyer).

Methyl ether MeA'. (116°). 7S.G. 9-9007. C.E. (0°-10°) -001174. S.V. 149·6 (Elsässer, A. 218, 315); 148·3 (R. Schiff, A. 220, 834). S.H. (21°, 45°) 491 (Kopp). Smells like bananas.

bananas.

Ethyl ether Eth'. (184°). (E.); (135° cor.) (Perkin). S.G. 2 .8861 (E.); 4½ .8714; 25 .252 (P.). C.E. (0°-10°) .001034. S.V., 1784 (E.); 178-0 (S.). M.M. 7-615 at 18°. Oil, sol. alcohol. Smell.s like rennet apples and water-mint (Pierre a. Puchot, A. Ch. [4] 2J, 284). Converted by sodium into oxy-decoic acid, ethyl ethoxy-decoate (Hantzsch, A. 249,

64), an acid C_mH₁,O₂ [c. 127°] (295°), and other bodies (Greiner, Z. [2] 2, 460; Wanklyn, C. J. 17, 371; Geuther a. Greiner, J. 1865, 319).

**n-Propyl ether PrA'. (156°). S.G. 2, 8809. C.E. (0°-10°) 000997. S.V. 197·5 (Elsässer); 196·8 (Schiff).

**Isopropyl ether PrA'. (142°). S.G. 2, 870; 13°854 (Silva, A, 153, 136).

**Di-chloro-propyl ether C₂H₂Cl₂A'. (245°) at 737 mm. S.G. 11 1·149. Formed from epichlorhydrin and isovaleryl chloride (Truchot. A, 138, 298). (Truchot, A. 138, 298).

Isobutyl ether C.H.A'. (169°) (Elsässer, A. 218, 328); (173°) (P. a. P.). S.G. 2 .8736 (E.). 2 .8884 (P.a. P.). C.E. (0°-10°) .001027. S.V. 223'4 (E.).

Isoamyl ether C₃H₁A'. (188°) (Kopp; R. Schiff, A. 234, 344); (196°) (Balard); (190°) (Balbiano, J. 1876, 348); (194°) (Kahlbaum). S.G. 2 '870 (Balbiano). S.V. 244·5. V.D. 6.1. Smells, when dissolved in alcohol (7 pts.), like apples.

Octyl ether C₈H₁,A'. (250°). S.G. 14 962 (Zincke, A. 152, 6).

Cetyl ether C₁₆H₁₃A'. [25°]. (280°-290°) at 202 mm. S.G. 22 982 (Dollfus, A. 181, 982).

Allyl ether C3H3A'. (154°). Oil (Cahours a. Hofmann, A. 108, 296).

 a. 100 main., A. 108, 2001.
 Glyceryl derivative v. Geneerin.
 Chloride Pr.CH. COCl. (114°) at 726
 mm. S.G. 29 9887. μ_β 1·4213. R_∞ 49·14.
 Liquid, easily decomposed by water (Béchamp, G. B. 49.24). R_∞ 1.14. C. R. 42, 224; Brühl, A. 203, 24).

Bromide C.H., OBr. (143°). Liquid.

Iodide C.H., OI. (168°) (Cahours, C. R.

44, 1252).

Anhydrids (C₃H₂O)₂O. Mol. w. 186. (215°) (Chiozza, A. 84, 106). Converted by hydrated BaO₂ into the oily peroxide (C₃H₂O)₄O₂ (Brodie, Pr. 12, 655).

Aceto-valeric anhydride (C.H.O).OAc.

(147°-160°) (Autenrieth, B. 20, 3187).

Amide C.H., CONH., [128°] (Letts, B. 5, 669; Hofmann, B. 15, 982); [135°] (Schmidt a. Sachtleben, A. 193, 102). (231°). Silky plates, v. sol. water and alcohol.

Anilide C.H., CO.NHPh. [115°] (Chiozza, A. Gl. [3] 39, 201; Kelbe, B. 16, 1200; cf. Dumas, C. R. 25, 475, 658; Dessaignes, A. 68. 333). Sl. sol. hot water, v. sol. alcohol and ether.

Fr.CH.CN. Isobutyl cyanide. (129°) (R. Schiff, B. 19; 587). V.D. 289. Formed by hard Nitrile Mol. w. 83. S.G. 9 823. Pr.CH2.CN. ammonium valerate or valeramide with P.O. ammonum valerare or valeraming with P₂O₃ (Dumas, Malaguti a. Leblanc, C. R. 25, 358). Occurs among the products of oxidation of gelatin and case by chromic acid mixture (Schlieper, A. 59, 15; Guckelberger, A. 64, 72), of the action of chlorine on leucine (Schwanert, A. 102, 228), and of the action of conc. HNO, on castor oil (Hell a. Kitrosky, B. 24, 980). Formed also, together with valeramide, by heating valeric also, together with valeramue, by heating valera-toid with potassium sulphoryanide (Letts, B. 6, 669). It is also got by the action of cold Ac.0 on the oxim of valeric aldebyde (Dollfus, B. 25, 1915). Prepared by digesting isobutyl iodide with KCy and alcohol (Erlenmeyer a. Hell, 4. 160, 266). Liquid, smelling like almonds, dissolving in about four times its volume of water Sodium converts it, on heating, into cyanbutine C₁₂H₂₇N₃, crystallising in stellate groups of needles, which yield B'HCl and B'₂H₂PtCl₃, and is converted by nitrous acid into C18H2 (OH)N. [89°] (E. von Meyer, J. pr. [2] 37, 407).

Active valeric acid CHMeEt.CO,H. Methylethyl-acetic acid. Hydrotiglic acid. (177° i.V.). S.G. $\frac{34}{178}$ 938 (Saur). S.V. 129 1 (Lossen, A. 254, 60). Occurs in the essential oil from the fruit Angelica Archangelica (R. Müller, B. 14,

Formation.-1. By oxidation of isoamyl · alcohol .- 2. By reducing tiglic acid with HI and P (Schmidt a. Berendes, A. 191, 117).—8. By heating methyl-ethyl-malonic acid (Bischoff a. Conrad, A. 204, 151).—4. From methyl-ethylacetoacetic ether (Saur, A. 188, 257).—5. By feducing angelic acid (Schmidt, A. 208, 261).-6. By reducing bromo-hydro-tiglic acid (Pagen-Steeher, A. 195, 121).—7. By the action of NaOEt and Et on propionyl-propionic acid (Israel, A. 231, 219).—8. By oxidation of the corresponding aldehyde (Lieben a. Zeisel, M.

Properties .- The acid obtained by synthetic methods is inactive, but when obtained by oxidation of active amyl alcohol it is dextrorotatory, but is mixed with inactive isovaleric acid. By oxidation of an amyl alcohol [a] == acid. By oxightion or an amplification $|a_1\rangle = -4.4^\circ$ Guyes and Chavanne (C. R. 116, 1454) obtained a valeric acid (174°), $[a]_D = +13.6^\circ$, S.G. $\frac{23}{2}$ 938. By oxidation of an amplialcohol $[a]_D = -5.2^\circ$ at 22° Rogers (C. J. 63, 1130) got a valeric acid (175°), S.G. $\frac{23}{2}$ 936, $[a]_D = +13.9^\circ$ at 22°. Methyl-ethyl-acotic acid can be separated acting a solid through this rated from isopropyl-acetic acid through the greater solubility of its silver salt. Dilute KMnO, oxidises methyl-ethyl-acetic acid to CMeEt(OH).CO.H.

Salts.—CaA'₂5aq: needles. S. (of CaA'₂) l.—*BaA'₂: gummy mass.—ZnA'₂. Needles, ore sol. cold than hot water.—CuA'₂: bluish-'een, crystalline pp.—AgA': groups of needles. 1.13 at 20° (C. a. B.); 1.11 at 1° (Sedlitzky, r. 8, 568).

Ethyl ether EtA'. (133 5° i.V.). S.G.

Nitrile C.H., N. (125°). S.G. 2 8061. ormed by adding Na and EtI to a solution of cetonitrile in benzene (Hanriot a. Bouveault,

valerie in oeuzene arianriot a. Bouveault, l. [2] 51, 173). Liquid. Valerie acid CMe, CO.H. Tri-methyl-acetic cid, [35°]. (163.5° i.V.). S.G. 22 005. S. 2.2; 20°. Heat of neutralisation: Gala. Werner, l. 1914. 12, (2) 46, 801. Formed by heating its nitrile ith alcoholic potash or conc. HGlAq at 10° (Butleroff, A. 165, 322; 170, 151; 173, 355; 1. 5, 478). Formed also by action of CrO, on inacolin (Friedel a. Silva, B. 6, 146, 826) and n wi-methyl-pyruvic acid (Glücksmann, M. 10, 77). Monometric crystals. Does not yield a romo-derivative on heating with Br, either lone or in presence of P (Reformatzky, B. 23,

D90).
Salts.—NaA'&aq. Prisms, v. sol. water.—
H.A'. Needles, fh. sol. water.—Ca\(\frac{1}{2}\) 5aq.—s
aA'\(\frac{1}{2}\) aq. S.\(\frac{2}{2}\) at 19.—SrA'\(\frac{1}{2}\) 5aq.—BaA'\(\frac{1}{2}\) 5aq.—ZaA'\(\frac{1}{2}\) at 2° (Landau, M. 14, 767).—MgA'\(\frac{1}{2}\) 8aq.—ZnA'\(\frac{1}{2}\) aq. S. (of ZnA'\(\frac{1}{2}\)) 1'' at 20°. The cold aturated solution becomes filled on warming

with a solid salt, which dissolves up again on cooling.—PbA',--PbHA's: needles.—CuA'aq: greenish pp.—AgA'. S. 1·1 at 1°; 1·27 at 27°

(Stiasny, M. 12, 599).

Methylether MeA'. (101°) (Butleroff).

Ethylether Eth'. (118.5° i,V.). 9 .875.

Test-butyl ether C.H.A'. (135° i.V.).

Amyl ether CMe, CH.A'. (165°) (Tissier,
Bl. [2] 24, 589).

Chloride CMe, COCl. (106°).

Anhydride (CMe, CO).O. (190°).

Anide CMe, CO.NH₂. [154°]. (212°).

Formed by heating the aumonium salt in sealed tubes & 230° (Famchimont a. Klolbie, B. T. C. tubes at 230° (Franchimont a. Klobbie, R. T. C. 6, 238). Long needles. Decomposed by pure HNO, (S.G. 1-53) with evolution of N.O.

Methylamide CMe, CO.NHMe. 191°1. (204°).

Dimethylamide CMe_xCO.NMe_x. (186°). Ethylamide CMe_xCO.NHEt. [49°]. (204°). Diethylamide CMeg.CO.NEt_x. (203°). S.G. 15 ·891.

Nitrile CMesCN. Tert-butyl cyanide. [16°]. (106°). Formed, together with a polymeride (160°), by the action of tert-butyl iodide on dry potassio-mercuric cyanide below 5° (Butleroff, A. 170, 151; Freund a. Lenze, B. 23, 2806; 24, 2161). Crystalline mass with pungent smell. On heating with aniline hydrochloride it yields phenyl-valeramiame, which forms an oxalate [192°]. Hydroxylamine forms the amidoxim CMe, C(NH.): NOH [116°].

References .- AMIDO-, BROMO-, CHLORO-, IODO-, NITROS, NITROSO-, and OXY- VALERIC ACIDS. 12-VALERIC ALDEHYDE

CH. CH. CH. CH. CHO. (103°) S.G. 11 819. Formed by distilling calcium n-valerate with calcium formate (Lieben a. Rossi, A. 159, 70; Zander, A. 224, 81).

Zanner, A. 224, 51).

Isovaleric aldehyde (CH₂),CH.CH₂.CHO.

Valeral. Mol. w. 86. (92·5°). S.G. 18 8041;
25 7921 (Perkin, C. J. 45, 477). µ_B 1·3934,

R. 40·66 (Brühl). V.D. 43·08 (calc. 43)
(Schröder, B. 4, 400, 468). S.V. 118·5. Formed by oxidation of isoamyl alcohol (Dumas a. Stas, A. Ch. [2] 73, 145; Parkinson, A. 90, 114; Kolbe a. Guthrie, A. 109, 296). Formed also by distilling calcium iso-valerate with calcium formate (Limpricht, A. 97, 370), by the distillanormate (LIMPPICEN, A. VI, 570), by the distillation of isovalerates (Chancel, A. 60, 318; Ebersbach, A. 106, 262; Schmidt, B. 5, 600), by oxidation of gluten (Keller, A. 72, 84) and castor oil (Arzbächer, A. 73, 202), and by the action of

SO, on leucine (Schwanert, A. 102, 226).

Properties.—Neutral oil, with pungent fruity odour. Polymerises on keeping. Mixes with alcohol and ether. On heating with ammonium sulphocyanide it yields a dark-red liquid, sol. alcohol ether, and HOAc (Brodsky, M. 8, 87). Alkaline sodium nitroprusside gives a violet-red colour, destroyed by HOAc (Von Petto, A. 267, 876). Combines with sodium bisulphite, form-

ing (O,H,₀O)NaHSO,
Reactions.—1. Readily oxidised to valerio
Reactions of the forms mono and dischloroacid.—2. Chlorine forms mono- and di-chloro-valeric aldehydes, and, at 140°, oily C.H., Cl.O. (204°), which is converted by alcoholic soda into C_1H_1 , C_1 , C_2 , C_3 , C_4 , C_5

valerate and other bodies (Fittig, A. 117, 68) .-6. Sodium-amalgam and water slowly form isoamyl alcohol (Wurtz, A. 134, 201).—7. Sodium isoamyl alcohol (Wurtz, A. 134, 201).—7. Sodium forms isoamyl alcohol, sodium valerate, decyl alcohol $C_{16}H_{12}O$ (203°), an oil $(C_{16}H_{13}O)_a$ (250°–290°), the compound $C_{16}H_{19}O_{1a}$, cand the acid $C_{16}H_{19}O_{2}$ (Borodin, Z. 1864, 553; E. 5, 480).—8. KOH at 0° produces an oily polymeride, lighter than water, not capable of combining with NaHSO, and yielding isovalgric aldehyde and the compounds $C_{16}H_{16}O$ and $C_{26}H_{26}O$, on distillation (Borodin, B. 6, 982). This polymeride, left in contact with Na₂CO₃Aq, 57ten forms needles of C₂₆H₁₆O, [70°2,—9. Heating forms needles of C₂₀H₁₂O₃ [70°] —9. Heating with KOH forms the aldehyda C₁₀H₁₈O and a compound C₂₀H₁₈O₃ (260°-290°). S.G. '90.— 10. Heating with sinc at 1806 forms decenoic aldehyde $C_{10}H_{11}O$ (190°), S.G. 2 862 (Riban, C. R. 75, 96; Kekulé, A. 162, 77) and other products.—I1. ZnEt, produces the oil $(C_{10}H_{11}O)$, in large quantity (Beilstein a. Rieth, A. 126, 242). ZnMe2 followed by water, forms methyl-isobutylcarbinol (Kuvsinoff, J. R. 1887, 204).—12. Dry carbinol (Kuvsinoii, J. H. 1881, 2041,—12. Dry K₂CO₂ at 50° forms an oily polymeride, which is reconverted at 180° into the aldehyde. Bodling with K₂CO₃ yields C₁₀H₁₀O (v. supra), C₂₀H₃₀O₂ (265°-270°), and C₁₃H₂₀O₂ (235°-240°) (Gass a. Hell, B. 8, 369).—13. Dry K₂CO₃ added to moist incovaluric additional forms efter some days isovaleric aldelyde forms, after some days, crystals of a polymeride [84°], which is reconverted at 108° into the original aldehyde. Converted 105° into the original aldenyde, (Bruylants, B. 8, 414).—14. PH, I forms a compound (C₂H₁₀O),PH₄I, crystallising from ether in plates [119°], converted by cold potash into (C₂H₁₀O),PH₂OH, crystallising in prisms [125°], insol. water (De Girard, A. Ch. [6] 2, 33; C. R. 94, 215).-15. On heating with hypophosphorous acid in an atmosphere of hydrogen the compound (C₂H₁₀O₃H₂PO₂ [160°] is formed. It yields BaA'₂aq (Ville, C. R. 109, 71).—16. AcCl at 100° combines, forming chloro-amyl acetate C,He.CHCl,OAc (Maxwell Simpson, Pr. 27, 120). 17. m.-mido-benzoic acid forms C₁₁H₁,NO₂ c. 430°].—18. Dry HCl forms (C₁H₁,CHCl)₂O (180°) (Bruylants, B. 8, 414).—19. Conc. NH₂Aq forms isovaleric aldehyde - ammonia C₂H₂.CH(NH₂)OH 7aq [58°] (Erdmann, A. 130, 211; Petersen, A. 132, 158; Ljubavin, B. 6, 1460). 1460), which yields, on allowing its alcoholic solution to stand, or on boiling with potash, the solution to stand, or on boiling with potash, the oily 'throxyamylamine' C₁H₃₃NO₃, fortaing B'HCl [113°] and B'₂H₄PtCl₃. AgNO₃ seacts with isovaleric aldehyde-ammonia, forming (C₂H₁₁N)₂AgNO₃ and (C₂H₁₁N)₃AgNO₃ (Goldschmidt, B. 11, 1200; Mixter, J. 1878, 438).—20. Alcoholic NH, at 150° forms valeritrine, hydrovaleritrine, and other bodies. Valeritrine, C. H. N. is a very notable liquid (250°. nydrovalentrine, and other bodies. Valeritrine C₁₂H₂₁N is a very unstable liquid (250°–260°), yielding B'HHgCl₂ [88°], B'₂H₄PtCl₄, and B'C₁H₂N or C₁H₃N is a liquid, yielding crystaline B'HCli₄, B. 2-87 at 22°, not melted at 180° (Ljubavin, B. 6, 565).—21. H₂S passed into an aqueous solution forms thiovaleric aldehyde CHS (69°) An isomerica (115°) is get to C.H., S [69°]. An isomeride (115°) is got, to-gether with a polymeride [94.5°], by heating gener with a polymeride [947], by heating isovalegit aldehyde with sulphur at 250° (Barbaglis, B. 18, 1574; 17, 2654; G. 11, 95; 16, 426).—22. CS, and NH_AAq form carbovaleraldine C, H_m, N_S, (Schröder, B. 4, 469; Mulder, A. 168, 237), which melts at 109°

(Guareschi, A. 222, 811).—28. NH_BGS.OEt and HCl form C₂H₁₆(NH.CS.OEt), [108°] (Bischoff, B. 7, 1078).—24. H₂Se passed into an agneous solution of valeric aldehyde forms C₄H₁₆Se [56:5°].—25. Acetons and dilute NaOH yield Pr.CH₂CH:CH:CC.CH₄ (180°) (Barbier a. Bou-

veaut, C. R. 118, 198).

O x im C.H., CH:NOH. Mol. w. 101. (163°).
S.G. ³⁰ *8934 (in vacuo): μ_D 1 *437 (Petraczek, B. 15, 829; Trapesonzánz, B. 26, 1428). It is a syn. oxim, because it yields valeronitrile when mixed with Ac,O and ether (Dollfus, B. 25, 1915).

Isovaleric orthaldehyde. Amylidene glycol. Acetyl derivative C, H, CH(OAc)2. (195°). Formed by heating isovaleric aldehyde with Ac.O at 200%

Bensoyl derivative C₄H₂.CH(OBz)₂. [111°]. (264°). Formed by heating the aldehyde with Bz₂O at 260° (Guthrie a. Kolbe, A. 109, 298).

Di-methyl ether C,H, CH(OMe), (124°). S.G. 10 .852. Formed from isovaleric aldehyde S.G. 12 852. Formed from isovaleric aldehyde (2 vols.), MeOH (5 vols.), and HOAc (1 vol.) (Alsberg, J. 1864, 486).

Di-ethyl ether C₄H_n.CH(OEt). (168°).

S.G. 12 835. Formed in like manner.

Di isoamyl ether C₄H₉CH(OC₅H₁₁)₂ (c. 248°). S.G. ² ·849. Ethyl isoamyl ether

C.H. CH(OEt)(OC, H.1). (c. 205°). S.G. 12 ·875. Formed by the action of Na on an ethereal solution of isovaleric ether (Greiner, Z. 1866,

Valeric aldehyde CHMeEt.CHO. Formed by reducing tiglic aldehyde with iron and HOAc (Herzig, M. 3, 123; Lieben a. Zeisel, M. 7, 56), and by warming CH.:CH.CHEt.OH with dilute (1 p.c.) H₂SO₄ (Kondakoff, J. R. 20,

154).
Valeric aldehyde CMe, CHO. [3°]. (75°).
S.G. 12 .7927 (Tissier, Bl. [2] 24, 558).
Di - isovaleric aldehyde v. DECENOIG ALDE-

Reference .- DI-BROMO-, CHLORO-, IODO-, and OXY- VALERIC ALDEHYDE.

VALEROGUANAMINE C.H., N. i.c.

PrCH, C:N.C(NH) NH.C(NH) Butylguanamine. . [173°]. Formed by heating guanidine isovalerate (Bandsowski, B. 9, 240; Haat, J. pr. [2] 43, 76). Flat plates (from water). Weak base.—B'HCl: needles, v. sol. water.—B'H, SO,.—B'AgNO,. VALEROLACTIDE v. OXY-VALERIO ACID. -B'HCl:

VALEROLACTONE v. OXY-VALERIC ACID. VALERONE r. DI-ISOBUTYL REPONE. VALERONITRILE v. Nitrile of VALERIO

VALEROVALERIC ACID v. VALERAL

VALERY ACETOPHENONE TO PHENYL CIPHINO STATE OF THE COLOR OF THE COLOR

BUTYL METHYLENE RETONE.

VALERYL CHLORIDE v. Chloride of VALERIC

ACED.

VALERYL-CYANAMIDE v. CYANIO ACIDS.

VALERYL-CYANAMIDE v. PENTINENES and also BRORO- and DI-GHLORO-VALEBYLENE.

VALERYLENE TETRABROMIDE v. TETRA-BROWO-PENTANE.

VALERYLENE HYDRATE v. PENTENYL ALCOHOL

HYDROCHLORIDE VARERYLENE CHLOBO-AMYLENE.

VALERYL-VALERIC ACID. Ethyl ether C₁₂H₂₂O₃ i.e. CH₂Pr.CO.CHPr.CO₂Et. (206°) at 722 mm. Formed by the action of sodium on isovaleric ether (Greiner, Z. 1866, 461; Wohlbruck, B. 20, 2335). il, sol. alcohol and bruck, B. 20, 2335). ether.

VALYLENE C.H. Mol. w. 66. (50°). A product of the action of alcoholic potash on valerylene dibromide (Reboul, A. 135, 372). Liquid, with odour of garlic and prussic and. Ammoniacal Cu₂Cl, ppts. yellow C₂H₂Cu, which yields the pure hydrocarbon on treatment with dilute HClAq. Bromine at 0° forms crystalline C₂H₂Cr₂. Ammoniacal AgNO, yields a white pp. of C.H.Ag.

VANADATES v. VANADIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 851.

VANADIC ACIDS v. VANADIUM OXYACIDS, p. 851.

VANADIUM. V. At. w. 51.2. Mol. w. not Melts at a very high temperature; probably higher than m.p. of Mo, which does not melt at 1700°-1800° (Moissan, C. R. 116, 1225). S.G. 5.5 at 15° (Roscoe, T. 1869, 679). For emission-spectrum, obtained by using electric

sparks, v. Thalen (A. Ch. [4] 18, 243)

Historical.—In 1801 Del Rio announced the discovery of a new metal in a lead ore from Zimapan in Mexico (G. A. 71, 7); to this metal he gave the name erythronium, but at a later time he thought the metal was only impure chromium. In 1830 Sefström found a new element in the bar-iron and refinery slags where iron-ore from Taberg in Sweden was smelled (P. 21, 43); this element he called vanadium (from a Scandinavian deity Vanadis). In the same year (P. 21, 49) Wöhler found that the lead ore examined in 1801 by Del Rio contained lead vanadate; and he showed that the metal which Del Rio had called erythronium, and had then supposed to be impure chromium, was really wanadium. In 1831 Berzelius supposed he had prepared vanadium by heating an oxychloride in NH, and also by heating the highest oxide with K (P. 22, 1); but in 1867 Rescoe (T. 1863, 1; 1869, 879; v. also 1870, 317) showed that one of the substances which until then had been taken to be the element V was a nitride, and that another substance, taken to be V, was an orgice of this element. Roscoe obtained pure V by heating VCl₂ to redness for many hours in dry H. Roscoe was led to doubt the accuracy of the statement of the properties and at. w. of V that had been accepted on the authority of Berzelius, because he found that several compounds of V and Pb were isomorphous, but that, it was impossible to assign comparable formulato these compounds if the at. w. given by Berzelius for V were accepted (v. T. 1868. 1 et seq.).
Berzelius gave the value 68.5 to the at. w. of
V; he assigned the formula VO, VO, and VO,
(O, 8) to the three offles, and classed V with
Cr. Mo, and W. Roscoe's researches showed
that the at. w. of the metal is 51.2, that the
sxides are best represented as V,O, V,O, and
V,O, that the substance thought to be V,was it was impossible to assign comparable formula

really chiefly V₂O₂, that the compound supposed by Berzelius to be VCl₂ was VOCl₂ and that V must be classed with P and As.

Occurrence.—Small quantities of compounds of V are found fairly widely distributed; the element does not occur uncombined. The chief minerals that contain V compounds are mottramite (Cu-Pb vanadate), descloisite (Pb-Zn vanadate), dechenite (Pb-Zn-Cu vanadate), roscocite (Al vanadate with K silicate), vanadinite (vanadate of land with lead chloride), and some other minerals, which generally contain vanadates of Cu, Pb, Zn, or Ca, Small quantities of compounds of V are found in all pisolitic limonites (Böttger, C. C. 1873. 514), in some pitchblendes, clays, and basalts, and in a few other rocks. Compounds of V have also been found, in small quantities, in the slag from copworks (Karsten, P. 52, 629; Witz a. Osmond, Bl. [2] 88, 49); in many specimens of pig-iron (v. Riley, C. J. 17, 21; cf. Hodges, C. N. 26, 238; Walz, Am. Ch. 6, 453; in some meteorites (v. Apjohn, C. J. 27, 104); in contributed with a state of the contributed o in caustic soda and sedium phosphate (Schöne a. Rahmelsberg, B. B. 1864. 681; Donath, D. P. J. 240, 318); and according to Lockyer (Pr. 27, 279), probably in the sun.

Preparation.—1. From the refinery slag of the Taberg iron-ore. The finely-pow-dered slag is heated with KNO, and Na.CO, the fused substance is digested with boiling water, and solution of a salt of Ba or Pb is added to the filtered liquid; the ppd. Ba or Pb vanadate is decomposed by boiling with a slight excess of H2SO, Aq, and the solution is filtered from BaSO. or PbSO,; the filtrate is neutralised by NH,Aq and concentrated, and pieces of NH Cl are placed in the liquid until some NH Cl remains undissolved; the NH, VO, which is thus ppd. as a white crystalline powder is washed with conc. NH,ClAq, and then with alcohol, and is then decomposed by heating strongly in an open vessel, whereby V₂O₅ is produced (Berzelius, P. 22, 1). Wöhler (A. 78, 125) employed a very similar process for preparing V₂O₅ from timonite.—2. From vanadinite. L'Hôte (C. R. 101, 1151) recommends to mix finely-powdered vanadinite (approximately 3Pb, V₂O, PbCl₂) vanadinite (approximately 3Pb,V₂O₃.PbCl₂) with four times its weight of lampblack and a with four times its weight of imposes and a little oil, to heat strongly in a closed vessel, and then to heat to 300° in a stream of dry Cl, whereby VOCl, is formed, and distilled over into a cooled U-tube; other compounds of V are readily prepared from VOCl,—3. From the cobalt-ore of Mottram in Cheshire. This source of V compounds was discovered by Poscoe (v. C. J. [2], 6, 326). The Cheshire Keuper sandstone contains carbonates of Cu, carbonate of Pb and galena, black cobalt-ochre, fron oxides, and salts of As, Ag, Ma, and Ba. The compound of V was probably vanadinite.
The sandstone was crushed, and the metallic compounds were dissolved by HClAq; bleaching powder and milk of lime were added till the reaction was alkaline; and it was from the pp. thus obtained that Roscoe prapared a and its compounds. The lime pp. con-tained chiefly As, Cu, Fe, Pb, V, and Ca in combination with SO, and PO,; it was heated in a furnace with ground coal to remove As, then roasted with a quarter its weight of Na, CO,

and lixiviated with water; the solution was saturated with H.S and filtered, and H.S was boiled off; crude oxide of V was then ppd. by NH_Aq; the oxide was dried and heated with cone. HNO_Aq to oxidise it to vanadic acid, which was then boiled with saturated (NH_)_CO_Aq, and the somewliat soluble NH_ vanadate was crystallised from water, and then strongly heated in an open vessel; the V_O, thus obtained was suspended in water, into which NH, was passed; the solution of NH_ vanadate was filtered from silica, phosphates, &c__evaporated to dryness, and heated in an open vessel until V_O, remained.

The metal vanadium is paspared by reducing VCl₂ in H (for preparation of VCl₂ v. Vanadium disciplinations, p. 844). The process is conducted in perfectly pure and dry H; every trace of moisture and air must be excluded. The pure and dry H is passed for 12 hours through a porcelain tube, connected (by specially arranged paraffin-joints) by a glass tube, to the H apparatus; the VOl₂ is then placed in the porcelain tube (a special arrangement for loing this is desgribed by Roscoe), and H is passed through the apparatus for 6 hours. The porcelain tube is then gradually heated to full redness, and the passage of H is continued so long as HCl is given off, after which the tube is allowed to cool for several hours in the stream of H. The process occupies from 40 to 80 hours according as from 1 to 4 g. of VCl₂ are used. The V thus obtained contains traces of H and O. Reduction proceeds more quickly at a white heat, but the product is not so pure; it generally contains c. 95 to 96 p.c. V. (For details, and figures of the apparatus, v. Roscoe, T. 1869. 679; 1870. 317; or C. J. [2] 8, 344; 9, 23.)

Moissan (C. R. 116, 1225) obtained V containing from 17.5 to 25.7 p.c. C. by heating a minute of the contains trace of the contains trace of the contains trace of the contains trace.

a. Moissan (C. R. 116, 1226) obtained V containing from 17.5 to 25.7 p.c. C, by heating a mixture of C and one of the oxides of V in an electric furnace, using a current of 70 volts and 1,000 ampères; with a current of 70 volts and 850 ampères reduction proceeded very slowly.

Sio ampères reduction proceeded very slowly.

Vanadium, mixed with V₂O₃, was obtained by Roscoe (l.c.) by strongly heating a mixture of one of the chlorides of V with Na in an atmosphere of H, and lixiviating with water; the admixed black, powdery V₂O₃ can be removed from the heavier, grey, lustrous, metallic powder, by repeated washings with water, and a substance containing c. 91 p.c. V can be obtained.

The substance supposed by Berzelius (P. 22, 1) to be V, and obtained by heating V₂O₃ with K, was shown by Roscoe to consist chiefly of V₂O₄. The black powder which Uhrlaub (F. 108, 134) prepared by heating V oxychloride in NH₂, ar I which he supposed to be V, was found by Schafarik (W. A. B. 38, 5) to be VN₂ (cf. Roscoe, l.c.). Properties.—A light-grey, lustrous powder; under the microscope at 3 seen to be composed

Properties.—A light-grey, lustrous powder; under the microscope at 3 seen to be composed of crystalline, silver-white particles. Does not become coherent and dense when strongly compressed. S.G. 5.5 at 15°. Not magnetic. Is not oxidised in, air at the ordinary temperature, nor by moistening and then drying in vacuo. Has not been melted, except perhaps when reduced from the oxides by C in an electric furnace (v. Moissan, C. R. 116, 1225). When powdered V is thrown into a Bunsen flams it burns brilliantly; when strongly heated in O it forms

V₂O₂; and when slowly heated in air it perhaps forms V₂O, then V₂O₂, V₂O₄, and finally V₂O₂. Burns in Cl., forming VCl.; combines with N to form VN; also combines with N V is insoluble in HClAq; it dissolves in hot conc. H₂SO₄ and in HNO₂Aq. V dissolves in molten NaOH, giving off H, and forming st vanadate. V acts on glass vessels in which it is heated, forming a compound with Si; it also alloys with Ph(R₁, L₂C₄).

forming a compound with St.; it also alloys with Pt (R., I.c.).

The at. w. of V has been determined (1) by reducing V₂O₂ to V₂O₃ by heating in H (Berzelius, P. 22, 15 [1831]; Rossoe, T. 1868, 8); (2) by oxidising, V₂O₃ to V₂O₃ by HNO₃ (B., I.c. [1831]); (3) by analysing (V₂O₃)(SO₃)₂4H₂O (B., I.c., p. 18 [1831]); (4) by ppg. VOCl₃ by AgNO₂Aq, removing excess of Ag from the filtrate, evaporating to dryness, heating, affil weighing the V₂O₃ produced (B., I.c. [1831]); (5) by determining the weight of Ag required to ppt. the Cl from VOCl₃; also by weighing the AgCl ppd.; also by filtering from AgCl, evaporating, and weighing the V₂O₃ obtained (Roscoe, T. 1868, 23); (6) by determining V.D.s of, and analysing, VCl₄ and VOCl₃ (g. v.). The results obtained by Berzelius (with the necessary corrections on account of the wrong formulæ used by him; v. Roscoe, I.c.) gave values for at. w. of V varying from 49·3 to 52·5; Roscoe's values from the reduction of V₂O₃ to V₂O₃ varied from '51·13 to 51·55, and from the analyses of VOCl₃ from 50·32 to 51·877. The S.H. of V has not been determined.

S.H. of V has not been determined.

Vanadium is both metallic and non-metallic in its reactions. V₂O₄ interacts with attong acids to form divanadyl salts, V₂O₄(SO₄), &c.; hypovanadates V₂O₄(DM), are also derived from a hydrate of V₂O₄; V₂O₅ interacts with conc.

H.SO₄ to form V₂O₄, SSO₅ and V₂O₅2SO₂, xH₂O;

V₂O₅ also forms V₂O₅, H₂O (=HVO₂) and V₂O₅, 2H₂O (=HV₂O₂), which react as acids, and salts of the acid H₂VO₄ are also known;

V₂O₅ also combines with various acidic oxides (P₂O₅, MO₅, &c.) and basic oxides, to form complex, salt-like compounds. The sulphides of V dissolve in alkali sulphide solutions; several thiovanadates have been isolated, e.g. (NH₄)₄VS₄; and also thio-oxyvanadates, e.g. Na₄VS₂O. The haloid compounds of V are generally decomposed by water to oxyhaloid compounds.

Vanadium is placed in Group V., with N, P, As, Nb, Sb, Di, Er, Ta and Bi. V is the second member of the even series family of this group, the family consisting of N, V, Nb, Ta and an unknown element with an at. w. between those of Th (-232) and U (-239). Group V does not show a marked division into families; the gradation of properties from N to Bi is fairly regular, nevertheless the families (1) N and P, (2) W, Nb and Ta, (3) As, Sb and Bi are distinctly indicated. No hydrides of members of the vanadium family have been isolated with exptainty. The highest oxides, M₂O₃ are salforming; all of them interact with alkalis to form salts containing the elements M in the acidic radicles; V₂O₃ also forms basic salts (VO)₂R_p, with strong soids; normal salts have not been obtained by the reactions of M₁O₃ with acids. Oxyacids of V, viz. H7O₃ and H₁V₂O₃, have been isolated, but definite oxyacids of Nb and Ta are unknown. Both Nb and Ta form chlorides, corresponding with their highest

oxides M.O.; but the highest haloid compound ornose myo, we are migress matter compounds of V is VX, corresponding with V₂O, coxysholid compounds of V of the form of VX, exist (VOCl₂, VOBr₂) (v. Nitreger Group of Elements, vol. iii. p. 571).

In cognidering the relations between vanations of the constant of

dium and the elements of Group V., the position of V in series 4 must be taken into account: as compared with the elements that form series 3, in which series P is placed, the elements, of the vanadium series are metallic (V is preceded by Ti, Sc. Ca and K, and is followed by Cr. Mn. and the iron elements); the elements of the vanadium series are nearly as metaltic, and also as non-metallic, as Rb, Sr, Y, Nb, Mo, -, and the Ru metals, which elements form series 6, i.e. the niobium series. Hence V would be expected to be distinctly more like a metal, in its chemical relations, than P, and about equal to Nb in its metallic and non-metallic tendencies. As V is the second member of the even series family of Group V., it might be expected to resemble N, which is the first of the even series elements of this group; but it is to be remembered that the differences between the first and second even series members of the groups (i.e. the differences between Li and K, Be and Ca, B and Sc, C and Ti, N and V, O and Cr, F and Mn), become more marked in passing from Group I. to Group VII., and it is also to be remembered that the resemblances between the first even series members and the succeeding odd series members, become more marked as the atomic weights increase; F is more like Cl and Br than O is like S, Se, . and Te; but O resembles S, Se, and Te more than N resembles P, As, Sb, &c.; and C is more like Si, Ge, Sn; &c., than B is like Al, Ga, In, &c.; but C less resembles Si, &c., than N resembles P, &c.

Reactions and Combinations .- (Roscoe, T. 1869. 679; 1870. 317.) 1. Heated in air, V burns to V₂O₄; lower oxides are first formed if the temperature is low. - 2. Does not decompose water at 100° .- 3. Heated to redness in chlorine water at 100°.—8. Heated to redness in chloring burns to VCI,; heated in bromine produces VBr,; does not combine with iodine.—4. Heated with excess of sulphur, V forms V,S, (v. Kay, C. J. 37, 728).—5. Heating in a stream of pure nitrogen produces VN.—6. V combines directly with stition and also with flatinum.—7. Molten polash or sola dissolves V, forming an alkali vanadate and giving off H.—8. V dissolves in combination of the conc. sulphuric acid (? forming a vanadyl salt); also in nitric acid, probably forming a basic nitrate; also, slowly, in hydrofluoric acid (? forming VF.).

Detection and Estimation .- Small quantities of compounds of V give a colorrless borax of microcosmic salt bead in the outer flame, becoming green in the reducing flame; if much, V compound is present the bead is yellow in the blue; after reduction the solution bleaches indigo very rapidly, and soon absorbs O. Solutions of vanadates, either neutral or acidified by acetic acid, give finely-divided black pps. with tincture of calls, and the liquids appear like ink.

When an acidified solution of a vanadate is shaken with an ethereal solution of H₂O₂, the latter solution becomes dark red (Werther, J. pr. 88, 195).

Vanadium is generally estimated by convertvandum is generally estimated by converting it into an ammonium salt, strongly heating this in air, and either weighing the V₂O, thus produced or heating in H and weighing the V₂O₃ that remains. For a volumetric method of estimating V²v. Gerlach (B. 10, 1216).

Vanadium, acidə of, v. Vanadium oxfacids, and

SALTS AND DERIVATIVES THEREOF, p. 851.
Vanadium, bromides of. Only one bromide of V has been obtained.

VANADUM TIBERONIDE VBr., Mol. w. not known; from analogy of PBr., AsBr., &c., the formula VBr., is probably molecular. Formed by heating Vor-VN to redness in vapour of Br. Also by passing Br vapour over a mixture of Also by pussing Br vapour over a mixture of v_{2} 0, and C kept at a red heat; VOBr, is formed, then VOBr, and then VBr, sublimes (Roscoe, T. 1870. 317). Usocoe (L.c.) recommends to prepare VBr, by placing pure VN in a porcelain boat in a tube of hard glass, driving out all air by dry CO., then passing vapour of Br through the tube while that part where the boat is placed is heated to redness, when brown vapours are given off and condense on the cooler parts of the tube, and finally driving out all traces of Br by a stream of dry CO₂. VBr, is a greyish black, opaque, amorphous, very deliquescent solid; loses Br even in a sealed tube; heated gently for air gives V2O2, and at a higher temperature V2O3. Dissolves in water, without giving off any Br, forming a brown liquid which goes green on addition of a few drops of HClAq; this reaction is said by R. to be characteristic of a salt of V₂O₂.

Vanadium, chlorides of. Three chlorides have been isolated: VCl₂, VCl₃, and VCl₄, V burns when heated in Cl, forming VCl₄, and the other chlorides are formed by reducing VCl, by The V.D. of VCl, has been determined, and the formula VCl, is molecular; the formula VCl, is probably molecular, from the analogy of AsCl., PCl., BiCl., &c.; VCl., AsI., Pl. and BiCl. are the only haloid compounds of the form MX. that have been isolated in Group V.; the mol. w.s of these compounds have not been deter-

mined.

VANADIUM TETRACULORIDE VCI. 192'08. Prepared by Rosco (7. 1869. 601).

Formation.—1. V or VN is heated in Cl.—

The vapour of VOCl₁, mixed with excess of

Cl, is passed slowly over a long layer of sugar-

charcoal heated to redness.

Preparation.—VN is heated to redness in a tube of hard glass, in a current of pure, dry Cl, which must be free from air. The first few drops of distillate are rejected, as they contain traces of VOCl, formed from traces of oxide in the nitride used. Elife dark-red liquid that is formed is saturated with dry Cl, then heated for some hours in a current of elry CO, in a vessel to the containing the property of the proper connected with an upright condenser, and then

fractionated.

Properties and Reactions.—A thick, dark, brownish red liquid; boils at 154° under 760 mm. pressure. •S.G. 18584 at 0°, 18868 at 8°, 18159 at 30°. V.D. 98°1 at c. 200°. Does not solidify at any temperature above -- 18°. Slowly decomposes to VCl, and Cl at ordinary tempera-

tures, more quickly when exposed to light, and rapidly when heated. Gives off white fumes in the air. Dissolves in water, forming a blue solution, which does not bleach; this solution is oxidised by KMnO,Aq to HClAq and V,O,Aq. 2VCl, taking up O. Reacts violently with alsohol and ether, torming deep-boloured liquids. When heated with Br in a sealed tube, VCl, is formed. VCl, does not combine with Cl to form a higher chloride. H2S reacts with VGI, to form

a higher chloride. H₂S reacts with VGl₄ to form VCl₂, HCl, and S (Kay, C. J. 38, 736).
VANDIUM TRICHLORIDE VCl₂. Mol. 4v. not determined, but formula is probably molecular from analogy of PCl₃. AsCl₃. &t. Prepared by heating VCl₄ in a retort as leng as Cl is given off, and heating the residual solid to 160° in a stream of dry CO₂ (Roscoe, T. 1869, 691). Also by heating pure V₂s, in a stream of dry, air-free Cl, separating S₂Cl₂ by repeatedly distilling the liquid product, and heating the residue at 140° in dry CO₂ to remove the last traces of S Cl. in dry CO₂ to remove the last traces of S₂Cl₂ (Halberstadt, B. fo, 1619). Lustrous, peach-blossom coloured tablets, resembling CrCl₂; S.G. 8.0 at 18°. Deliquesces very rapidly in air to a brown liquid, which goes green on addition of a drop or two of HClAq; this solution is oxidised by KMO,Aq, 2VCl, taking up 2O, to HClAq and V₂O₂Aq. Soluble in alcohol and in ether. Heated in air forms V₂O₃. Heated in H is re-

duced to YCl, and then, gradually, to V.

VANADIUM DICHLORIDE VCl.. Mol. w. not known. Formula possibly V.Cl.. Prepared by passing vapour of VCl., mixed with a large excess of pure, dry H, through a glass tube heated to dull redness. The distillation of VCl. should be slow, and the mixture of vapour of VCl4 and H should be brought at once into the heated part of the tube. Forms applie-green, micaceous, hexagonal plates; S.G. 3·23 at 18° ; very hygroscopic. Dissolves in water, forming a violet solution, which bleaches indigo and litmus, and reacts as a solution of a salt of V_2O_2 . Dissolves in alcohol and in ether. The solution in water is oxidised by KMnO₄Aq to HClAq and V₂O₄Aq, 2VCl₄ taking up 30. Heated in H, is slowly reduced to V; heating to whiteness in

NH, produces VN (Roscoe, l.c.).

Vanadium, ferrocyanide of, v. vol. ii. p. 837. Vanadium, fluorides of. Only one fluoride, VF, has been isolated; there are indications of the existence of a higher fluoride in solutions in conc. HFAq.

VANADIUM TRIFLUORIDE VF. 3H2O. Mol. w. not known; formula probably molecular, from analogy of tritalides of other elements of Group V. Prepared by evaporating a solution of V₂O₂ in HFAQ at 100°, and crystallising from water containing a little HFAQ. A white cryswater containing a name rinay. A wince cays-talline crust, consisting of rhombohedra. Easily soluble in water; solution reacts acid. Insoluble in cone alouhol. Efforesces in air; loses some water at 100°, and all at 130°, with absorption of O; V₂O₃ is formed on heating to redness in air. An aqueous solution reduces Ag salts to Ag, Hg and Cu selts to mercurous and cuprous Ag, Hg and Cu sens to mercurous and cuprous salts; alralis or alkali carbonates ppt. V₂O₂xH₂O from VF₂Aq (E. Petersen, J. pr. [2] 40, 44).

Vanadofluorides. (Fluovariadites.) A number of compounds of the forms VF₂xM²F.

and VF₂.xM¹¹F₂ were obtained by Petersen (l.c.) by adding various fluorides to solutions of V₂O₂.

in HFAq, and crystallising. These salts are generally greenish coloured, and crystalline; most of them are soluble in water, but not in KFAq; they lose water of crystallisation from 100° to 200°. The vanadofluorides may be regarded as salts of hypothetical acids HVF., regarded as saits of hypothetical adus 1.74., H₁VF₈, and H₂VF₈; they may also be formulated as double saits (g. supra). The following saits are described by Fetersen (l.c.):
. Commonium canadoftuorides NH₄VF₄.2aq,

(NH₁)₂VF₃. aq, and (NH₁)₂VF₃.

Cadmium vanadofiuoride CdVF. 7aq (Piccini a. Giorgis, G. 22 [1] 55).

Cobalt vanadofluoride CoVF , 7aq. Nickel vanadoftuoride NiVF, 7aq.

Potassium vanadoftuoride K,VF, aq

Sodium vanadoftuoride Na,V,F,1, aq

2VF,5NaF, aq (7 Na,VF, aq).

Zino vanadoftuoride ZnVF, 7aq (P. a. G.,

l.c.).
Vanadoxyfluorides. (Fluoxyvanadates.) These salts are generally produced by dissolving V₂O₂ in HFAq, adding metallic fluorides, and crystallising; also by dissolving V₂O₃ in solutions of metallic fluorides, and crystallising; some of them are obtained by treating solutions of V2Os in metallic fluoride solutions with reducing agents, and then crystallising. vanadoxyfluorides have been examined by Baker (C. J. 33, 388 [1878]), Ditte (C. R. 105, 1067; 106, 270 [1888]), Piccini a. Giorgis (G. 18, 186 [1889]; G. 22 [1] 55 [1892]), and Petersen (B. 21, 3257 [1888]; more fully in J. pr. [2] 40, 193, 271 [1890]). There are still considerable discrepancies between the results obtained by the different observers. For a criticism of Baker's results v. Petersen (J. pr. [2] 40, 289-92). The vanadoxyfluorides belong to two main classes: (1) those obtained by dissolving Voo, in HFAq, adding a fluoride (or carbonate), and crystaldissolving V_2O_3 in solutions of fluorides, and crystallising; (2) those obtained by partially reducing solutions of V_2O_3 in HFAq, then adding fluorides, and crystallising. The first class of salts may be divided into (i.) those wherein one atom of O in V2Os is substituted by 2F, and which, therefore, are represented as xMF.yVO.F $(V_2O_3, gives \ V_2O_4F_2=2VO_2F)$; and (ii.) those wherein 30 in V_2O_3 is substituted by 6F, and which, therefore, are represented as xMF,yVOF, (V₂O₃ gives V₂O₂F₅=2VOF₃). Salts of the second class are regarded as compounds of MF with VOF2, and VOF2 is looked on as obtained vor, and vor, is looked on as obtained by substituting 20 in V₂O₄ by 4F (V₂O₄ gives V₂O₅F₄=2VOF₂). The salts derived from V₂O₄ i.e. xMF.yVO₅F and xMF.yVOF₈, are often called fluorythroadates, and those derived from V₂O₄ and xMF.yVOF₈ are often called fluorythroadates. V₂O₄, i.e. cMF₂VOF₂, are often called fluory hypovanadates; the former class of salts will here be called vanadoxyfluorides, and the latter hyprbanadoxyfluorides.

Ammonium vanadoxyfluorides. Three salts are described by Baker (C. J. 38, 388 [1878]), and also by Piccini a. Giorgis (G. 22 [1] 55, [1892]; the formulæ given by the different experimenters do not agree.

Lamellar summonium vanadoxystuoride.

This salt was obtained by Baker by dissolving V₂O₂ in NH₄HF₂Aq, and then odding more NH₄HF₂; it separates in small yellow, pearly.

hexagonal plates. P. a. G. obtained the sait by dissolving V₂O₂ in a slight excess of HFAq, adding NH₂F in the ratio 3NH₂F:2V₂O₃, and evaporating. B. gives the formula 6NH₂F.V₂O₄F. If both formula are expressed as 3NH₂F:2VO₂F, then x=13 in Baker's formula and =2 in the formula of P. a. G. A sait obtained by Petersen (J. pr. [2] 40, 193, 271 [1890]), by a similar process to those used by B. and by P. a. G., was formulated by him as 7NH₂F.4VO₂F.HF.

Pyramidal ammontum vanadoxyfluoride. Obtained by Baker by adding NH, HF, to a solution of the lamellar salt; P. a. G. prapared the salt by dissolving V₂O₅ in excess of HFAq, and exactly neutralising the hot solution by NH₂Aq. This salt crystallises in yellow, simple pyramids (Baker). The formula assigned by B. is 12NH,F.V.O.,EVOF., while that given by P. a. G. is 3NH,E.VO.F.; Petersen gives the same formula as P. a. G. If Baker's formula is expressed as 3NH,F.VO.F., x must be put = 13,

and $y = 1\frac{1}{2}$.

Acicular ammoniumvanadoxyfluoride. Baker obtained this salt by dissolving the pyramidal salt in warm HFAq and allowing to cool; P. a. G. prepared it by a similar reaction. This salt crystallises in pale-yellow acicular prisms; when dry it has the odour of HF; it acts on glass. The formula given by P. a. G. is SNH, F.2VOF, ad; Baker assigned to this salt the formula SNH, HF, 2VOF, but his analyses were, admittedly, not very trustworthy.

Adopting the formulæ given by P. a. G. for

the three ammonium vanadoxyfluorides, these salts are represented as

(1) 3NH₄F.2VO₄F = (NH₄)₃V₂O₄F₅ (2) 3NH₄F.VO₂F = (NH₄)₃V₂O₄F₄ (3) 3NH₄F.2VOF₅ = (NH₄)₃V₂O₄F₉.

A few of the other vanadoxytluorides seem to belong to one or other of these types; P.a.G. and also Petersen, describe a potassium vanadoxy-fluoride $8KF.2VO_aF = K_aV_aO_aF$, belonging to the same form as the lamellar ammonium salt. But most of the vanadoxyfluorides described belong to forms which are not represented by the ammonium salts. The following are the principal salts :-

Ammonium salts. 9NH,F.5VOF,3HF; 7NH,F.4VOF,HF (Petersen).

**NH. A. VOT., HF (received).

**Potassium salts 2RF.VO,F; 2RF.VOF;

8KF.2VOF, HF; 4KF.VF, VOF, (P.).

**Sodium salt 3NaF.VOF, VOF, a.] (P.).

Zinc salts. ZnF2.VO,F. 7aq (P. a. G.);

ZnF₂.ZnO.2VOF₃. 14aq (B.). In none of these compounds does the atomic ratio of V to O exceed 1:2. According to Ditte (C. R. 105, 1067; 106, 270 [1889]), many compounds of alkali fluorides with V₂O₃ are formed by heating the constituents together, digesting by heating the constituents together, digesting with water, and crystallising; the atomic fatio of V to O in these compounds, as given by Ditte, is 2:5. The formulæ assigned to the compounds may be generalised & xV₀, yMF; M = K or N₀, x=1,3, and 4, and y + 1,2,4, and 8. Ditte (l.c.) says that crystals of V₀,4NH,F.4aq are obtained by dissolving V₀, in hot cone. NH, Maq, and that this compound is formed, along with V₀O,8NH,F.4aq, when V₂O, is dissolved in cold

cone. NH,FAq; but the experiments of Baker, Piccini a. Giorgis, and Petersen, all agree in assigning to the compounds formed in these reactions, formulæ wherein the atomic ratio of V to O does not exceed 1:2.

Hypovanadoxyfiuorides. (Fluoxyhypovanadates.) These compounds are formed by partially reducing mixtures of V₂O₂ and fluorides, or carbonates, dissolved in HFAq. If sufficient the F is assigned to the metal present to form the normal fluoride, then the atomic ratio of V to the remaining F in these compounds is 1:2, and

the remaining F in these compounds is 1:2, and that of V to O is 1:1; the formulæ are written xMF.yVoF.

All the salts described by Baker and Piccini a. Giorgis, except one, belong to the form 2MF.VOF.

The salt of the formulæ may evidently be yritten M. (orM!)VOF.

Ammonium hipporanadoxy/tuoride

2NH.F.VOF., aq(*= (NH.).2VOF., aq) was propared by Baker (C. J. 33, 395) by passing H.S into a solution of V.O.; in HFAq. concentrating, filtering, and adding NH.F. The same salt was prepared by Piccini a. Giorgis (C. 22 | 1) 55) by electrolytically reducing a solution of NH.YO, in HFAq, after adding NH.F.; also by reducing NH.YO, in HFAq, after adding NH.F.; also by reducing NH.YO, in HFAq, and HFAq, and cutralising by NH.Aq, and HFAq by SO₂Aq, neutralising by NH₂Aq, and adding NH₃F; and in each case dissolving the crystals that were formed (said by P. a. G. to be 3NH,F.VOF2) in hot HFAq, and crystallising. Petersen (J. pr. [2] 40, 196) also obtained this salt. The salt crystallises in clear blue monoclinic forms; a:b = 9653:1 (Baker, l.c.).

Petersen (J. pr. [2] 40, 197) described two other ammonium hypovanadoxyfluorides,

7NH,F.4VOF, 5aq and 3NH,F.VOF '7NH_kF.4VOF_x-faq and 3NH_kF.VOF_x.

The other hypovanudoxyfluorides described by P. a. G. (i.c.) are 2KF.VOF_x and MF_x-VOF_x 2aq where M = Cd, Co, Ni and Zn. The K salt was prepared by reducing V₂O_s in HFAq by SO_xAq and adding KF; the other salts by dissolving MO, or MCO_s, along with V₂O_s in HFAq, and reducing electrolytically. According to Petersen (i.c. pp. 199, 200), the salts 7KF.3VOF_x and SNaF.3VOF_x 2aq also exist.

P. a. G. (i.c.) remark that the tendency to form highly fluorinated compounds increases in

form highly fluorinated compounds increases in the family V, Nb, Ta as the atomic weight inthe tanniy V, No, Ia as the atomic weight increases; thus, VO₂F is not affected by a little HFAq, while Nb₂OF forms NbOF₃, and TaOF₄ is converted into TaF₅. They also point out that the three compounds, ZnF₂,VO₂F. 7aq, and ZnF₂,VF₃, 7aq, all crystallise with the same number of molecules of water, all contain the same number of atoms, have the same crystalline form, and are geometrically iso-

morphous.

VANADUM PENTAPLUONDE VF. According to
Petersen (J. pr. (2) 40, 271), this compound
exists in a solution of V.O. in conc. HFAq. No compound was isolated, nor is any trustworthy evidence given of the existence of VF, in solution.

Vanadium, haloid compounds of. When V is heated in excess of Cl the tetrachloride VCl. is produced; heating in Br produces the trifromide VBr., V does not sombine with I. The haloid compounds of V belong to the forms VX., VX., and VX.; X = Cl in each case, X = Br or F in the one case of VX. The formula VX. is molecular; the other formulæ are probably molecular. VCl. BiCl., AsI, and PI, are the

only dihalides known of members of Group V. Attempts to prepare halides higher than VX, have failed. Solutions in water of the haloid compounds of V behave like solutions of the corresponding oxides in haloid acods; VCl.Aq like corresponding oxides in hatch away vol. Aq like a solution of v.O. in HClAq, VX.Aq like a solution of v.O. in HXAq, and VOL.Aq like a solution of v.O. in HClAq. VCl. is decomposed by heat to VCl. and Cl. and heating VOl. with H produces VCl. VF. combines with metallic fluorides to form vanadofluorides, man v of which fluorides to form vanadoftuorides, finany of which belong to the form Mr₂VF₂ or. Mr¹VF₃ (v. p. 844). Several oxychlorides and oxybromides of V have been isolated: VOX₃ and VOX₂, where X = Cl or Br; also VOCl, Vo₂U₁, and VO₂Cl; the existence of other oxybromides also is probable. No oxyfluoride has been isolated with certainty. But many compounds exist which may be regarded as containing the oxyfluorides VO₂F, VOF₃, and VOF₂ respectively; the compounds VO₂F.xMF and VOF₃.xMF are obtained by dissolving V₂O₂ and fluorides in HFAq and crystallising; they are described as vanadoxyfluorides (p. 844); the compounds VOF₂xMF are obtained by partially reducing solutions of V₂O₃ and fluorides in HFAq, they are described as hypovanadoxyfluorides (p. 845).

Vanadium, iodides of. No iodide of V has been isolated. No reaction occurs when vapour of I is passed over VN heated to redness, nor do I and $V_{\bullet}O_{\bullet}$, react at any temperature (Roscoe, C. J. [2] 9, 28). I does not react with $V_{\bullet}O_{\bullet}$ when digested therewith for a long time in presence of water or alcohol (Guyard, Bl. [2] 25,

Vanadium, nitrides of. V and N combine directly. Two nitrides are known.

Vanadium mononitride VN. Mol. w. not

known. Obtained by heating V in a stream of pure N; also by saturating VOCl, with dry NH., and heating to full whiteness in a stream of white heat in a stream of NH_s. Better prepared by heating NH_qVO_s in the air, and then heating the residue to a full white heat in a stream of dry NH_q (Roscoe, C. J. [2] 8, 844). VN may also be prepared by heating V_qO_s to whiteness in NH_s (R., l.c.). VN is a greyish-brown, metal-like powder; heated in

a greysan-prown, metal-like powder; heated in air it is oxidised to V₂O₂ and then to V₂O₂; heated with soda-lime it gives off NII,.

VANADIUM DINTIRIDE VN... A black powder; exposed to air gives off NII, and is oxidised. Prepared by saturating VOCl₂ with dry NII, heating the solid so obtained in a glass tube distribution. long as NH₂G sublimes, washing the residue with water containing a little NH₃, and drying in vacuo over H₂SO₂ (Roscoe, C. J. [2] 6, 349); examined by Unrlaub, who did not succeed in

examined by Unriaub, who did not succeed in determining its composition (P. 103, 184; cf. Schafarik, W. A. B. 33, 5).

Vanadium, oxides and hydrated pages of. By gently heating V in air the oxide V₂O₂ is possibly farmed, and, off continued heating, oxidation proceeds to V₂O₃, V₂O₃, V₂O₄, and finally V₂O₅. The oxides V₂O₄, V₂O₅, and V₂O₂ are also formed by reducing V₂O₄ by heating with Hor K. Saverel oxides intermediate held. with H or K. Several oxides intermediate between, F.O. and V.O. seem also to exist. The oxides V.O., V.O., V.O., and V.O. are feebly basic; V.O. and V.O. are also be dide. The oxides of V correspond in composition with the oxides of N; corresponding oxides of Bi

are known. The names generally given to the oxides of V do not, unfortunately, tally with the oxides of v do not, unto tamasely, sany wan the names given to the corresponding oxides of N; thus, V₂O₂ is generally called hypovanadous oxide, while NO is called nitric oxide; V₂O₃ is called variadic oxide, while the name nitrogen peroxide is often quite wrongly applied to NO.

The mol. w. of none of the oxides of V is known.

? Vanadium monoxide (? V₂O). When the
powdered metal is ... slowly heated in a powdered metal is ... slowly heated in a current of air it glows brightly, with absorption of oxygen, forming in the first place a brown oxide (V₂O or V₂O₂); and on further heating this oxide again glows, and passes through the black trioxide and blue tetroxide to pentoxide' (Roscoe, C. J. [2] 8, 357). This statement seems to contain all that is known of an oxide lower than V.O.

than V_2O_2 .

VANADIUM DIOXIDE V_2O_2 . (Hypovanadous oxide.) This substance was supposed by Berzelius (P. 22, 1) to be V; Roscoe (T. 1868. 1) proved it to be an oxide with the atomic ratio V:O=1:1. The mol. w. is not known; the formula is generally written V_1O_2 rather than V_2O_3 at the double formula is on the whole VO, as the double formula is, on the whole, more in keeping with the reactions of the compound.

Formation.—1. By heating one of the higher oxides with K (Berzelius, l.c.).—2. By passing vapour of VOCl₃, mixed with much dry H, over red-hot charcoal (Schafarik, A. 109, 85).—3. By strongly heating V₂O₃, and V₂O₄, mixed in the ratio V₂O₄:V₂O₅, out of contact with air (Petersen, J. pr. [2] 40, 193).

Preparation.—A mixture of much dry H and vapour of VOCl. (a. p. 854) is passed through

vapour of VOCl₃ (q. v. p. 854) is passed through

a hard glass tube containing powdered charcoal and kept red hot. Some solid oxychlorides are deposited on the cooler parts of the tube, while the V₂O₂ remains mixed with the C. The contents of the tube are then strongly heated in a current of dry H to remove traces of Cl comrated from the C (Roscoe, C. J. [2] 6, 334). When Zn, Cd, or Na-amalgam is added to a solution of V2O, in H2SO, Aq (prepared by dissolving the oxide in hot conc. acid and diluting with 50 pts. water), the liquid becomes blue, green, and finally lavender. The lavender solution absorbs O very rapidly; exposure to the air for a few seconds causes the colour to change to deep chocolate-brown. By determining the quantity of standardised KMnO, Aq decolourised by the lavender solution, Roscoe (C. J. [2] 6, 834 proved that this solution contained V.O. probably combined with SO. After passing air into the lavender solution until it becomes air into the lavender solution until it necomes permshently blue, the solution contains V_{\bullet} ; if the free acid in the lavender solution is neutralised by zino, and the liquid is then exposed to the air until permanently brown, and slittle acid is then added, a green solution is forthed which contains V_{\bullet} (R. 1.c.).

December and Reactions.—A light-grey.

rommed which contains v_*O_* (K., i.e.).

Properties and Reactions. — A light-grey, lustrous powder; or a lustrous, metal-like, crystalline crust, S.c. 8:64; very brittle; fuses at a very high temperature. eHeated to redness in sir, V₂O₂ burns to V₂O₂; heated in O, burns to V₂O₂. Insoluble in water; disolves in dilute acids, giving a lavender solution, which bleaches strongly: from these solutions KOHAs at strongly; from these solutions KOHAq of

NH,Aq ppts, a brown ayarared oxide, which rapidly oxidises (Brierley, C. J. 49, 824). According to Petersen (J. pr. [2] 40, 194), V,O, dissolves in HFAq, and on evaporation, solution of the residue in water, and evaporation over the ThSO, blue, microscopic crystals are ebtained, which are perhaps, VOF, zaq; no analyses were made. Addition of alkali fluorides to V,O, in HFAq produces various compounds of the form xVOF ... WHY (v. HYPOYANADOXYFLUORIDES, p.

845).

HYDBATE OF VANADIUM DIOXIDE. By adding NH,Aq to a lavender-colbured solution of V,O, φ in H,SO,Aq), Brierley (C. J. 49, 824) obtained a deep-purple gelatinous pp. which he said was hydrated V₂O₂; the pp. rapidly oxidised in the

Vanadium trioxide V_2O_3 . (Vanadous oxides Vanadium sesquioxide.) Mol. w. not known. This compound was represented by Berzelius as

 $\nabla O \ (\nabla - 68.5, O - 8)$

VO (V=68°5, O=8).

Formation.—1. By heating V₂O₃ to redness in H (Schafarik, A. 109, 85). The presence of traces of P₂O₃ prevents reduction (Roscoe, C. J. [2] 6, 331).—2. By heating V₂O₃ in a carbon crucible (Berzelius, P. 22, 1).

Preparation.—Pure V₂O₃ is heated in perfectly pure and dry H until the substance ceases to lose weight: the tube is allowed to coal com-

to lose weight; the tube is allowed to cool completely in H, and then a stream of dry air is passed through it (Roscoe, C. J. [2] 6, 331). When a solution of V_2O_3 in cone. H_2SO_4 is much diluted, and then treated with Mg until the liquid is green, this solution contains V,O,, combined with SO, (v. Vanadous salts, infra). A similar solution is obtained from the lavender solution of V_2O_2 in H_2SO_4Aq (prepared from V_2O_3 in H_2SO_4 , v. supra) by neutralising free acid by zinc, exposing to the air, and adding a little

acid (Roscoe, C. J. [2] 6, 337).

Properties and Reactions.—V₂O₃ is a black powder, resembling graphite; or, formed by reducing VOCl, by H, it is a black, lustrous, crys-illine crust. S.G. 4.72 at 16°. Does not fuse the blowpipe flame. When warm V_2O_3 is exosed to the air it glows and oxidises to V_2O_3 ; and even at the ordinary temperature it takes up the strong of th ',O. (Sabatier a. Sendereus, C. R. 115, 236). leating to redness in H.S produces V,S. (Kay, I. J. 87, 728). V₂O₃ dissolves in hot conc. L₃O₄, forming V₂O₃.∞SO₃ (v. Vanadeus Saltes, Myab, V₃O₂ dissolves in HFAq, and VF₃.№I₂O as been isolated from this solution (v. Vanadum). RIFLUORIDE, p. 844).

HYDRATE OF VANADIUM TRIOXIDE. By adding

Hybrate of vandoum trioxide. By adding (OHAq, or NH₂Aq, to an aqueous solution of 1,0,480,9H₂O (n. infra) Brierley (C. J. 49,824), bitained a dirty green, gelatinous fp., which ridited rapidly in air. According to B., this p. was hydrated V₂O₂.

VANADOUS SALTS V₂O₂.xX (X = acidic raids) or V₃R₂ (Ru = acidic raids). Only one lait derived from an oxyscid fits been certainly solated; it has the composition V₂O₂.4SO₂.xH₂O₃. The formula may be written V₂H₂(SO₂).yH₂O₃. Vanadous thrasulphate, or acid vanadous supplements, or acid vanadous supplements, v₂O₂.4SO₂.xH₂O or V₃H₂(SO₂).yH₂O₃.

A hydrate with x = 3 or y = 2 was obtained

by Gerland (B. 10, 2111 [1877]) by heating a solution of V₂O₄ in a large excess of conc. H₂SO₄ for a long time at 120°, and treating the blue crystalline crust-thus formed (consisting chiefly of V₂O₄.3SO₂.xaq, v. Hypovanadus saltes, p. 848) with boiling water, when V₂O₄.4SO₂.8H₂O remained. G. sppposed that reduction of V₂O₄

remained. G., supposed that reduction of V₂O₄ was effected by dust in the air.

Brierley (C. J. 49, 822 [1886]) prepared
V₂O₃.4SO₄.9H₂O(=V₂H₄(SO₄), 8H₂O) by electrolysing a solution of V₂O₄ in H₂SO₄. The solution was prepared by reducing V₂O₄ in concl.
H₂SO₄. Agater dilution, by SO₂. The deep-blue solution was placed in a Pt digh which formed the negative electrode, and a porous pot containing dilute H.SO.As was arranged so that it just touched the surface of the liquid in the Pt dish; a plate of Pt immersed in the H.SO.As formed the positive electrode. The Pt dish was warmed during the process, so that electrolysis and evaporation proceeded together. Blectrolysis was continued until the liquid was deep green, and a drop placed in a little water showed no trace of blue colour. Conc. H₂SO₄, equal to twice the bulk of the green liquid, was added; after 24 hours the green, sandy pp. was collected, with the green sandy pp. was collected. washed with conc. alcohol, and dried over H₂SO₄ in coal-gas. The salt dissolved in water, and alkali ppd from this solution a dirty-green gelatinous substance, said by B. to be $V_{Q,p,xH,Q}$. This pp dissolved in an aqueous solution of $V_{xQ,p}ASO_{x}9H_{yQ}$, forming a chocolatebrown solution, giving a lustrous green solid or evaporation, which dissolved in water to form a brown solution. B. concluded that the brown solution contained a compound of V₂O₂ and SO₂

solution contained a compound of V₂O₂ and SO₂ more basic than V₂O₂ASO₃.

Gerland (B. 11, 106 [1878]) 4uentions the normal winadous sulphate V₃(SO₂), (-V₂O₂ASO₃) as if he had prepared it; no details are given.

VANADIUM TETROKIDE V₂O₄. (Hypovanadio oxida.) Mol. w. not known. Represented by Berzelius as VO₂(V = 63:5, O = 8).

Fornation.—1. By allowing V₂O₃ to absorb of from the air (cf. Hypovanado-vanado oxida.), 851).—2. By strongly heating a mixture of

O from the air (cf. HYPOVANADO OXIDES, p. 851).—2. By strongly heating a mixture of 5 pts. V₂O₃ and 6 pts. V₂O₃, in absence of air.—3. By the electrolysis of molten V₂O₄ (Buff avoided in a stream of CO₂ (Crow, C. J. [2] 15, 453).

Preparation.—A solution of V₂O₄ in H₂SO₄ obtained by reducing V₂O₅ in conc. H₂SO₄ by SO₂, is ppd. by Na₂CO₂A₃, and the pp. is washed and dried by heating in vacue (Barzallus P. 22.

and dried by heating in vacuo (Barzelius, P. 22, and dried by heating in vacuo (Barzelius, P. 22, 1).—2. V₃O₄ is exposed to the air for some months, until the colour has changed to blue (Roscoe, G. J. [2] 6, 338].—3. V₂O₄ is dissolved in hot cone. HClAq; when Cl ceases to be given off the liquid is saturated with H₂S, filtered from S, evaporated to dryness at 100° and the V₂O₄CD, 22q thus formed is heated to redness in a stream of dry CO₂ (Ctow, l.e. pp. 457, 458).

Properties and Reactions.—A blue, lustrous, crystalline nowder: nemared w heating VO Cl.

Properties and Reactions.—A blue, lustrous, crystalline powder; prepared by heating V₂O₂Cl₃ in CO₂ it forms a dark-green, amorphous powder (Grow, Lc.). Infusible at a high temperature. Insoluble in water. When kept in a loosely-stoppered bottle V₂O₃ gradually absorbs O, forming V₂O₃ (Crow, l.c.). Dissolves easily in acids, forming bright-brue liquids; the same solutions are obtained by the action of moderate

reducers, such as SO,Aq, H,SAq, or H,C,O,Aq, on solutions of V,O, in acids, also by passing air into V,O, in H,SO,Aq until the liquid becomes permanently blue (Roscoe, I.c.; v. infra, HPPO-VANADIC SALTS). Petersen (J. pr. [2] 40, 194) supposed that the blue microscopic crystals he obtained by dissolving V₂O₄ in excess of HFAq and evaporating were VOF₂. xaq, but he did not obtain enough to make an analysis. V₂O₄ dissolves readily in alkali solutions, forming hypo-vanadates, M₂V₄O₅ (q. v. under Vanadotte ox-acids, and salts and derivatives thereof, p. 858)

HYDRATES OF CHYPOVANADIC OXIDE. By adding Na₂CO₂Aq, drop by drop, to₅ a colution of V₂U₄ in HClAq or H₂SO₄Aq, till the supernatant liquid was colourless, filtering rapidly in CO₂, and drying on a porous tile over H₂SO₄ in vacuo, Crow (l.c.) obtained the black, amorphous heptahydrate V₂O₄, 7aq; and on heating this in CO₂ for some hours at 100° he obtained the trihydrate

V₂O₄, Saq.

HYPOVANADIC (or variedyl) SALTS
V₂O₄, xX (X = acidic oxide). Only a few compounds of V₂O₄ with acidic oxides have been studied more isolated. The sulphates have been studied more represented as V₂O₄.2SO₃.yH₂O. The compound V₂O₄.2SO₃ may be called the normal sulphate; V₂O₂,2SO₃ may be called the normal sulphate; the formula may be expressed as V₂O₂,(SO₄), or VO.SO₁,... The compound V₂O₄.3SO₅.6H₄O may be called acid sulphate; the formula may be expressed as V₂O₂,SO₄(SO₄H)₂.5H₂O or (V₂O₂)H₂(SO₄),5H₂O₅, or it may be written V₂O₄.2SO₂,H₂SO₄.5H₂O; When the formulæ of the compounds of V₂O₄ with acidio oxides are written V₂O₄.X the compounds of a compound of the compounds of V₂O₄ with acidio oxides are written V₂O₄.X the compounds of a compound of the compounds of V₂O₄. pounds are generally called hypovanadic salts; when the formulæ are written V₂O₂·xR (R= acidic radicle) the name divanadyl salts is usually given to the compounds; and when these compounds are regarded as VO.xR, it is customary to call them vanadyl salts. Hypovanadic sulphates are obtained (1) by dissolv-

H2SO, and heating to the boiling-point of the liquid for a long time. The salt separated as a green-blue powder; insoluble in water, cold or het; insoluble HClAq and H₂SO₄. (G. does not say how the salt was obtained pure for analysis; no analyses are given of the salt prepared exactly as described above.) Various hydrates are described by G. obtained by different processes. Crow (C. J. [2] 15, 456 [1876]), obtained he heptahydrate by repeatedly treating hexalty fracted trisulphate (v. infra) with absolute alcohol.

Hypovanadic trisulphate, or acid divanadyl Hypovaniaci trisuipnate, or acta avamacy sulphate, V_*O_* 380, xH_*O or $(V_*O_*)H_*(SO_*)_*, yH_*O$ [y=x-1]. (Acta vanadyl sulphate $(VO.SO_4)_*, H_*SO_*, yH_*O.)$ Hydrates with x=4 and 3 (or y=3 and 2) were prepared by Gerland (B. 10, 2, 109); and a hydrate with x=6 (or y=5) by Crow (C. J. [2] 15. 455).

By dissolving V₂O₄ in a large excess of conc. H₂SO₄, heating for a long time at c. 120°, and drying the small, blue, transparent crystals that formed on a porous tile over H₂SO₄, Gerland obtained a substance which gave analytical results approaching those required by the formula V₂O₄.3SO₃.4H₂O. The salt was not obtained quite free from admixed V₂O₃.4SO₃.xH₂O. This tetrahydrate was partially decomposed by cold ing with alcohol and other and drying over H_2SO_4 , had the composition of a trihydrate, V_2O_4 3SO₃3H₂O₄.

Crow obtained a hexahydrate V₂O₄, 3SO₄, 6H₂O₅, by reducing by SO₄ a solution of V₂O₅ in conc. H₂SO₄, heating at 100° for some time, drying the light-blue crystals that separated on a tile, removing acid by washing with ether, and drying by pressure between paper. The crystals deliquesced in air to a blue syrup; they were insoluble in ether, and scarcely soluble in absolute alcohol.

The formulæ of the various hydrated hypovanadic sulphates are as follows :-

Vanadyl sulphates. Hypovanadic sulphates; Divanadyl sulphates; V₂O₂·(SO₄)₂ V₂O₂·(SO₄)₂·3H₂O V₂O₂·(SO₄)₂·4H₂O VO.SO, (Gerland). 2(VO.SO,).3H₂O (G.) VO.SO,.2H₂O (Crow, confirming V₂O₄·2SO₃·3H₂O V₂O₄·2SO₃·4H₂O Berzelius). Berzeitus).
2(VO,SO₄).7H₂O (G., also C.)
VO.SO₄.5H₂O (G.)
2(VO.SO₄).18H₂O (G.)
2(VO.SO₄).H₂SO₄.2H₂O (G.)
2(VO.SO₄).H₂SO₄.3H₂O (G.)
2(VO.SO₄).H₂SO₄.5H₂O (C.) V2O (SO)2.7H2O V2O4.2SO4.7H2O V₂O₂(SO₄)₂,10H₂O V₂O₂(SO₄)₂,10H₂O V₂O₂(SO₄)₂,18H₂O (V₂O₂)H₂(SO₄)₃,2H₂O (V₂O₂)H₂(SO₄)₃,3H₂O ₄(V₂O₂)H₂(SO₄)₅,5H₂O V₂O₄.2SO₃.1H₂O V₂O₄.2SO₃.10H₂O V₂O₄.2SO₃.13H₂O V₂O₄.3SO₃.4H₂O V₂O₄.8SO₃.6H₂O

ing V₁O₄ in hot cone. H₂SO₄ and boiling; (2) by dissolving V₂O₄ in cone. H₂SO₄ reducing by SO₂ dithionate by adding BaS₂O₄Aq to V₂O₂(SO₂)Aq, or H₂CO₄, and evaporating; (3) by dissolving V₂O₄ and evaporating; (3) by dissolving v₂O₄ filtering, and evaporating in vacue: the salt was V₂O₄ in cone. H₂SO₅ and beliling in the air for some time. In reaction (5) V₂O₅, xSO₅ seems to be formed and then partially reduced, by dust or products of combustion of coal-gas, to V₂O₄, xSO₅; the products are mixtures or V₂O₄, xSO₅; the products are mixtures of V₂O₅, xSO₅ and V₂O₄, xSO₅ (Gerland, B. 11, 98).

Hypovanadic disulphate, v₂O₄, xSO₅ or v₂O₇ (SO₂).

(Vanadyl sulphate, V₂O₄, xSO₅ or v₂O₇ (SO₂).

(Vanadyl sulphate, V₂O₄, xSO₅ or v₂O₇ (SO₂).

(Vanadyl sulphate, V₂O₅, xSO₅ or v₂O₇ (SO₂).

(Vanadyl sulphate, V₂O₅, xSO₅ or v₃O₇ (SO₂).

(Vanadyl sulphate, v₄O₅, xSO₅ or v₅O₇ (SO₂).

(Vanadyl sulphate, v₅O₅ or v₅O₇ (SO₂).

(Vanadyl sulphate, v

pounds of V₂O₄ with As₂O₃, B₂O₃, CrO₃, MoO₃, and a few other acidio oxides (#. Lehrbuch [5th ed.] 3, 1053).

VANADUM PENTOXIDE V₃O₄, (Vanadic oxide. Vanadic anhydride.) Mol. w. not knewn. Represented by Berzelius as VO₃ (V=68*5, 0=8).

**Example from -1. By strongly heating any of the company of th

Formation .- 1. By strongly heating any of the lower oxides in air or O .- 2. By heating NH. VO. in air to dull redness.—3. By decomposing VOCl, by water.—4. By heading V₂O₂.4SO₃. 9aq to bright redness (Brierley, C. J.

Preparation .- Pure VOCl, is decomposed by water, and the ppd. V₂O₄ is washed till the washings are free from acid (HClAq is produced) and heated until dry (Schafarik, J. pr. 76, 142). For the preparation of V₂O₃ from vanadinite and other sources of V compounds, v. Vanadium, Pre-

paration of (p. 841).

Properties.—A pale-yellow powder, with a reddish tinge. When heated to full redness out of contact with any reducing agents, V2O3 melts, and solidifies on cooling to a mass of yellow-red, crystalline needles, appearing ruby-red by transmitted light; should the V_2O_3 used contain V_2O_4 , which is often the case when the V_2O_3 is prepared by heating NH4.VO3, the solid obtained by fusion and cooling appears violet to nearly black, and does not seem to be crystalline (Berzelius, P. 22, 1). As molten V₂O₃ cools nearly to its solidifying-point much heat is given out, and the mass glows until solidification is complete (B., l.c.). V2Os is said not to be changed at a white heat, provided no trace of a reducing agent is present (B., l.c.); but according to Read (C. J. 65, 313 [1894]) molten V₂O₃ gives off O, producing V₂O₃, which on cooling in air takes up O, forming steel-blue crystals of V₂O₄. The crystals of V₂O₄ are rhombic (c. Nordenskjold, P. 112, 160). S.C. (crystalling) 25 5 4 00 (Cal-Agerit I. 17, 160). (crystalline) 3.5 at 20° (Schafarik, J. pr. 76, 142). V₂O₃ is odourless and tasteless; it reddens moist V₂O₂ is odouriess and sateless; it reduces most litmus paper; 1,000 pts. boiling water dissolve scarcely 1 pt. V₂O₃ (B., l.c.). With molten alkalis or alkali carbonates V₂O₃ produces vanadates (q.v. p. 851). V₂O₃ dissolves in conc. H₂SO₄, HClAq, HNO₂Aq, or HFAq (cf. Vanadic surrs, p. 850).

According to Ditte (C. R. 101, 698), V₂O₃ exists in three forms; (1) red, obtained by heat-

ing NH, VO, in a closed crucible, treating with HNO, and repeatedly heating to redness; (2) yellow, obtained by heating NH, VO, to 440° in a stream of air; and (3) crystalline, obtained by treating the yellow form with HNO,, and then fusing. D. says that the red form is somewhat soluble in water, 1,000 c.c. dissolving 8 g. at 20°; that the yellow form is very slightly soluble, and the crystalline form is insoluble, in water. He also says that the red form absorbs water from the air, producing hydrates with 2H,0 and 5H,0; and that addition of NHCl, KCl (and other salts). to an aqueous solution of the red variety causes so an aqueous solution of the red variety obtains ppn. of a hydrate of the yellow form of V_2^{20} , which hydrate, when dry, is a dark-red powder o having the composition $V_2O_1.2H_2O_2O_3$ and is almost insoluble in water. (No analyses

are given by D.)

Reactions.—1. When heated and kept molten, V₂O₂ is formed, and this absorbs Q as it cools in air and forms V₂O₂ (Read, C. J. 65, 313 [1894]).

Heated to reduces in hydrogen till it ceases to lose weight, V₂O₃ is reduced to V₂O₃ (Schafarik,

A. 109, 85); traces of P₂O₃ prevent the reduction (Roscoe, C. J. [2] 6, 831).—8. Heating with potassium produces V₂O₃ (Berzelius, P. 22, 1).—4. V₂O₃ is produced by heating V₂O₃ in a carbon expedible (B., l.c.). For action of Mg, Zn, &c. on solutions of V₂O₃, v. Vanadic satus, (p. 850).—5. When mixed with carbon and heated in chlorine, V₂O₃ yields VOCl₃ (Roscoe, C. J. [2] 6, 342).—6. Electrolysis of molten V₂O₃ produces V₂O₄ (Buff a. Wöhler, A. 110, 277).—7. According to Ditte (C. R. 103, 55), f-kion with potassium cyanide produces 110, 277).—7. According to Ditte (C. R. 108, 55), frion with potassium cyanide produces V_QO₂ (N, K_QO, and OQ, being also formed). Carnot (S. R. 104, 1803, 1850; 105, 119) says that a boiling solution of potassium cyanide produces KVO₃ (CO₂ and N being given off); and that by dropping V_QO, into excess of boiling KONAq there is formed K₂V₁O, (with evolution of N and CO₂). No analyses are given either by D. or C.—8. Ditte (C. R. 103, 55) asserts that the products of the interaction of V₂O₃ and potassium iodice or bromide are K₂V₂O₄, KVO₄, and I or Br. The reactions are said to occur and I or Br. The reactions are said to occur between V_2O_3 and molten KI or KBr; and KIAq is said to react in the same way as the molten salt.—9. When V₂O₅ is heated with molten boron triaxide, a pale-yellow glass is formed, which is said by Guyard (Bl. [2] 40, 354) to be a vanadio borate; no analyses, composition, or methods of borate; no analyses, composition, or memors of purification are given.—10. V₂O₃ dissolves in hot cone. sulphuric acid, forming V₂O₅.xSO₃, genearally along with more or less V_QO₄.xSO₄ (v. Vanabos acids, p. 850).—11. V₂O₃ dissolves in cone. hydrochloric acid; Cl is given off on heating; after the passage of H2S followed by evaporation at 100° the oxychloride VO, Cl. rag is obtained (Crow, C. J. 30, 457; cf. Vanadium dioxymono-chloride, p. 854).—12. By dissolving V₂O₈ in conc. hydrochloric acid in presence of platinis chloride, Brauner (M. 3, 58) obtained large tablets having the composition 2(VOCl, PtCl,). 21aq.-13. An oxylodide 2VOI, 9aq is obtained, according to Ditte (C. R. 102, 1310), by adding excess of hydriodic acid to a warm aqueous solution of red V₂O₃, removing free I by shaking with silver powder, filtering, and evaporating in vacuo. (No analyses are given.) -14. V₂O₃ dissolves in hydroftuoric acid, forming a pale-yellow solution, the colour of which becomes deeper on dilution (Piccini a. Giorgis, G. 22 [1] 55). Petersea (J. pr. [2] 40, 271) supposed that a solution in cone. HFAq contained VF₃; but he did not separate this compound, nor does he give any direct evidence in favour of its existtence beyond the preparation from the solution tence beyond the preparation from the solution of V₂O₃ in HFAq of a compound which may be represented as **XF.VF*, VOF*, and other compounds of the forms **xMF.yVOF*, and **xMF.yVOF*, and **xMF.yVOF*, and adding metallic fluorides to colutions of V₂O₃ in HFAq, and crystallising, vanadoxyfluorides are formed; these cympounds are of the forms **xMF.yVOF*, and **xMF.yVOF*. are of the forms xMF.yVOF, and xMF.yVO,F (v. WANADOXYFLUORIDES, P. 844). 15. Vanadoxyfluorides are also formed by dissolving V2O, in alkali fluoride solutions, and drystallising (of infra, Combinations, No. 5).-16. It a solution of V.O. in hydrofluoric acid is partially reduced, and then evaporated with metallic fluorides. hypovanadoxyftuorides (q. v. p. 845) are formed; these salts are of the form xMF.yVOF, -17. By boiling V.O. with hydrogen peroxide solution, a

black liquid was obtained that deposited a blackbrown crust of indefinite composition (Cammerer,

Chem. Zeit. 19, 957).—18. By fusion with alkali or alkali carbonates vanadates are formed (v. Vanadates, p. 851).

Combinations.—1. With water, but not directly, to form V₂Q.H₂O and V₂O₂2H₂O (v. Metavanadic acid and Pyrovanadic acid, under VANDIUM OXYACIDS, AND SALTS AND DÉMIVATIVES THEREOF, p. 851).—2. With various acidic oxides: (1) With SO, to form V₂O, xSO, formed oxides: (1) With SO, to form V₂O_xxSO₃, formed by dissolving V₂O₃ in hot conc. H₂SQ₄; (2) with As₂O₃ to form V₂O₃xAs₂O₅; (3) with P₂O₅ to form V₂O₃xP₂O₅; (4) with I₂O₆ to form V₂O₃xAs₂O₅; (5) with MoO₃ to form V₂O₃xMoO₃; (7) with P₂O₃ and SiO₄ to form V₂O₃xWO₂; (7) with P₂O₃ and SiO₄ to form V₂O₃xP₂O₃ySiO₂. Most of these compounds combine with the stronger leaves M O₃ and O₃ of the form at this compounds. bases M2O and MO to form salt-like compounds. The compounds of V₂O₃ with SO₃ are described as vanadic sulphates under Vanance sates (infra); the compounds with other acidic oxides are described respectively as arseno-vanadic acids and salts, iodo-vanadic acids, molybdo-vanadic acids and salts, phospho-vanadic acids and salts, phospho-silico-vanadic acid, and tungsto-vanadic acids and salts, under VANADIUM OXYACIDS, AND BALTS AND DERENATIVES THEREOF (v. pp. 853-4).—

8. With vanadium tetroxide to form oxides intermediate between V₂O₄ and V₂O₅ (v. Hyro-yanado-yanado-vanadic oxides, p. 851).—4. With vanadium trioxide to form V₂O₄; produced by heating equivalent weights of the two oxides out of ontact with air (Berzelius, P. 22, 1; Petersen; J. pr. [2] 40, 193).—5. With alkali fluorides. According to Ditte (C. R. 105, 1067; 106, 270), several compounds of the form xV.Q., yMf are formed by fusing V.Q., with alkali fluorides, extracting with rate of all awarellicing. tracting with water, and crystallising; D. gives formulæ where x = 1, 3 and 4, y = 1, 2, 4 and 8, and M = K and Na; but he does not give analyses of the salts (v. Vanadoxyfluorides, p. 844).

Hyprates of vanadic oxide. The hydrates $V_2O_s.H_2O=HVO_s$ and $V_2O_s.2H_2O=H_4V_2O_r$ have been isolated; these compounds are acids (v,Vanadic acids, p. 851). Ditte (C. R. 101, 698) asserts, without giving analyses, that a penta-hydrate V₂O₅.5H₂O is formed by absorption of water from the air by the red form of V.O. (v.

VANADIUM PERTOXIDE, Properties, p. 640),
VANADIO SALTS V₂O₂cX (X = acida.)
oxide). A few compounds of this form have been isolated. The sulphates have been better studied than the other salts. Two sulphates, $V_2O_3.2SO_3.xH_2O$ and $V_4O_3.8SO_3.xH_2O$, have been If x is taken to be 2 in the first sal. isolated. If x is taken to be x in the nrss sat, and 3 in the second, then the formulæ may be written as (VO),2SO,H,SO,H,GO and (VO),SO,2H,SO,H,O expectively; ((VO),SO,2H,SO,H,O = V,O),2SO,2H,O; (VO),SO,2H,SO,H,O = V,O,3SO,3H,O]. If the salts are anhydrous, as seems most probable from the analyses, then the formulæ may be written (VO),SO,2SO, respectively. (VO₂)₂SO₄·SO₅ and (VO₂)₂SO₄·2SO₅ respectively. Neither of the salts can be regarded as the nor-

98), and Münzig (C. C. 1889 (ii.) 908). The salt seems to be without water of crystallisation; Fe (l.c.) says it crystallises with H2O. V2O, is dissolved in hot conc. H₂SO₄, and the solution is boiled for a considerable time, when small crystals separate, some of which are brown and some ruby-red, lustrous, and transparent. The crystals are heated in a bath of molten lead until SO, ceases to be given off (G., Lc.). According to Münzig (l.c.), the orange-coloured crystalline powder that separates when V_2O_3 is added to boiling conc. H.SO, until the acid is saturated is V₂O₂.2SO₂. By keeping a solution of V₂O₃ in a large excess of conc. H₂SO₄ at 130°-150° for a long time, Gerland (l.c.) obtained a hard, opaque, sealing-wax red, crystalline crust composed of

Y₂O₂, and SO₃ in approximately the ratio V₂O₃:2SO₄.
Y₂O₄:2SO₅ [= (VO₂)₂SO₄.SO₃] is described by G. (i.e.) as a clear red, crystalline, deliquescent solid; addition of a drop or two of water ppts.

 $V_2O_3xH_2O_5$ Vanadic trisulphate $V_2O_3.3SO_3(?xH_2O)$. This salt seems to have been of tained by Berzelius (Lc.). Ditte (C.R. 102, 757) gave x the value 3; Gerland's analyses (Lc.) were inconclusive the percentage of water found varying from 3 to 73. G. (Lc.) prepared this salt by long-continued boiling of a solution of V₂O₂ in a large excess of conc. H₂SO₄; small crystals separated, some of them brown and some ruby-red and transparent (probably regular octahedra). When the boiling was not continued for so long a time, G. noticed that fine, golden-yellow, lustrous needles separated. The composition of the crystals in each case was very nearly that required by the formula V₂O₄.3SO₃. More or less V₂O₄.2SO₃ was always formed; G. found that addition of a little HClO, prevented the formation of much V₂O₄.2SO₃. V₂O₅.3SO₃ is very deliquescent; soluble in

cold water or alcohol; a slight rise of temperature suffices to ppt. V₂O₂.xH₂O. By adding to a solution of this salt in cold water the proper quantity of K₂SO₄, G. (l.c.) obtained small, amber-yellow crystals, which, after a few washings with cold water, pressure between paper, and drying over H₂SO, had the composition of the double salt V₂O, 2SO₃K₂O. 6aq. The same crystals were obtained by using the tion of the double salt V_2O_s , $2SO_s$, k_2O , 6ag. The same crystals were obtained by using the disulphate V_2O_s , $2SO_s$. Replacement of K_sSO_s by $(NH_s)_2SO_s$ produced the double salt V_2O_s , $2SO_s$, $(NH_s)_2O_s$, Aa_sSO_s or $MgSO_s$, by the trisulphate $(V_sO_s, 3SO_s)$ crystallised unchanged. Gerland (B, 11, 102) found that when a solution of V_sO_s in both cone. H. SO_s we leavely

tion of V₂O₅ in hot. conc. H₂SO₄ was largely diluted and dialysed, H₂SO₄Aq passed rapidly through the dialyser, along with small quantities of V compounds, until the liquid in the dialyser contained V.O. and SO. in the ratio V.O. 3SO. after which SO. Aq passed very slowly through, and the composition of the substance in the dialyser gradually approached V₂O₂.2SO₄. By dialysing a diluted solution of V₂O₅ in cold conc. H2SO, the conditions being the same as in The sulphates are obtained by distifue V_1 , V_2 and V_3 are obtained by distifue V_4 , V_4 and V_5 , V_6 and V_7 , V_8 , V_8 and V_8 , $V_$ H.SO, contains loose, easily decomposed compounds of V_2O_5 and H_2SO_4 , but that a solution of V_2O_5 in hot H.SO, contains V_2O_4 .3SO,, which gradually loses SO, until V_2O_5 .2SO, is formed. Solutions of V_2O_4 in cone. H.SO, may be reduced to sulphates of lower oxides (Roscoe, C. J.

2] 6, 3344 Rammelsberg, B. B. 1880. 787) :—Zn, Cd, or Na-amalgam causes reduction to lavender solutions of $\nabla_2 O_2 x S O_3$; Mg effects reduction to green solutions of $\nabla_2 O_3 x S O_3$; and $H_2 S$, $S O_{21} O_2 x S O_3$; and $G O_3 x S O_3$; and

V₂O₄.xSO₅. By fusing V₂O₅ with B₂O₅ (Guyard, Bl. [2] 25, 354) obtained a green glass, which he took to be a vanadic borate; no analyses or descrip-

tions are given.

The compounds of V2Os with As2Os, I2Os, P2Os MoO₃, and WO₃ respectively—or some of these compounds—may perhaps be regarded as vanadic arsenates, iodates, &c.; v. Arseno-vanadic acids AND SALTS, IODO-VANADIC ACIDS, &c., p. 853.

HYPOVANADO-VANADIC OXIDES. Several oxides seem to exist intermediate between V2O4 and V₂O₄. Roscoe noticed that V₂O₄ gradually absorbed O and H₂O from the air, forming a greenish solid; Brierley (C. J. 49, 30) found that a pale grass-green substance was formed after some months, having the composition V₂O₄.2V₂O₅.8aq = V₂O₇.4aq. By dissolving this solid in dilute H₂SO₄Aq, and neutralising by KHOAq, B. obtained 2V₂O₄.4V₂O₅.5K₂O. aq. By gently heating the compound

2V₂O₄,3V₂O₅,3(NH)₂O. faq (v. Hypovanadovamdates, p. 853), B. (i.c.) obtained a darkgreen solid that absorbed water from the air, and then had the composition $3(V_2O_1, V_2O_2)$. 8aq = $3V_4O_8$. 8aq (cf. Ditte, C. lt. 101, 151; also Manasse, A. 240, 23).

Compounds of SO, with oxides intermediate between V_2O_4 and V_2O_5 are formed by the reducing action of zinc on solutions of V_2O_5 in H₂SO₄ (v. Rammelsberg, B. B. 1880. 787).

Vanadium oxyacids, and salts and deriva-tives thereof. Two oxyacids have been isolated, HVO, and H₄V₂O, corresponding with HPO, and H.P.O.; salts of these, also salts of the tribasic acid H₂VO, and several more complex salts, are known. Salts derived from the hypothetical hypovanadic acid V₂O₁(OH)₂ (=2V₂O₁H₂O) have also been prepared; and several compounds are known which are most eimply regarded as xV₂O₄.yV₂O₅.2MO, and which may be called hypovanado-vanadates. V₂O₅ also combines with several acidic and basic oxides simultaneously to form compounds of the general form. $x\nabla_{z}O_{z}yX:xMO$; these compounds are generally described as arseno-vanadates, phospho-wana-

described as arseno-vanadates, phospho-wanadates &c.

VANADIC ACIDS. Two vanadic acids,
HVO, and H,V,O,, have been isolated; esalts of
the third acid, H,VO, are known, but the acid
itself has not certainly been prepared.

Metavanadic acid. Monohydrate of vanadic oxide
vanadic acid. Monohydrate of vanadic oxide
V,O,H,O.) Gerland (B. 9, 872 [8876]) prepared
this acid by adding an excess of NH,ClAq to
cold CaSO,Aq, then adding NH,VO,Aq sill a
permanent pp. formed, heating to 75°, washing
the lustrous yellow scales that slowly separated
with dilute H,SO,Aq and SO,Aq (to remove
V,O.), then washing with water, and drying at

100° until the smell of NH, ceased. Manasse (A. 240, 52) obtained HVO, by decomposing cone. solutions of the Ca, Mg, or Sr salt by a little HNO₂Aq, and washing the pp. with dilute HNO₃Aq, and then with hot water. Metavanadic acid forms golden-yellow crystalline scales; it is unchanged in air; dissolves very slightly in water; insoluble in absolute alcohol; soluble in NH,Aq, KOHAq, or NaOHAq. By adding NH,VO,Aq, to CuSO,Aq, filtering from the pp. that formed, and dialysing for several days, By adding Gerland (I.c. p. 874) obtained a solution in the dialyser of vanadic acid, which remained clear when heated, and on continued evaporation gave a pp. of red amorphous V_QO_x. Metavanadic acid forms a series of salts (v. Metavanapares, infra).

This compounds is used as a colour in place of gold bronze, under the name of vanadium bronze. According to Guyard (Bl. [2] 25, 856), the substance commonly known as vanadium

bronze is really an ammonium vanadate.

Pyrovanadic acid H₁V₂O₂. (Tetrabasio vanadic acid. Dihydrate of vanadic oxids vanadic acid. Dihydrate of vanance oxuse V₂O₂,2H₂O₃) This acid is obtained by decomposing a fairly cone, solution of an alkali vanadate of the form M₂V₂O₁₁ or M₂V₂O₁₆ (v. Tethavanamers and Hexavanamers, p. 852) by HNO₃Aq, washing with cold water, and drying in the air (von Hauer, J. pr. 80, 321). According to Ditte (C. R. 101, 698), the red form of V₂O₅ (v. p. 849) absorbs H₂O from the air, forming V₂O₂,2H₂O, and also V₂O₅SH₂O. Pyrovanadic acid is described as a brown, amorphous powder. acid is described as a brown, amorphous powder, resembling FeO,H,; dried over H,SO,, it is said to lose half its water. Very slightly soluble in water; the solution is clear yellow; it reddens ntmus. H₄V₂O₇ is insol. in absolute alcohol; it dissolves readily in NII₃Aq. For salts of this acid v. Pyrovanadates (p. 852).

VANADATES. The greater number of the vanadates belong to the series (1) MVO₃, (2) M,VO₃, (3) M,VO₄, (4) M,VO₃, or (5) M,VO₃, (8). Series (1), (2), and (3) may be called normal salts; the formule may be written as (1) M₂O₄VO₅, (2) 2 M₂O₄VO₆, and (3) 3M₂O₄VO₅. Series (4) and (5) may be called acid salts; the formule may be written as (4) M₂O₄VO₅, and (5) M₂O₃VO₄. Acid salts are also known intermediate between sories (1) and (4); the chief of these are (6) 3M₂O₄VO₅ = M₂V₂O₅, (M₂O₄VO₆ = 1:1; 1, (7) 3M₂O₄VVO₅ = M₂V₃O₄(M₂O₄VO₅ = 1:1; 1, (1). A few salts of the form 4M₂O₄VO₅ = M₃V₃O₅(M₂O₄VO₅ = 1:1; 1, (1) may be called basic salts. Some salts, especially those of Sie and Tl, belong to more complex fogurs. VANADATES. The greater number of the

forms. Roscoe (C. J. [2] 9, 28) has shown that the alkali orthovanadates, M,VO, or 3M,O.V.O, are asily decomposed in aqueous solution at the ordinary temperature to pyrovanachtes M.V.O., and MOHAq; but that orthovanachtes are formed, rather than meta- or pyso-vanadates, by fusing V₂O₂ with alkali carbonates; further, that aqueous solutions of alkali pyroganadates are readily decomposed by CO, to alkali carbonates

and metavanadates.

METAVANADATES MIVO, or M.O.V.O. Ammonium metavanadate NH.VO. with dilute H.SO,Aq and SO,Aq (to remove tained by dissolving V2O,EH.O in excess of V2O,), then washing with water, and drying at NH,Aq, warming, and allowing to evaporate Forms a white, crystalline crust. Dissolves slowly in cold water, quickly in boiling water. Dissolves Decomposed by heat, giving V_2O_s when air is present. According to Berzelius (P. 22, 1), when a solution of $V_2O_sxH_2O$ in excess of when a solution of V₂U₃xH₂U in excess of NH₂Ag is allowed to evaporate without having been heated, NH₄VO, separates in lemon-yellow crystals (v. B., l.c.; Roscoe, C. J. [2] 6, 322; Ditte, C. R. 102, 918; Norblad, B. 8, 126; Wagner, D. P. J. 223, 633; Böttger, C. C. 1873

Barium metavanadate Ba(VO_s), aq. A yellowish-white, pp.; obtained, along with red crystals, by ppg. (Manasse, A. 240, 23). Sl. sql. in water. Loses H₂O when heated to c. 200° (Berzelius; Norblad,

Potassium metavanadate KVO₁, xaq. Formed by dissolving V₂O₂ in KOHAq in the ratio V₂O₃:KOH. Various hydrates have been obv₂0₅:ROEE. various nyurates have been obtained as white crystalline solids, melting to a clear yellow liquid, which solidifies to white, lustrous KVO₆ (v. Berzelius, Lc.; Ditte, C. R. 104, 902, 1061, 1168).

104, 902, 1001, 1108).
Sodium metavanadate NaVO₃. Obtained by,
Roscoe (C. J. [2] 9, 31) by fusing V₂O₃ and Na₂CO₃,
in the ratio V₂O₃:2Na₂CO₃, dissolving in water,
crystallising Na₄V₂O₇. 18aq, and passing CO₂
into an aqueous solution of this salt, when NaVO₃ crystallised out and Na CO, remained in solution. Small yellowish-white crystals, probably monoclinic prisms, melting readily and solidifying to a yellow crystalline mass (cf. Norblad, l.c.). Hydrates with 2, 4, and 5 H.O have been ob; tained (cf. Ditte, l.c.).

tained (cf. Ditte, l.c.).

The other metavanadates that have been prepared are Cd(VO₃)₂ (Ditte, C. R. 104, 1705) (Ca(VO₃)₂ 4aq (von Hauer, J. pr. 69, 385; 80, 324; Manasse, A. 240, 23; cf. Roscoe, C. J. [2] 9, 32); Co(VO₃)₂, 3aq (D., l.c.; Radau, A. 251, 114), forms double salts with KVO₃ (R., l.c.); Pb(VO₃)₂ (R., l.c.; D., l.c.); LiVO₃ 2aq (Ditte, C. R. 104, 1168); Mg(VO₃)₂ 4aq (Radau, l.c.); Manasse, l.c.); Mn(VO₃)₂ 4aq (Radau, l.c.); AgVO₂4NH, 2aq (D., l.c.); Sr(VO₃)₂, 4aq (Norblad, l.c.; Manasse, l.c.); Zn(VO₃)₂, 2aq (D., l.c.).

Onyhoyandates M₃VO₄ or 3M₂O. V₂O₃.

Potassium orthoyanadate K, VO₄. Obtained

Potassium orthovanadate K₂VO₄. Obtained by fusing V₂O₄ with K₂CO₅; decomposed by water, giving KOHAq and K₄V₂O₇ (Rammelsberg, B. B. 1883, 8).

perg, B. B. 1853. 3).
Sodium orthovanadate Na, VO, xH,O! Roscoe
(C. J. [2] 9,39) obtained the salt with 16H,O
by fusing V,O, and Na,CO, in the ratio
V,O, 3Na,CO, allowing to cool, dissolving in as
little colic water as rossible, quickly adding excess of conc. alcohol, allowing to stand for some
hours, washing the crystals that formed with small
quantities of alcohol, and drving on a rorons nours, washing the crystals that formed with small quantities of alcohol, and drying on a porous plate over H₂SO₄ in vacuo (cf. Czučnowicz, R 120, 34; Rammelsberg, B. B. 1885, 3). Baker (C. J. 47, 853) obtained Na₂VO₄mH₂O with c=8(?), 10, and,12; he also obtained the double satt Na₂VO₄NaF19H₂O. The crystalline forms are given by B and the various hydrates of are given by B, and the various hydrates, of Na, VO, are shown to be isomorphous with cor-Na, VO, are shown to be isomorphous with corresponding arsenates and phosphates. Na, VO, Aç changes to Na, V,O,Aq and NaOHAq; the change occurs slowly at 'ordinary temperatures, and rapidly at higher temperatures (R., l.c.).

The other orthovanadates that have been pre-

pared are Ca₁(VO₄)₂. CaCl₂(Hautefeuille, U. R. 103, 600; 104, 501); Pb₄(VO₄)₂ and 3Pb₄(VO₄)₂ PbCl₂(R., l.c.); Ag₃VO₄ (R., l.c.); Tl₃VO₄ (Carnelley, C. J. 26, 323).

C. J. 20, 523).

PYROYANDATES M¹₄V₂O₇ or 2M₂O.V₂O₄.

Barium pyrovanadate Ba₂V₂O₇. Obtained, as a white amorphous powder, by adding BaCl₂A₀ to freshly-prepared Na₂VO₄A₁, washing, and drying at 100°. The salt is slightly soluble in water (Roscoe, C. J. [2] 9, 83).

Potassium pyrovanadate K₁V₂O₇. Hard, deliquesgent monnellinic prisms. formed by adding

liquescent monoclinic prisms, formed by adding KOHAq to KVO,Aq, rapidly evaporating to a syrup, and placing over H₂SO₄ (Norblad, B. & 126).

Na, V20,.16H2O. Sodium pyrovanadate Formed by fusing V₂O₅ and Na₂CO₅ in the ratio V₂O₅:2Na₂CO₂, disso ving, and orystallising; also v₂V₅:2Na₂V₉, anserving, and orystalising; also by exposing Na₃VO₄Aq to air free from CO₂ until addition of alcohol ppts. silky scales (Na₄V₂O₂) (Roscoe, *l.c.*, p. 31). White six-sided tables; e. sol. water, insol. alcohol. Na₄V₂O₄Aq is decomposed by CO, to Na, CO, Aq and NaVO, Aq

(R., l.c.).
The other pyrovanadates that have been pre-The other pyrovanatates that have been prepared are 2Ca,V2O,. 5aq (Roscoe, l.c.; cf. Ditte, C. R. 104, 1705); Cu,V2O,. 3aq (von Hauer, l.c.); Pb,V2O, (Ditte, l.c.); 2Pb,V2O,. PbO (Roscoe, l.c.); Li,V,O,. 6aq (von H., l.c.); Mn,2V,2O, (Ditte, l.c.); Ag,V2O, (Roscoe, l.c.; Ditte, l.c.); Tl,V2O, (Carnelley, C. J. 26, 323); Zn,V2O, (D., l.c.).

TETRAVANADATES M,2V4O,1 or M,2O.2V4O, (also called diagnadates).

called divanadates).

Ammonium tetravanadate (NH₄). V_4O_{11} , raq; x=3 or 4. Formed by adding a little acetic acid to boiling NH₄VO₄Aq and evaporating in vacuo; also by saturating NH₂Aq with V_2O_3 in a closed, warmed flask, and allowing to evaporate; red prismatic crystals with a goldenyellow sheen (Berzelius, P. 22, 1; Rammelsberg, B. B. 1883. 3; von Hauer, l.c.; Ditte, C. R. 102,

918). Potassium tetravanadate = 3, 4, 7, and 10. Obtained by saturating K₂CO₃Aq at 80° with excess of V₂O₃ and allowing to cool; also by adding acetic acid to V₂O₅ in KOHAq, concentrating at 80°, and letting cool. (Ditte, C. R. 104, 902, 1061, 1168; cf. Norblad, B. 8, 126). Orange-coloured tablets (v. also Gibbons, C. N. 80, 267).

Chip ons, C. N. 80, 207).

The other tetravanadates are CaV₁O₁₁, 9aq (Manasse, A. 240, 23); PbV₂O₁₁ (Ditte, l.c.); Li₂V₂O₁₁, 9aq (Norblad, l.c.); MgV₂O₁₁, 9aq. (B., l.c.; vop. Hauer, l.c.); NiV₂O₁₁, 3aq (Radau, A. 251, 114); Na₂V₂O₁₁, 9aq (Berzelius, P. 22, C; von Hauer, l.c.; Norblad, l.c.); SrV₄O₁₁, 9aq (B., l.c.; vop. V. l.c.) von II., l.c.).

HEXAVANADATES M, IV, O16. xH, O or M.O.3V.O., $2H_2O$ (also called trivanadates). These salts have been described by Norblad (B. 8, 126) and Ditte (C. R. 104, 90% 1061, 1168). The chief are those where $M_2 = (NH_4)_2$

Cd, Ca, K₂ and Na₂.

The principal vanadates belonging to other

The principal vanadates belonging to other The principal vanadates belonging to other series than those already mentioned are the following:—(1) $3M_{\star}O_{\star}AV_{\star}O_{\star}$ (= $M_{\star}\Pi V_{\star}O_{\star}$), M = Ca and Sz (v. Manasse, Lc.); (2) $3MO_{\star}OV_{\star}O_{\star}$ (= $M_{\star}\Pi V_{\star}O_{\star}$), M = Ba, Mg, K_{\star} (d. Manasse, Lc.; Radau, A. -251, 114); (3) $2MO_{\star}SV_{\star}O_{\star}$ (= $M_{\star}\Pi V_{\star}O_{\star}$), M = (NH_s)_p, Ba, Li_s, Mg, K_s, Na_s (v. Ditte, Lc. p also C. R. 96,

l.c. ; 1048 ; Manasse, Norblad, l.c.) ; (4) 4M₂O.V₂O₃(=M¹,V₂O₃), M=Li and Na (v. Ditte, i.e.).

Several other vanadates not belonging to any of these series have also been described; for Ca

of these series nave also open described; for Ca and Sr satts (and double satts). v. Manasse (Lc.); and for Tl salts v. Carnelley (C. J. 26, 323).

HYPOVANADATES, Salts of hypothetical hypovanadic acid V.O.(OH). (=2V_2O., H_O). These salts belong to the form M.V.O., xH_O (= M_O.2V_2O_xH_O). The formation of the NH, when the salts was described by Regrating a garden. and K salts was described by Berzelius; a series of salts was prepared and examined by Crow (C. J. [2] 15, 458). The alkali salts are obtained by treating fairly conc. VO₂ClAq (v. HYDRATED VANADIUM DIOXYMONOCHLORIDE, p. 854) with excess of caustic alkalis, allowing the pps. to settle in closed vessels, washing with alkali solution, then with dilute alcohol containing a little acetic acid, and finally with alcohol alone, and drying between paper. The salts of Pb and Ag are obtained by ppn. from a solution of the K salt. The salts form brown to black crystalline powders; the alkali salts dissolve in water. Crow prepared salts with M2 = (NH4)2, Ba, Pb, K2, Ag2,

and Na... HYPOVANADO-VANADATES. Salts of the form $nV_2O_1 mV_2O_2 pM_2O_2 H_2O$. Alkali salts of this series were obtained by Brierley (C. J. 49, 32) by reducing $V_2O_2A_2$ by SO_2 , adding V_2O_3 in alkali, then a slight excess of alkali, and then acetic acid; pouring into alkali acetate solution, washing the pps. with alcohol, and drying over The salts crystallise in greenish-black,

CaCl₁. The saits crystallise in greenish-black, or black, prisms. The following were prepared: (1) 2V₂O₄,V₂O₂,2Na₅O.13H₂O; (2) 2V₂O₄,V₂O₂,2K₂O.6H₂O; (3) 2V₂O₄,V₂O₂,(NH₃).O.14H₂O; these salts are soluble in water: (4) 2V₂O₄4V₂O₅5K₂O.H₂O; (5) 2V₂O₄4V₂O₅3(NH₃)₂O.6H₂O; these are insoluble in water. soluble in water.

COMPLEX VANADIC ACIDS AND SALTS. Vanadio oxide V₂O₃ combines with several an-hydrides, such as As₂O₃, I₂O₃, P₂O₃, &c., and many of the compounds thus produced combine with basic oxides. The compounds of V₂O₃ with certain anhydrides are generally regarded as acidic; and the compounds formed of V₂O₅, anhydrides, and bases are usually classed as salt-like substances. It is quite likely that many of the compounds of V₂O₃ with anhydrides, such as As₂O₄, F₂O₃, &c., would be better classed as salts, just as the compounds of V₂O₃ with SO₃ are classed as salts.

ARSENO-VANADIC ACIDS AND SALTS. By boiling ARSENO-VANDIC ACIDS AND SAITS. By BOILING V₂O₃ with excess of H₂ASO₄Aq, and concentrating the solution, Fernandez (B. 17, 1632) obtained lustrous, golden-yellow crystals of V₂O₂As₂O₃, 11aq (cf. Friedheim a. Schmitz-Dumpnt, B. 23, 2600). Gibbs (P. Am. A. 2%, 50) obtained xV₂O₄.yAs₂O₅, saq (x and y probably either 5 and 8, or 7 and 6), by decomposing a privature of Na vanuadate and arsenate by mixture of Na vanadate and arsenate by a mixture of Na vanadate and arsenate by HNO, Aq. For various compounds of the form mV_*O_*, mA_*, O_*, pMO , where m and n are 1 and n, 2 and 3, 1 and 2, 2 and 1, &c., and p varies from P to 5, v. F. a. S. D. (l.c.):

1000-variant across. Ditte (Q. R. 102, 357) says that compounds of V_*O_* and I_*O_* are formed by heating V_*O_* with conc. HIO, Aq; he gives formulæ, but no analyses.

MOLYBDO-VANADIC ACIDS AND SALTS. For descriptions of numerous compounds of the forms also $xV_2O_*yM_0O_*$, eaq, $xV_2O_*yM_0O_*pMO_*$ eaq, and also $xV_2O_*yM_0O_*pMO_*$, $xpMO_*pMO_*$, $xpMO_*pMO_*$. Gibbs $(P. \Delta m. A. 18, 232)$.

PHOSPHO-VANDIC ACIDS AND SALTS. Various compounds of V₂O₃, P₂O₃, and H₂O are described by Gibbs (P. Am. A. 21, 50); Ditte (C. R. 102, 757) also assigned formulæ to substances ob-

of the form $\mathbf{z}V_{s}Q_{s}, \mathbf{y}P_{s}O_{s}$, neMO. zaq, v. Gibbs (l.c.); and cf. Friedheim (l.c.).

F. divides the compounds formed by reacting with V2O, on alka I phosphates into two classes, which he calls · luteo- and purpurco- compounds.

Luteo- compounds are formed by (1) the interactions of phosphoric and vanadio acids in solution; (2) the interactions of solutions of phosphates and vanadates in presence of small quantities of acids; (3) the interactions of solutions of phosphates and vanadic acid; (4) the interactions of vanadates and phosphoric acid, by heating solutions nearly to beiling and eva-porating. These compounds are yellow, granu-lar, and indistinctly crystalline; the alkali compounds are very slightly soluble in water, solution being accompanied by decomposition. The following luteo- compounds are described by F.:

V₂O₃,P₂O₃2H O. 9nq. V₂O₃,P₂O₃(Nif₁)₂O.H O. 2aq, 2V₂O₃,P₄O₃(Nif₄)₂O. 7aq, V₂O₃,P₂O₃K₂O.H₂O. 2aq, and 2V₂O₃P₂O₄K₂O. 7aq.

Purpureo compounds are formed by dissolving vanadic acid in conc. solutions of alkali phosphates, and by adding phosphoric acid to cone solutions of alkali vanadates; in each case the solutions should be strongly heated. The purpurco- compounds described by F. belong . to the form 12V2O3.P2O6.7M2O. 26aq; they are dark-red crystalline substances, sol. in water.

F. regards the luteo- compound of the form V_{2.0}, P_{2.0}, 2H_{2.0}, 9aq as acid phosphate of the radicle VO, thus (VO₂)H₂PO, 9aq; he compares this with the acid orthophosphates MH_PO₁. The compounds of the form MH.PO. The compounds of the form V.O. P.O. M.O.H.O. xaq are looked on as double heid phosphates of alkali metal and VO, thus NH₄(VO₂)HPO. The luter-compounds 2V₂O₃P₂O₃M₂O₄xaq are formulated by F. as double compounds of alkali metavanadates and double compounds of alkali mets-angdates and (VO.)H.PO.; thus 2VO.,P.2O.,K.Q.2H.Q. 5ac = 2(KVO.,(VO.)H.PO., 2½aq). The purpureo-compounds which belong to the form 12V.Q.P.O.,7M.Q. xaq are looked on by F. as double compounds of scil vanadates and acid phosphates; this view of their constitution is expressed by the statement 12V.Q.,P.O.,7M.Q. xH.O = P.Q.,2M.Q.H.Q. + 12V.Q.,5M.O + (x-1)H.O. These views of F. are considerably modified in a

These views of F. are considerably modified in a later paper (Zeit. f. anorg. Chemie, 5, 437) where the purpureo- compounds are looked on as divanadates with some V₂O isomorphously replaced by P₂O. According to F., many of the substances described by Gibbs and by Ditte do not exist. Berzelius (P. 22, 1) described a compound of V2O2, P2O2, and SiO2 with H2O, which may be

named phospho-silico-vanadic acid.

TUNGSTO-VANADIC ACIDS AND SALTS. pounds of V₂O₅ with WO₅ and bases that have been described are very numerous, and the formula, given are generally excremely complex (v. Gibbs, P. Am. A. 18, 232; Rosenheim, A. 251, 197, 234; and especially Friedheim, B. 17, 1505; 23, 1505; 24, 1173).

Vanadium, oxybromides of. Two compounds of V with O and Br have been isolated; and VOBr, corresponding with two of the five oxychlorides. According to Schafarik (W. A. B. 33, 14; 47 [11] \$\theta 51\$), other exybromides also

VANADIUM OXYDIBROMIDE VOBr2. (Vanadyl vanadion oxyddromide vodr. (*Anadio dibromide.) A brown, def quescent powder. Prepared by heating VOBr. (*). infra); decomposition to VOBr. and Broccurs slowly at temperatures below 180°, and suddenly at 180°. Heated in air forms V.O.; dissolves in water, forming a blue solution (Roscoc, U. J. [2] 9, 26). forming a blue solution (Aloscov, O. 1.12) of 1.27. Ditte (C. R. 102, 1310) says that a compound VOBr₂.4H₂O is formed, as dark-gleen deliquescent crystals, by treating red V₂O, with HBr. D. writes the formula V₂O, Br₂.2HBr.7H₂O.

VANADIUM OXYTRIBONIDE VOBr₃. (Vanady)

tribromide.) Prepared by passing vapour of pure Br over V₂O₂ heated to redness, condensing the yellowish white vapours that are formed, removing excess of Br from the red liquid by heating to 40°-50° at c. 100 mm. pressure in a current of perfectly dry air, and then distilling in vacuo (Roscoe, C. J. [2] 9, 24). VOBr₃ is s red, very hygroscopic liquid that boils, at 1300-136° at 100 mm. pressure; S.G. 2.9673 at 0°, 2.9325 at 11.5°; decomposes slowly at the ordinary temperature, and suddenly Lt 180°, to VOBr. and Br (R., l.c.).

Vanadium, oxychlorides of. Five compounds of V with O and Cl have been isolated: VOCl, VOCl₂, VOCl₃, V₂O₂Cl, and VO₂Cl. xaq.

VANADIUM OXYMONOCHLORIDE VOCI. (Vanadyl monochloride.) Obtained by the regulated reduction of VOCl, by H. The mixed vapours are passed through a red-hot tube; VOCl is deposited near the end whereat the vapours enter the tube. A brown, light, flocculent powder; insol. in water; easily dissolved by HNO, Aq

(Roscoe, C. J. [2] 6, 347).

VANADUM OXYDICHLORIDE VOCI2. dichloride.) Prepared by heating a slight excers of VOCI, with zinc for some days in a sealed tube, at 400°, cutting off the part of the tube on which the sublimate of VOCL, has formed (V2O4 and ZnCl, are the other products), quickly placing it in a wider tube, and removing VOC, by heating in a stream of dry CO, at 130°. Also obtained by passing vapour of VOCla and H through a red-hot tube; VCCla is deposited part the end of the tube whereat the gases enter, and V.O.Cl at the further end of the tube (Moscoe, Lc., p. 348). Luctrous, grass-green, deliquescent tablets; S.G. 288 at 13°; clowly decomposed by water; soluble in dilute HNO, Aq. A compounds with PtCl₄, having the composition 2(VOCl₂.PtCl₄). 21aq, is said by Brauner (M. 3, 58) to be formed by dissolving V₂O₃ in conc. HClAq in presence of PtCl,Aq.

VANADIUM OXYTRICHLORIDE VOCl₂. *(Vanadyl

trichloride.) Mol. w. 173.27.

Formation.—1. By heating V₂O₂ gently in a stream of Cl (Berzelius, P. 22, 1).—2. By heat. ing a mixture of V2O, and C in Cl.

Preparation .- A mixture of V2O, and sugarcharcoal is heated to redness in a stream of dry H, and allowed to cool in that gas; a stream of dry Cl is then passed over the mixture, which is heated to redness, and the product is condensed; the liquid thus obtained is heated for some boars in a flask with an inverted condenser, in a current of dry CO₂, and then rectified over Na (Roscoe, C. J. [2] 6, 342).

Properties and Reactions .- A clear, mobile, lemon-yellow liquid (Berzelius, l.c.; Roscoe, l.c.; Schafarik, A. 109, 85). S.G. 1.836 at 17.5°, 1.828 at 24° (R., l.c.); 1.86534 at 0°, 1.63073 at b.p. (Thorpe, C. J. 37, 348). B.P. 127·19° (T., Lc.). S.V. 106·25. Does not solidify above -15° (B., Lc.). V.D. 88·38 at 186° (R., Lc.; cf. T., C. N. 24, 827; Schafarik, Lc.). Gives off thick, yellowish-red fumes in the air. Dissolves in a little water, forming a thick, red liquid; dissolves in much water, forming a clear yellow liquid; dissolves in absolute alcohol with a red colour, but the solution soon becomes blue, owing to reduction. Heated to 60°-70° in a closed tube with ether forms needles of the composition VOCl, Et,O (Bedson, C. J. 29, 309).

V2O2Cl. DIVANADIUM DIOXYMONOCHLORIDE (Divanadul monochloride.) Yellow-bronze, microscopic crystals, resembling mosaic gold; formed by passing VOCl, and H through a red-The crystals are deposited on the hot tube. part of the tube farthest from the end whereat the gases enter (Roscoe, C. J. [2] 6, 348). Insoluble in water; soluble in HNO₃Aq. This compound was thought by Schafarik (A. 109,

85) to be V.

HYDRATED VANADIUM DIOXYMONOCHLORIDE VO.Cl. raq. (Hypovanadic chloride V.O.Cl. raq.) Formed, as a brown, deliquescent solid, by passing H.S into a solution of V.O. in hot HClAq, filtering from S, and evaporating (Crow, C. J. 30, 457). Heated in a stream of dry CO, gives off HCl and H2O, and leaves V2O4-40 C: (l.c.) gives the hydration as V₂O₄Cl₂. 5aq.

Vanadium, oxyfluorides of. No compound of Vewith O and F has been isolated with certainty. V2O2 dissolves in excess of HFAq; on evaporation, solution in water, and evaporation over H.SO., Petersen (J. pr. [2] 40, 194) obtained blue, microscopic crystals which he supposed might be VOF, xaq, inasmuch as a solution of these crystals in HFAq treated with fluorides yielded salts of the form xMF.yVOF, (v. Hypo-VANADOXYFLUCRIDES, p. 845). P. did not obtain enough of the blue crystals for analysis.

Vanacium, oxyiodides of. According to Ditte (C. R. 102, 1310), an oxylodide 2VOL-9K₂O is formed, as a black, deliquescent mass, by adding formed, as a black, deliquescent mass, by adding excess of HIAq to a warm solution of red V₂O₃, removing free I by shaking with finely-divided Ag, filtering, and evaporating in vacuo. The compound is said to react with NH₂Aq, civing (NH₄)₂V₂O₃. D. writes the formula as V₂O₁I₂.2HI.8H₂O; but no analyses are given.

No reaction occurs when I is heated with V₂O₄ (Roscoe, C. J. [2] 9, 28); nor when V₃O₅ is digerted with water, or alcohol, and I (Guyard,

Bl. [2] 25, 351). V.O. and I.O. probably combine (v. Ditte, C. R. 102, 757, 1019).

Vanadium, exysulphides of. None of these compounds has been certainly isolated. Ozysulphides may perhaps be formed by decomposing alkali thiovanadates in solution by dilute

and airdit into sandages in solution by different acids (o. Kay, C. J. 87, 728).

Vanddum, salts of. Compounds of the oxides V₂O₃, V₂O₄, and V₂O₅ with acidic oxides have been isolated; the formula of one or two of the compounds may be written as desired. from oxyacids by replacing H by V, but it is simpler, and more in keeping with the facts that eare known, to represent all the compounds by the general formula $V_2O_x.yX$, where X is an acidic oxide. The best-studied compounds of acidio oxide. V₂O₄ with acidic oxides may be represented as salts of the radicle V2O2 (divanadyl), or of the radicle VO (vanadyl); and the compounds of V2Os with acidic oxides as acid salts of the radicle VO₂. The sulphates have been better studied than the other salts; the following table presents the compositions of the sul-

I. Vanadous sulphates (v. p. 847): $V_2O_1.48O_3.xaq = V_1.H_2(SO_4)_4.yaq (y=x-1)$; ?? $V_2O_2.8SO_3 = V_2(SO_4)_3$. II. Hypovanadio sulphates (v. p. 848):

V₂0₄.2SO₄ = V₂O₂(SO₄)₂ = (VO)SO₄; V₂O₄.3SO₃, xx_0 = V₂O₂. H_2 (SO₄)₃, yx_1 (y = x - 1) = (VO.SO₄)₂. H_2 SO₄ yx_0 . III. Vanadic sulphates (v. p. 850):

Y₂0.2SO₂ = (YO₂)₂SO₃O₃ for if the salt contains xaq then Y₂O₃2SO₃, xaq = (YO₂)₂SO₃.H₂SO₄, yaq (y=x-1); Y₂O₃SO₂ = (YO₂)₂SO₃; or if the salt contains xaq, then $V_2O_4.3SO_3$. $xaq = (VO_2)_2SO_4.2H_2SO_4$. yH_2O

(y=x-2).

Alkalis probably ppt. V2O3. xaq from solutions of vanadous sulphates (v. p. 847); from solutions of hypovanadic sulphates alkalis ppt. V₂O₄. xaq (v. p. 848). V₂O₂ dissolves in oxyacids, forming lavender

olutions which probably contain V2O2. xX, where

\(\) is an acidic oxide (v. p. 846).

Various salts of V₂O₃, V₂O₄, and V₂O₃ besides he sulphates probably exist, but they have not

\[
\] been thoroughly examined (v. Hyrovanadic latts, p. 848; Vanadic salts, p. 850; Aiseno-/Anadic acids and salts, p. 853; Iodo-vanadic icids, p. 853; Molysdo-vanadic acids and salts, p. 853; Foreign salts, p. 2.853; PHOSPHO-VANADIC ACIDS AND SALTS, p. 853; and TUNGSTO-VANADIC ACIDS AND SALTS, p. 854).

Tanadium, silicide of. Roscoe (C. J. 23 8,

358) says that V acts on glass or porceann vessels when strongly heated therein, forming a compound with Si; tubes in which Vchlorides are reduced by heating in H get coated with a grey lustrous mirror of this compound. No details or

analyses are given.

Yanadium, silicofluoride of. By boiling

Y.O. with H.SiF.Aq and alcohol, Guyard (Bt.

[2] 40, 352) obtained a greyish, uncrystallisable

[2] 40, 552) obtained a greyish, uncrystallisable mass which he took to be a silicofluoride of V; no analyses or details of preparation are given.

Vanadium, sulmides of. Berzelius (P. 22, 1) described two compounds of V and 8, one often a solution of an alkali shiovanadate by dilute acid, and the other by heating VO on HS R wave the formula VS and ing V.O. in H.S. B. gave the formula VS, and Na, VOS, 5aq. Obtained by saturating 80 e.e

VS, to the compounds he described. The sul-phides of V were re-examined by Kay in 1880 C. J. 37, 728), who found that the pp. obtained (C. J. 37, 728), who found that the pp. obtained by adding dilute HClAq or H_SO_Aq to a solution of sodium ganadate saturated with H_S, or to solution of V_O, in an alkali hydrosulphide, contained O, but probably had not a sedinite composition; and that the product of heating V_O, in H_S is the trisulphide V_S, Kay prepared three sulphides, V_S, V,S, and V,S, corresponding to three of the four oxides; the sulphide discolve in solutions of bled including sulphides dissolve in solutions of alkalisulphides.

probably forming thioranadates (q. v. infra).

Vandium disurrence V.S., (Hypovanadous sulphids.) Propaged by heating V₂S, to full redness, for a long time, in H quite free from O. Forms black lustrous plates, or a brownish-black powder; S.G. 4-2 to 4-1. Absorbs O very quickly when heated in air, giving V_2O_3 , V_2O_4 , and then V_2O_5 , with evolution of SO_4 . Not acted on by boiling HClAq, dilute or conc., nor by boiling dilute H.SO.Aq, or cold conc. H.SO. Dissolves in hot conc. H.SO.; dissolves in HNO.Aq. Slowly acted on by NaOHAq or KOHAq, hot or cold: dissolves in (NH₄)₂SAq or KHSAq, forming purple to reddish-brown solutions (Kay, Le. 775)

(Vanadous VANADIUM TRISULPHIDE V2S2. sulphide.) Formed by strongly heating V.O. in a stream of H.S. (Berzelius, Le.; Kay, Lo. p. a stream of H.S (Berzelius, Lc.; Kay, Lc. p. 736); also by heating any chloride of V, or VOCl., to redness in H.S (K., Lc.); and by strongly heating VO. ing V2O, in a stream of vapour of CS2 so long ing V₂O₂ in a stream of vapour of CS₂ so only as any reaction occurs (K. Lc.). Forms dark, lustrous plates, or a black amorphous powder; S.G. 37 to 40. Oxidised by heating in air, finally to V₂O₂, giving off SO₂. Scarcely acted on by dilute HClAq or H₂SO₂A₃, and or cold, nor by cone. HClAq; readily oxidised by HNO, Aq. Soluble in (NH,) 2SAq or KHSAq, forming purplered to golden-red solutions; also somewhat soluble in KOHAq, NaOHAq or NH, OHAq (Kay, l.c.).

VARADIUM PENTASULPHIDE V₂S₃. (Vanadia sulphide.) Prepared by mixing V₂S₃ with \$\frac{1}{3}\$ its weight of pure powdered S, heating to fusion (c. 400°) in a narrow tube quite filled with CO, and scaled, cooling, and dissolving out excess of S with CS. A black powder; S.G. 30. Heated in a gas that does not react with it, V2S, gives in a gas that does not react with 13, v₃S₃ gives off S and leaves V₂S₃; heated in air gives off SO₂, forming V₂O₃ and finally V₂O₃. Behaves towards bacids similarly to V₂S₃. Dissolves in hot NaOHAq; also in (NH₄). SAq or KHSAq, forming

yellow to red solutions (Kay, I.c. p. 738). Vanadium thio acids, and selts thereof. compound of V with H and S has been isolated, but some thiovanadates, and also some oxythiovanadates, have been prepared by Krüss a.

throwandates, have been prepared by Kuss.
Ohmanis (B. 23, 2547).
Athinonium bito-orthovanadate (NH.), VS.,
Obtained, in pusple crystals, resembling
KMfO., S.G. 1-62, by passing H.S into a solution of NH, VO, in NH, AQ 23G. 898; the solution is saturated in the cold, and is kept cold while H.S is passed in. A brown pp. is formed, and this dissolves after passing in more H.S to a dark-violet liquid, from which the salt crystal lises after some time.

Sodium monoxy-thio-orthovanadate

NaOHAq S.G. 1.122, with H.S, adding a solution of 8 g. Na, V,O, in 6 c.c. water, cooling the liquid by ice, and passing in H,S for 4 hours. The salt was also obtained without water of crystallisation by Krüss (Zeit. f. anorg. Chemie, 3, 264) by fusing a mixture of V₂O₃, Na₂CO₃, and S, until excess of S was removed. Small crystals, that melt at the ordinary temperature to a red, oily liquid (K. a. O., *l.c.*).

Sodium trioxy-thio-orthovanadats

Na, VO, S. 10aq. Obtained by heating Na, V2O, Aq to boiling, adding freshly prepared NaSHAq, cooling by ice, and adding alcohol. A red oil, that solidifies to a crystalline mass which melts at 18° (K. a. O., l.c.).

Ammonium monoxy-thio-p rovanadate (NH₄)₄V₂OS₅. Formed by passing H₂S into a cooled solution of NH₄VO₅vin NH₃Aq S.G. greater than '898, and allowing the liquid to stand for some months, when crystals separate having S.G. 1.715 (K. a. O., l.c.).

Potassium monoxy-thio pyrovanadate

K.V.OS. 3aq. Obtained by passing H.S into KVO, in KOHAq S.G. 1.472, air being excluded and the liquid cooled by icer Crystals resemble KMnO₄; S.G. 2·144; loses all water slowly at 150°. By evaporating the mother-liquor from this salt in vacuo, large crystals of the salt 2K₄V₂OS₄. 3aq are obtained (K. a. O., l.c.) M. M. P. M.

VANADOX,YFLUORIDES and Hypovanad-

oxyfluorides; v. pp. 844-5.
VANADYL COMPOUNDS; compounds of the radicle VO: v. VANADIUM OXYBROMIDES (p. 854), VANADIUM OXYCHLORIDES (p. 854), and Hypo-VANALLIC ACID v. Methyl derivative of

PROTOCATECHUNG ACID.

VANILLIN v. Methyl derivative of Pro-TOCATECHUIC ALDEHYDE.

VANILLO-DIACETONAMINE v. AGETON-

VAPOUR DENSITIES. The term 'vapour density' is now generally employed to signify the specific gravity of a gas referred to hydrogen For descriptions of the principles of the methods used in determining vapour densities, v. Densities, relative, vol. ii. p. 374; and for an account of the application of vapour densities to finding molecular weights, v. ATOMIC

AND MOLECULAR WEIGHTS, vol. i. p. 340.

VEGETABLE PROTEÏDS v. PROTEÏDS. VERATRALBINE v. JERVINE.

VERATRIC ACID v. Di-methul derivative of

PROTOCATECHUIC ACID.

Homo-wrattic soid v. Di-oxy-phenyl-acetic

VERATROLE v. Di-methyl ether of Pyro-CATECHIN.

VERATRUM ALKALOIDS

Veratrine U₁₂H₁₈NO, & Cevadine. [205°]. 8. 12 at 16° Occurs in the seeds of Veratrum Sabadilla (Meissmer, N. J. T. 5, 3; Pelletier a. Caventou, A. Ch. [2] 14, 69; Ccuerbe, A. Ch. [2] Carenton, A. Ch. [2] 14, 05; Ottoroe, A. Ch. [2] 52, 352; Merck, ch. 95, 200; Ar. Ph. 231, 135; Delondre J. Ph. [3] 27, 417; Weigelin, C. C. 1872, 259; Schmidt, Ar. Ph. [3] 10, 511; B. 9, 1115; A. 185, 224). Occurs also in the root of Sarracenia purpurea (St. Martin, Z. [2] 2, 442;, Hétet, C. R. 88, 185). Prepared by extracting

the seeds with boiling alcohol containing a little tartario acid, concentrating the extract, adding water, filtering from resin, adding Na,CO,, and shaking with ether. The ethereal solution is shaken with dilute tartaric acid solution, and the acid solution mixed with Na,CO, and extracted with ether. The ethereal extract is mixed with ligroin and allowed to evaporate spontaneously, when a viscid mass first separates, followed by crystals which are recrystallised from alcohol (Wright s. Luff, C. J. 83, 888). If commercial veratrine [144°] be dissolved in alcohol at 70°, water added till turbidity ensues, and the solution evaporated at 50° to 60°, crystalline veratrine separates first, then a resinous mixture of veratrine and veratridine, while the mother-liquor contains veratridine and veratroin

veratrate (Rosetti, Ar. Ph. [3] 21, 81).

Properties.—Needles (from alcohol),
ether, insol. water. Inactive to light. poisonous, a small quantity producing vomiting and purging. Introduced into the nose it produces sneezing. Alkaline to test papers. Conc. H₂SO₄ forms a yellow colour changing to crimson, 1 pt. colouring 3,000 pts. H₄SO₄ (Vasmer, Ar. Ph. 2, 74). Conc. HClAq forms a yellot solutions. violet solution on warming. HNO, forms a red solution, becoming yellow. Veratrine mixed with sugar (3 pts.) is coloured by H₂SO₄ dark green and finally deep blue (Weppen, Fr. 13, 454). A solution of ammonium selenite (1 g.) in H₂SO₄ (20 c.c.) gives a yellow colour at 30°; in 3 hours a red pp. is formed, the liquid remaining yellow (Da Silva, C. R. 112, 1267). On heating with alcoholic potash or baryta it yields angelic acid and cevine (W. a. L.; Rosetti; "Stransky, M. 11, 482). ICl forms a yellow flooculent pp., sol. hot HClAq (Dittmar, B. 18, 1612). Conc. HClAq yields tiglic acid. Veratrine yields tiglic acid and (8) methyl-pyridine on distillation. On distilling veratrine with lime the products are (8) methyl-pyridine and its hexahydride and isobutyric acid (Ahrens, B. 23, 2705). Veratrine is not affected by bolling dilute H₂SO, Salts.—B'HCl. Amorphous.—B'₂H₂PtCl₄:

amorphous.—B'HAuCl, Yellow needles (from alcohol).—B'HAuCl, 2aq (Rosetti, J. 1883, 1351). -R'HHgCl₃. Crystalline pp., v. sol. alcohol.-B'₂H₂SO₄ (dried at 100°).—B'H₄. Reddisl Reddishbrown amorphous solid (Bauer, J. 1874, 861).

Benzoyl derivative C₂₂H₄₈BzNO₂. [170°—180°]. Brown crystals (containing 1½ aq) (from

ether).—B'HAuCl.

Dibroride C. H. Br. NO. Formed by allowing the tetrabromide to stand in contact with dilute KOHAq. Light-yellow amorphous

Tetrabromids C_{zt}H₁₈Br₄NO₂. Formed by whaking veratifihe with bromine-water. Yellow amorphous powder, insol. water, v. sol. alcohol and ether (Ahrens_{*}B. 23, 2701).

Cevine C_{zt}H₁₈NO₂ (W. a. L.); C_{zt}H₁₈NO₂ (Rogstit). Cevedine. [145°] (W. a. L.); [182°-185°] (R.). Formed by boiling veratrine with alcoholic NaOH (W. a. L.). Yellow resin, v. col. alcohol of sof ether. Exampons solution sol, alcohol, sl. soff ether. Ks aqueous solution becomes turbid on warming. Does not attack the mucdus membrane, gives a crimson colour with H₂SO, and a brown colour with cane-sugar and H₂SO. Its salts are amorphous.—B'HHgI₄ (dried at 100°). Precipitate. Veratridine C₂, H₂₂NO₁₁ (W. a. L.); C₂, H₂, NO₂ (Rosetti). Veratrine. [180° c (W. a. L.); [160°-155°] (R.). S. 3 at 15°. [180° cor.] the viscid mass which separates before veratrine when a solution of the crude base in alcohol-ligroin is evaporated be shaken with ether, cevadilline remains undissolved, while veratridine dissolves in the ether (Wright a. Luff). Amorphous resin, sl. sollether. Decomposed by alcoholic potash into versiric acid and verine C₂₂H₁₅NO₅ [c. 95°] (W. a. L.) or versiring C₃₅H₂₅NO₅ [143°-148°], (R.), an amorphous base, solether. Verstriding dissolves in boiling water, being converted into veratroin veratrate $C_{ab}H_{ab}N_{a}O_{1}C_{a}H_{10}O_{1}$ 2aq (Rosetti), which melts, when anhydrous, at 165°-170°. H₂SO₁ forms a yellow solution which turns crimson.—Salts.—B'HAuCl. Amorphous.—BH,SO, 10aq, crystal-

Cevadilline C₁H₂₃NO₅. Obtained as above (W. a. L.). Amorphous, sl. sol. ether, m. sol. benzene. Decomposed by alcoholic potash.

Salts.—B'HAuCl,—B'HHgI₂. Gelatinous.
Cevadilline is perhaps identical with the sa badilline C₄H₅₆N₂O₁*of Wiegelin (C. C. 1872, 229), to which Hesse (A. 192, 186) assigns the formula CH₅NO₅ while sabatrine C. H₅NO₅ (W.) C₁₁H₃₅NO₇; while sabatrine C₃₁H₃₆N₂O₁, (W.) or C₃₂H₄₅NO₉ (H.) was probably a mixture of decomposition-products (Wright a. Luff).

Veratrum about. The alkaloids in the root

of this plant, and in that of V. viride, are described under JERVINE

VERATRUMIC ACID is VERATRIC ACID.

(Trifolium pratense), in pumpkin seeds, in ergot, and in the blossom of Corylus avellana and Pinus sylvestris (E. Schulze, J. pr. [2] 32, 447; H. 10, 80, 326). Separated from asparagin by crystallisation from hot water. Minute silky prisms, v. sol. hot water, insol. alcohol. Its aqueous solution is neutral, gives no pp. with Pb(OAc), but is ppd. by AgNO, by pieric acid, and by phosphotungstic acid in presence of

HCl. Boiling hydrochloric acid forms guanine.—
Ag.C., H., N.O.. Gelatinous pp.
YERNONIN C., H., O.. Occurs in the root of
Vernonia nigritiana, used on the west coast of Africa as a febrifuge (Heckela. Schlagdenhauffen, C. R. 106, 1446). White powder, sl. sol. ether and chloroform, sol. alcohol. Conc. H2SO, gives a brown colour, changing to purple. Cardiac poison, 80 pts. being required to produce the effect of 1 pt. of digitalin. Decomposed by boiling dilute HCl into glucose and a resin

the seeds of Vicia sativa, V. Faba, and V. Faba minor (Ritthausen, J. pr. [2] 2, 3359.

Seeds with cold dilute H.SO. (1:50), neutralising with lime, filtering from CaSO., evaporating to dryness and crystallising from 86 p.c. alcohol.

The yield is 25 p.c.

Properties.—Tuffs of small needles, nearly
insol. alcohol. Loses 2H₂O at 160°. Sol.

alkalis and allaline earths, reppd. on newtralisation. Not affected by boiling baryta-water. Sol. dilute HCl and H.SO., but after boiling the colution gives a deep-blue colour with FeQ, and needles.

NH₂, and a violet pp. with baryta. Boiling KOHAq (S.G. 1·1) also forms divioin. When evaporated with HNO, (S.G. 1.2) the residue is edged with deep violet. Potash-fusion forms KCy.

Salts. - B'44H2SO. - B',11HCl. Slender needles.

Divicin C₃,H₃₆N₃₆O₁₆. By boiling vicin with water (5 pts.) containing H₃SO₄ (1 pt.) at 0° shere is formed crystalline (C₃,H₂,N₃,O₆)2§SO₄, which yields divicin on treatment with exactly the calculated quantity of KOHAq. Flat prisms (from water). Reduces AgNO, at once. Not pod by baryta. A little FeCl. followed by NH, gives a splendfil bac colour. B'SHNO, Whetstone-shaped crystals, got by adding HNO, to a

convicin C₂₀1²₁₂₈N₀O₁₁ 2aq. Obtained from powdered vetch seeds by extracting with alcohol, allowing vicin to crystallise from the extract, ppg, the mother-liquor with HgCl, and potash, decomposing the pp. with enqueous H.S, and evaporating. The mixture of vicin and convicin dissolves the vicin only. Thin plates (from water), often resembling leucine. Hardly sol. water), often resembling leucine. Hardly sol. cold water, sl. sol. alcohol. Not decomposed by boiling KOHAq (S.G. 1-1). Potash-fusion gives off NH, but forms no KCy. I sol. cold dilute HCl and H.SO. Its aqueous solution gives a flocculent pp. with Hg(NO₃)... VINACONIC ACID v. TRI-METHYLENE D

CARBOXYLIC ACID.

VERINE v. VERATRUM ALKALOIDS.

VERNÍN O₁₆H₂₈N₂O₈ 384. Occurs in young extended by milk of lime from powdered vetch plants (Vicia sativa), in young red clover a asclepids root (Tauret, C. R. 100, 277; Rl. [2] 43, 620. Occurs in two forms, sue soluble and one insoluble in water. Both forms are laworotatory, amorphous, sl. alcohol, insol. ether. Boiling dilute HCl yields an amorphous, inactive sugar, which does not ferment with yeast.

VINYL ALCOHOL CH.: CH.OH. This substance might be expected to be identical with aldehyde CH, CHO, but Poleck a. Thumsel (B. 22, 2863) suppose it to be present in ether that has been exposed to air and sunlight, and that its presence is indicated by the formation of a pp. C.H.OHgOHg.Cl. when a solution of mercury oxychloride in Na, CO, Aq is added to commercial ether. This pp. is white, and is converted by boiling potash into explosive greenish black acctylene mercury C.H.O.Hg. and by adding nitrio acid to its alkaline solu-tion into C₂HHg₂OCl₂, which is not explosive. H.S passed into water containing the compound C.H.O.H.O.Cl. yields (γ)-tri-thio-acetic aldehyde

VINYL-DIACETONAMINE v. ACETONAMINES. vinyL-Minus CH₂:CH.NH₂. Formed by the action of moist Ag₂O or of KOHAq on bromo-ethylamine hydrobromideat 48° (Gabriel, B. 21, 1049, 2665). Known only 2n squeous solution. Volatile with steam. Decomposes in aqueous solution gven in the cold. SO, converts it into taurine.

Salts.—*B'HCl. Poisonous. Its aqueous solution is decomposed by heat.—B',B,PtCl., Crystals, v. sol. water.—B',2BiI, Minute scarlet hexagonal leaves.—B'HAUCl., Golden crystals. B'C.H.N.O. [142°]. Slender yellow

–Di-iodovinylamine. VINYL BROMIDE v. BROMO-ETHYLENS. Vinyl tribromide of. TRI-BROMO-ETHANE. VINYL CHLORIDE v. CHLORO-ETHYLENE. VINYL ETHANE v. BUTYLEZE. VINYL-ETHYL-CARBINOL, v. PENTENYL

VINYL-ETHYLETE v. BUTINENE

VINYL ETHYL OXIDE CH. CH.OEt. (35.5° i.V.). S.G. $\frac{14.5}{17.5}$ 7625. Formed by heat-ing chloro-acetal CH₂Cl.CH(OEt)₂ with sodium at 140° (Wislicenus, A. 192, 106). Liquid, smelling like ether mixed with allyl compounds. Combines with Cl and Br. forming di-chloro, and di-bromo-di-ethyl oxide. A small quantity (1 g.) of iodine converts large quantities of the oxide (200 g.) into a viscid liquid. Dilute (1:4) H2SO4 forms aldehyde and EtHSO. .

Reference.—Chloro-vinyl-ethyl oxide. VINYL-ETHYL-PYRIDINE

C.H.NEt.CH:CH. (98°-102° at 21 mm.). Formed by heating C.H.NEt.CH. CH. OH, with conc. HCl at 170° (Prausnitz, B. 25, 2394). Oil, v. sol. ether.—B'₂H₂Hg,Cl₁₂. Neefles, sl. sol. hot water. VINYL IODIDE v. IODO-ETHYLENE.

VINYL-MALONIC ACID v. TRIMETHYLENE

DIGARBOXYLIC ACID.

VINYL OXIDE (C2H3)2O. (39°). Formed by the action of dry Ag₂O on vinyl sulphide (Semmler, A₂, 241, 90).

Reference.—HEXA-CHLORO-DI-VINYL OXIDE.

o.VINYL-PHENOL CH₂:CH.C₄H.,OH. Methyl ether CH₂:CH.C₄H.,OMe. o-Vinyl-anisole. (c. 198°). S.G. 16 10005, 30 10005. Formed from either of the methyl derivatives of o-oxy-phenyl-acrylic acid by successive treatment with HI and Na₂CO₂Aq (Perkin, C. J. 83, 211; 39, 429). Oil. Polymerises readily (at 150°), forming a glassy mass, which, however, on distillation, regenerates the original oil. It smells like high-boiling coal-tar naphtha. It forms a colourless compound with bromine.

p-Vinyl-phenol. Methyl ether
CH₂:CH.C.H.OMe. [3°]. (205°). S.G. ½5
1-0029; ½5 9956. Formed by distilling methoxyphenyl-acrylic acid (q. v.) and from the same acid by successive treatment with conc. HI (S.G. 194) and Na.CO.

Reference.-BROMOand NITRO-

PHENOL. VINYL-PIPERIDINE C,H10(C,H3)N (?) (147°). Formed by dehydration of oxy-ethyl-piperidine [32°] (Ladenburg, B. 22, 2587). Liquid, smelling like tropidine and conjine, v. sol.

YINYL-

Reference .- BROMO-VINTI - PIPERIDINE.

p. VINYL-ISOPROPYL-BENZENE O₁₁H₁₄ i.e. C.H.Pr.CH:CH₂ (204°). S.G. 14 p. 8902. Formed by distilling purels arylic acid at 21°0 r by boiling a-bromo-β-tumyl-propionic acid with Na₂CO₂Aq (Perkin, C. J. 1877, ii. 660). Oil, smelling like cuminic aldehyde. Partially polymerises on boiling, and also on keeping, forming a glassy mass, reconverted into the original hydrogarbon by heat. Yields C₁₁H₁₁Br, [71°]. .VINYL-PYRIDINE C,H,N i.c.

N < C(C,H_):OH > CH: (159°). S.G. 2 9985, Formed by passing a mixture of pyridine and Reducing agents form uranil (amido barbituric

ethylene through a red-hot tube (Ladenburg, B, 20, 1643). Formed also by distilling oxy-ethylpyridine under high pressure or in presence of KOH (Ladenburg, B. 22, 2585), and by the action of NaOHAq on β-bromo-β-pyridyl-propionic acid (Einhorn, A. 265, 229). Liquid smelling like conyrine, m. sol. water, v. sol. alcohol. De composed by distillation under atmospheric pressure, but boils at 81° under 29 mm. Oxidised by KMnO, to picolinic acid, and reduced in alcohone solution by Na to ethyl-pyridine.—Salts:
B'H.PtCl. [174°]. Crystals, m. sol. water.—
B'HAuCl. [144°]. Yellow needles.
Tetra-vinyl-pyridine C,H(C,H,),N. (277°).
S.G. 2 1°0515. Formed in the preparation of

γ-ethyl-pyridine by heating pyridine ethylo-igdide in sealed tubes at 320° (Karan, B. 25, 2776). Sl. sol. wakr.—B'.H.PtCl, [175°].— B'HAuCl, [148°].—B'HHgCl, [146°]. Needles.

VINYL-QUINOLINE v. QUINOLYL-ETHYLENE. VINYL SULPHIDE C.H.S i.e. S(CH:CH2)2. (101°). S.G. 913. Constitutes the chief part of the essential oil of Allium ursinum (Semmler,

A. 241, 90). Liquid, smelling like allyl sulphide. Reactions.—1. Dry Ag.O forms vinyl oxide.— 2. Moist Ag₂O gives aldehyde.—3. Alcoholic HgCl₂ forms crystals of C₈H₁₂Cl₄Hg₂S₂, which, when heated with potassium sulphocyanide, yields vinyl sulphocyanide.—4. PtCl, added to its alcoholic solution ppts. (C₂H₃) Cl₃Pt₂S₃, which is decomposed by animonium sulphide into vinyl chloride and dark-brown (C,H,),PtS,... 5. AgNO₃ forms (C,H,),2AgNO₃...6. Br gives (C,H,)tz),SBr. [295°]...7. Oxidising agents yield CO₂, oxalic acid, and H₂SO₃ only.

VINYL-TOLUIDINE so called is DI-p-TOLYL-DI-ETHYLENE-DIAMINE.

VIOLAQUERCITRIN v. this vol. p. 373. VIOLANTIN C.H.N.O. 4aq. Formed by mixing hot conc. solutions of nitroso- and nitrobarbituric acids (violuric and dilituric acids). Formed also by warming hydurilic acid with dilute HNO₂ (Baeyer, A. 127, 223). Yellowishwhite, crystalline powder, decomposed by water into its two component acids, but may be recrystallised from HOAc or 50 p.c. alcohol. It is also split up into its components by salts of the stronger acids.

VIOLURIC ACID C.H.N.O. i.e.

C₂O₂<NH C:NOH. Nitroso-barbituric acid. Mgl. w. 157.

Formation.—1. From hydurilic acid by the action of nitric acid (S.G. 1.2) or nitrout acid (Baeyer, A. 127, 200).—2. By heating dilituric (nitro-larbituric) acid with glycerin.—3. By warming ferçous diliturate with KCy.—4. By boiling an aqueous solution of alloxantin with hydroxylamine hydrochloride (Pellizzari, G. 17, 258).—5. Byadding hydroxylamine to an aqueous solution of alloxan (Ceresole, B. 16, 1133).— 6. By adding KNO, to barbituric soid (Baeyer, A. 130, 140).

Properties.—Trimetrio crystals (containing as); a:b:c = 83:1:1.92. M. sol. cold water, sl. sol. alcohol. Its aqueous solution is ppd. by scobol. FeSO gives a deep indigo-blue colour. HNO, forms ritro-barbituric seid. Br forms di-bromo-barbituric acid and nitrous fumes.

acid). Conc. HClAq forms hydroxylamine on heating.

Salts .- NH,A'. Dark-blue prisms .- KA'2aq. Balts.—NH,A'. Dark blue prisms.—KA'2aq.
Deep-blue crystals, v. sol. water, forming a blue solution; turned red by excess of KOH. A solution of the K salt in conc. HClAq deposits (KA'),HCl), 6aq in colourless efflorescent prisms.—BaA', 4aq. Red dimetric tables, nearly insol. cold water.—MgA', 6aq. Purple-red crystals.—PbA', 4aq. Small red crystals.—AgA'. •

Bensyl ether CONH.CONC.H.

[226°]. Formed by the action of benzyl chloride on silver violurate (Conrad a. Guthzeit, B. 15, 2849). Silvery scales, sol. hot water and alcohol. VIRIDIC ACID v. CAFFETANNIC ACID.

VIRIDINE C₁₂H₁₈N. (251°). S.G. 1024. A homologue of pyridine occurring in coal-tar (Thenius, C. C. 1862, 53). Yellowish oil, with slight greenish fluorescence, sl. sol, water, v. sol, alcohol and ether. — B'2H2PtCla. Greenish brown, insol. water, alcohol, and ether. The mercuric chloride double salt melts at 85° and crystallises from water.

Isomeride C12H16N. (230°-235°). Obtained, with other bases, by heating methyl-ethyl-acrolein with alcoholic ammonia (Hoppe-Seyler, M.

9, 651).—B'HAuCl., [93°].—B'HA!YCl., [135°].
VISCIN C_{[0}II.,O₀, (?). The glutinous constituent of the stalk, leaves, and berries of the mistletoe (Viscum album). Extracted from the bark by kneading with water, washing the sticky mass with 90 p.c. alcohol, and extracting the viscin with cold ether. The residue consists of viscaoutchin and woody-fibre (Reinsch, C. C. 1861, 145). Colourless, tasteless, semi-flaid mass, S.G. 10, decomposed by distillation, yielding oily viscene (226°) S.G. 85, which forms a crystalline Na salt with conc. NaOHAq. Viscaoutchin is very glutinous. Its S.G. is

978, and it is insol, alcohol and ether, sol, oil of turpentine.
VISCOSE is DEXTRIVE (q. v.).

VITELLIN v. PROTEÏDS. VITELLOSE v. PROTEÏDS.

VOLUMES, SPECIFIC: v. SPECIFIC VOLUMES.

VULPIC ACID C, HP,O, i.e. Methyl pulvate. [148°]. Occurs in Cetraria vulpina, a lichen growing in Norway, and used there, mixed with nux. vomica, as poison for wolves (Bebert, A. 2, 342; Strecker a. Möller, A. 113, 56; Spiegel, B. 13, 1629; 14, 1686; A. 219, 15). The lichen contains 2) to 4 p.c. of the acid, which may be extracted by warm milk of lime. Vulpic acid is also formed by dissolving pulvic anhydride in a solution of KOH in McOH. It appears to occur in the lichen Parmelia parieting (Berzelius; Stein, J. 1864, 553).

Properties.-Yellow plates or needles, sol. alcohol and ether, v. e. sol. chloroform, nearly insol. boiling water. Decomposed above 200° ind McOH and pulvic anhydride. Boiling milk of lime converts it into pulvic acid. Boiling

KOHAq forms di-benzyl-glycollio acid and CO₂.

Salts.—NH,A'. Yellow crystals, sol. water.

-BaA', 2aq. Yellow needlos (from water).

BaA', 2aq.—KA'aq. Light-yellow needlos sl. sol. water.

-AgA'. Pp. Blackens 2t 130°. Acetyl derivative C₁₈H₁₃AcO₄. [156°]. Colourless needles, insol. NaOHAq.

Methyl ether v. Di-methyl ether of Pulvio

Isovulpic acid C₁₈II₁₁McO. [124°]. Formed, in small quantity, together with pulvic anhydride, by heating vulpic acid at 200° (Spiegel). Thin golden plates (from alcohol). Forms orange

solutions in alkalis.

w

WACKENRODER'S SOLUTION. The soluion obtained by passing H2S for a long time nto nearly saturated SO₂Aq. The solution conains H₂S₂O₆, much H₂S₂O₆, H₂S₂O₆, and propably H₂S₂O₆, along with H₂SO₄, dissolved olloidal S, and a little S in suspension; v.

CHONGE CAUSE, P. 618: S IN SUSPENSION, F. C. (1908). Cause P. 638. WALDIVIN C₁₀H₂₁O₁₀. [230°]. S.G., 1:46. J. 17 at 15°; 3 at 100°. S. (alcohol) :33. Exracted by dilute alcohol from the powdered fruit of Simaba waldivia (Tanret, Bl. [2] 35, 104; 7. R. 91, 886). Hexagonal pisms (containing faq), v. sol. chloroform, insol. ether. Neutral to famus. Inactive to light. Tastes bitter. WATER. H.O. (Hydrogen monoxide.) Mol. w. 17.96. (For physical data v. Properties.). Occurrence.—Pure water is never found in

nature. The properties of different specimens of naturally occurring waters depend on the im-purities they contain, and these impurities are derived from the substances with which the water has come into contact; hence it is customary to classify natural waters in accordance with their origin, as rain-water, surface-water,

well-water, mineral spring-water, and sea-water. The composition of the substances found in these waters, and the properties of the waters themselves -that is, of the various more or less dilute aqueous solutions - are discussed in pp. 989-960 of vol. iv. of the DICTIONARY OF APPLIED CHEMISTRY. Solid water, more or less pure, is found as ice and snow. Water vapour is a constant constituent of the atmosphere. Agreat many minerals, and also many organic substances, contain water combined with other compounds.

Historical .- In 1781 Cavendish showed exnatoricat.—In 1781 Cavendins snowed ex-permentally that water was the only product of burning H and O mixed in certain proportions, and that almost the whole of the H and O dis-appeared. The account of the experiments made by Cavendish was published in 1784 (T. 1784. 116).

'When a mixture of inflammable and dephlogisticated air [i.e. in modern language, hydrogen and Gygen] is exploided in guch proportions that the burnt air is not much ploigisticated, the condensal liquor contains a little soid, which is always of the nitrous kind . . ; but if the proportions be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all soid, but

eems pure water, without any addition whatever; and as, when thay are mixed in that proportion, very little sir emains after the explosion, sluost the whole being con-lemed, it follows that almost the whole of the inflammable and dephlogisticated air is converted into pure water '(i.e.

Translated into modern language, this statenent would be taken as asserting that water is lormed by exploding a mixture of H and O in croper proportions. It is, however, worthy of note that Cavendish did not himself ipterpret his experimental results as we interpret them to-day. He regarded 'dephlogisticated air' oxygen] as 'nothing but dephlogisticated water, or water deprived of its phlogiston. He said: We must allow . . . that inflammable air [hydro-He said: gen] is either pure phlogiston... or else water united to phlogiston' (l.c. pp. 187, 140).

The formation of water by burning H and O was thought of by Cavendish as the restoration of phlogistone to water that had been deprived of this principle. 'Water,' he said, 'consists of dephlogisticated airs' united to fhlogiston.' Cavendish evidently thought of H and O as what we might now call forms of water; one or these was water with too little phlogiston, and the other was water with too much phlogiston; the explosion restored the phlogistic balance, and the properties of water were apparent. When Lavoisier had interpreted Cavendish's results, Cavendish spoke of Lavoisier's explanation as an hypothesis: 'According to this hypothesis we must suppose that water consists of inflammable air united to dephlogisticated air (l.o. p. 150). Cavendish established the fact that water is the product of burning a mixture of H and O in the ratio (approximately) of 2 vols. H to 1 vols?); but he stated this fact, in language that no longer carries a definite-meaning with it. Lavoisier added to the experimental basis whereon the fact rested, and he expressed the fact in language that still is clear, definite. and descriptive.

Formation .- 1. By the direct union of H and & by igniting a mixture of these elements. 2. By deoxidising metallic oxides, and many other compounds that contain O, by heating with H.-3. By the decomposition of many compounds containing H and O, by heat, or by reactions with other substances.

According to Freyer a. V. Meyer (B. 25, 622), a mixture of H and O in the ratio 2H:O does not explode when slowly passed through a giass tube at 606°, and the temperature of ignition of the wet, gaseous mixture is between 650° and 730°. Askenasya V. Meyer (A. 269, 49) found that when pure, dry electrolytic gas was passed at a moderate rate through a class tube heated to 518°, only o. 7 to 1.7 mgms. of water were produced in ten hours; and that a little more water, but still only a very small quantif, in proportion to the total quartity of H and O, was formed at 606°. Experiments made to determine the relation between the quantity of water formed and the time of the experiment showed that no constant relation could be arrived at, even when every precaution was taken to insure equality of conditions; the irregular action of the surfaces of the vessels was probably the cause of the irregularities in the results.

Davy (T. 1817) found that electrolytic gas did not explode when the pressure was so reduced

that the gas was rarefied to $\frac{1}{15}$ of its ordinary density. Thomas (C. J. 85, 215) found that the gas exploded at 168 mm. pressure. L. Meyer a. Seubert (C. J. 45, 586) found that the sparks from a Ruhmkorff coil caused the combination of c. 2 of a quantity of electrolytic gas at c. 70 mm. pressure, and that the remainder combined when the pressure was increased until it became the same as before the first explosion; this result is in keeping with Bunsen's determinations of the quantity of oxygen needed to prevent the explosion of CH+O (v. M. a. S., l.c. p. 588). Dixon (T. 1884. 634) noticed that electrolytic gas did not explode at a pressure under 70 mm., but that explosion occurred under 75 mm. pressure (cf. D., l.c. p. 642).

According to the experiments of Dixon (l.c.), the union of oxygen and hydrogen is not affected by the presence or absence of water'; dry electrolytic gas exploded by the spark at a pressure between 70 mm. and 75 mm., and the wet gas exploded at the same pressure.

The velocity of explosion of electrolytic gas was found by Berthelot and Vieille (C. R. 95, 151) to be 2,810 metres per second (cf. Explosion, vol. ii. p. 530).

Preparation.—Stas (Chem. Proport. 110) prepared pure water as follows. When large quantities were required, spring-water was very slowly distilled through a long copper tube, bent into zigzag form, completely filled with pure copper turnings that had been oxidised by strongly heating in O, the copper tube being surrounded by alumina and sand, and beated to full redness; the distillate was then distilled in an apparatus of platinum.

The second method recommended by Stas, especially when comparatively small quantities of pure water are required, is based upon destroying the organic matter in distilled water by the action of K manganate and permanganate. The process is described by Stas as follows :-

The process is described by Stas as follows:—

I preparel potassium manganate by reacting on manganese oxide with caustio potash and potassium chlorate. I shook up the powdered product with water, just sufficient to dissolve the manganate that had been formed, and allowed the mixture to settle in a closed vessel. I then added, 4 or 5 p.o. of the clear, dark-green solution to the spring water which was to be distilled, and allowed the components of this mixture to react for 24 hours. I then poured into the distillation, vessel one or two litres of the cone. solution of potassium manganate that had been mixed with an equal volume of cone. caustic potash solution; while the distillation was sufficiently cone. to make the salt as stable that its dilute solution could be beated for a long time without decomposition. I then filled the distillation vessel to a fa, with the water which had been in contact with the potassium manganate, and distilled in the ordinary way. When boiling began I moderated the heat, in order to prevent the liquid, which frothed much for ome minutes, from passing over. When the frothing has stepped, the water shay be boiled rapidly without the least inconvenience. When to the water has distilled over, that which they distill its completely free from orgatic substances, and also from mineral substances, if the upper parts of the distillation vessel is furnished with disphragmes to hold back the extremely small drops that are always carried over the water has prepared is perfectly.

Stassays that water thus prepared is perfectly free from organic matter. When he wished to obtree from organic master. What he whater absolutely free from any form of solid nfuter, Star re-distilled the water that had been purified as described above, using as condenser a long tube of platinum soldered, with gold. It is advisable to distil the water just before it is to be used.

On one occasion Stas used rain-water instead of well-water, and he found distinct quantities of ammonia in the distilled water thus prepared. To remove this he recommends to re-distil with 1.1 part of NaHSO, or KHSO.

To remove this he recommends to re-distil with roos part of NaHSO, or KHSO.

Composition of water.—The gravemetric composition of water was determined by Berzelius a. Dulong (A. Ch. [2] 15, 86) and by Dumas (A. Ch. [3] 8, 189) by passing pure H over a weighed quantity of red-hot CuO, and weighing the water produced and the copper which remained. The results gave the ratio H:O = 1:8 (B. a. D.) and 1:7-98 (D.). An extended series of measurements by the same method, with many precautions, by Dittmar a. Henderson (C. N. Cl. 127, 139, 151, 164 [1898]) gave the ratio H:O = 1:7-9827.

Several measurements have been made of the proportion by volume in which H and O combine to form water. Gay-Lussae in 1805, and Humboldt in 1805 (A. Ch. 53, 239), found the volumetric ratio of H:O to be 2:1. Morley, in 1891 (Am. S. [3] 41, 220, 276), determined the ratio of H:O to be 2:00023:1 by directly measuring the volumes of the gases. In 1892 Ledue (C. R. 116, 1248) found the ratio H:O = 2.0037:1, from determinations of the relative densities of H, O, and electrolytic gas. In 1893 Scott (T. 184, 543) completed a most carefully performed series of syntheses of water by sparking mixtures of H-and O, and determined the most probable value of the volumetric ratio H:O to be 2.00245:1.

Properties.—Water is a clear, transparent, almost colourless, tasteless, odourless liquid. A column of water appears slightly blue when looked at lengthwise. Bunsen (A. 72, 44) pointed out that the slight blue colour of water may be observed by looking at a shining white object through a column of water 2 metres long, contained in a tube brackened inside. V. Meyer (B. 15, 297) recommends to join five wide, thinwalled glass tubes, c. 40 mm. internal diameter, and each c. 14 metres long, by wide caoutchouc tubing, and thus to form a tube c. 7½ metres long; to lay the tube perfectly horizontal, and colose the end by smooth glass plates held in position by metallic clasps; then to cover the tube with black cloth. On looking through the tube the field of view appears quite colourless, but on now filling the tube with pure water (by means of brass tubes passing through the metallic clasps) a deep-blue colour is seen on looking through the colourn is seen on looking through the colourn is seen on looking

The boking-point of water is 100° under the pressure of 760 mm. Zeuner (Grundzigs der mechanischen Wärmetheorie, Tab. 19 [1877]) gives the following table, showing the increase of boiling-point with increase of pressure:—•

Pressure In atmos.	Boiling- point.	Pressure in atmos.	Boiling- point.
1 2	. 100 . 120·6 . 138·91 . 144 . 152·32 . 159·22	9 10 41 12	. 179.81 . 175.77 . 180.31 . 184.50 . 188.41
7	. 165.84	14 · ·	. 195 ;53 Frosh <i>(Trat</i>

An elaborate table is given by Broch (Trav. Mem. des Bureau internat. des Poids et Mes.,

1, 46 [1881]) based on Regnault's determinations; the table gives the b.p. of water for each '1 mm. from 680 to 800 mm. pressure. (The table is given in Landolt a. Börnstein's Physikalisch-Chemische Tabellen [Berlin, 1883], pp. 47-49.)

given in Landoit a. Börnatein's Physikalisch-Chemische Tabellen [Berlin, 1883], pp. 47-49.)

The melling-point of ice is slightly lowered by pressure. J. Thomson (T. E. 16) calculated that the m.p. would be lowered by n '0075° for an increase of n atmospheres; W. Thomson (P. M. [3] 37, 123) confirmed this calculation by determining the m.p. of ice at 81 and 16 8 atmos. Mousson (A. Ch. [3] 56, 252) kept water liquid. at _3.5° by greatly increasing pressure, and he found that at c. 13,000 atmos pressure ice melted at -3.5°.

The specific gravity of water is greater at 4° than at any other temperature. Exner gives the temperature of maximum density as 3°945° (older determinations are tabulated by Exner, W. A. B. 68 (ii.), 463 [1873]). The following table, showing the density and volume of water from 0° to 100°, is given by Volkmann (W. 14, 260 [1881]): it is based on the determinations of Hagen, Matthiessen, Pierre, Kopp, and Jolly:

or magen, m	W	,	
Temp.	Density (in vacuo) i.e. wt. of 1 c.c. water in grams.	Volume of 1 gram water in c.c.	
		,	
0	·999878	1.000122	
i	.999933	1 3000067	
2	·999972	1.000028 .	
3	•999993	1.000007	
4	1.000000	1.000000	
5	•999992	1.000008	
6	-999969	1.000031	
Ÿ	.999933	1.000067	
	-999882	1.000118	
' 8	999819	1.000181	
10	999739	1.000261	
11	•999650	1.000350	
12	• 999544	1.000456	
	-999430	1.000570	
$\frac{13}{14}$	999297	1.000703	
	999154	1.000847	
15	999004	1.000997	
16		1.001162	
17	-998839	1.001339	
18	•998663	1.001535	
19 .	•998475	1.001731	
20	998272	1.001939	
• 21	998065	1.002156	
2 2	997849	1.002383	
23	•997623	1.002563	
. 24	997386	1.002021	
25	997140	1.002808	
80	99577	1.00586	
85	994.77	1.00770	
40	▶ 99236		
45	•99035	1.00974	
· 250	•98817	1.01197	
55 ·	98584	1.01436	
• 60	98334	1.01694	
65	98071	1.01967	
70	97789	1.02261	
.7 5	• 97493	1.02572	
80	•97190	1.02891	
85	96876	1 03225	
90	•96549	1.03574	
95 '	96208	1.03941	
100	95856	1.04323	

Rossetti (P. Ergänsbd. 5, 268 [1871]) gives he densities and volumes of water for each legree from -10° to 100°, referred both to water it 0° and to water at 4° as unity. The S.G. of ce is c. 916 at 0° (water at 0°=1); according o recent determinations by Zakrzevski (W. 47, 155 [1895]) the value is .916660.

The expansion of water for various intervals of temperature has been measured by various between the base has been measured by various observers; putting $V_i = V_0$ (1 + at + $b_0^{i2} + c_0^{i2}$), the ollowing values are given by Kopp (F. 72, 1 1847); cf. Pierre, P. 86, 461; Weidner, P. 123, 300; Matthiessen, P. M. [4] 31, 149; Rosgetti, P. Ergänzbd. 5, 256; Hirn, A. Ch. [4] 10, 32):

Temp. - 000061045 0° to 25° 25° to 50° -:000065415 -:00005916 50° to 75° 75° to 100° - 00008645

For the expansion of water above 100° v.

Mendeléeff (A. 119, 1).

As water freezes it expands by c. ¹/₁₇ of its volume; one volume of water at 0° becoming 1.09082 volumes of ice at 0°. "It expands when heated at temperatures below 0°; Zakrzevski (W. 47, 155) gives the co-efficient of expansion 000077 (v. also Brunner, P. 64, 116; Struve, P.

66, 298; Marchand, J. pr. 35, 254).

The compressibility of water is small.

Röntgen a. Schneider (W. 33, 644) give the absolute compressibility at 17.95° as 0000462 per atmosphere of pressure (v. also Ramsay a. Young, T. 1892; and cf. Grassi, A. Ch. [3] 31, 437; and Rankine, P. M. [4] 1, 548; also Amaury Descamps, C. R. 68, 1564; and Calletet, C. R. 75, 77).

A table showing the volume of 1 kilo... of

saturated water vapour and the weight (in kilos.) of 1 c. metre of the vapour, at tempera-tures from 0° to 200°, is given by Zeuner (v. Lancolt a. Börnstein's Physikalisch-chemische Tabellen [Berlin, 1883], p. 53; cf. Dieterici, W. 38, 1). "According to Dieterici (l.c.) water vapour saturated at 0° behaves like apperfect

The vapour pressure of water varies from 1:0288 mm. at -19° to 20926.4 mm. at 230°; for complite tables calculated from Regnault's determinations v. Landolt a. Börnstein's Physikalischchemische Tabellen [Berlin, 1883] pp. 40-46 (the vapour pressure is given for each 1° from -19°

0000077183 -- 00000003734 ·0000077587 -- 000000035408 .0000000072848 ·0000031892 ·0000000024487

to 101°, and for each 1° from 101° to 230°). Ramsay a. Young (T. 1892) give a table of the vapour pressures of water up to 270°. In connection with the vapour pressures of water and ice, v. R. a. Y. (2. 1884. 470). For an expression representing the vapour pressure of water at any temperature up to 325°, v. Antoine (C. R_c 113,

The spec. heat of water increases as temperature rises; the quantity of heat required to raise 1 g. of water from t to to +1 is taken as unity in determinations of the spec. heats of other substances. The following table presents the data for S.H. of water at intervals of 10° from 0° to 230° (the memoits by the different observers are: Regnault, Acad. 21, 729, [1847]; Jamin a. Amaury, C. R. 70, 661 [1870]; Bostcha, P. Jubelbd. 549 [1874]; von Münchhausen, W. 1,

-						1
(air therm.)	Regnault	Jamin a. Amaury	Bosscha	v. Münchhausen	Henrichsen	Baumgartner
00	1:0000	1.0000	1:0000	1.0000	1.0000	1.0000
10.	1.0005	1.0111	1.0022	1.0043	1.0036	1.0031
20	1.0012	1.0225	1.0044	1.0085	1.0079	1.0061
80	1.0020	1.0341	1.0066	1.0128	1.0131	1.0092
40	1.0030	1.0459	1.0088	1.0170	1.0191	1.0123
50	1.0042	1.0580	1.0110	• 1.0213	1.0259	1.0154
60	1.0056	1.0703	1.0132	1¢0255	1.0335	1.0184
70	1.0072	1.0829	1 00.54	1.0298	1:0419	1.0215
80	1.0090	1.0957	1.6176	1.0340	1.0511	1.0246
90	1.0109	1.1087	1.0198	1:0383	1.0612	1.0276
100	1.0130	1 1220	1.0220	1.0425	1.0720	1.0307
110	1.0155	1.1355	.,1.0242	1.0468	1.0837	1.0338
120	1.0177	1.1493	1.0264	1.6510	1.0961	1.0368
130	1.0204	1.1002	1.0286 °	1.0553	1.1094	1.0399
140	1.0232	1.1775	1.0308	1.0595	1.1235	1.0430
150	1.0262	1.1920	□1 ₹330 €	1.0638	1.1384	1.0461
		405-		1. 1	-	
160	1.0294	1.2067	1.0352	1.0680	1.1540	1.0491
170	1.0828	1.2217	1.0374	1.0723	1.1706	1.0522
180	1.0364	1.2369	1:0396	1.0765	1.1879	1.0558
190	1.0401	1.2525	1.0418	1.0808	e 1.2060 c	1.0588
200	1.0440	1.2680	1.0440	* 1·0850	1.2249	1.0614
210	1.0481	1.2839	1.0462	€ £.0893	1.2447	€ 1.0645
220	1.0524	e 1.8001	1.0484	1.0935	1.2652	1:0675
280	1.0568	1.8165	1.0506	1:0978	1.2866	1.0706

WATER.

592; 10, 284 [1877 and 1880]; Henrichsen, W. 8, 83 [1879]; Baumgartner, W. 8, 648 [1879]).
The following values for S.H. of water, from

0° to 85°, are given by Bartoli a. Stracciali (A. Ch. [6] 29, 285); the values in the column 'calculated' were obtained by using the formula:

S.H. = 1.006630 Q00593962t ·000004338650t2 0000004255204 ·000000002819#

The unit is the quantity of heat given out by I gram water at 15° in cooling to 14°.

ţ0	S.H. calcd.	S.II. observed.
00	1.006630	1.00664
í	1.006041	1.00601
. 2	1.005463	1.00513
8	1.004898	1.00489
4	1.004350	1.00435
5	1.003820	1.00383
6	1.003307	1.00331
7	1.002824	1.00283
8	1.002362	1.00233
9	1.001927	1.00190
, 10·	1.001522	1.00149
11	1.001146	1.00111
12	1.00080	1.00078
13	1.000496	1.00048
14	1.000224	1.00023
15	0.999990	1.00000
16	0.999795	0 ·99983
17 18	0.999642	,0 ·99968
	0 ·999530	0.99959
19	0 999462	0.99951
20	0.999439	0.99947
21	0.999463	0.99950
22	0.999533	0.99955
23	0.999652	0.99964
24	0.999821	0.99983
25	1.000040	1.00005
26	1.000311	1.00031
27	1.000633	1.00064
28	1.000967	1.00098
29	1.001438	1.00143
80	1.001921	1.00187
31	1.002459	1.00241
32	1.003054	
33	1.003668 4	- ,
84	1.004408	
35	1.005170	

The S.H. of ice is considerably less than that of waters Regnault's determinations gave 474 be-

quantity of heat required to convert 1 g. of water at 100° into steam at 100°—is 585.77

gram-units, according to Favre a. Silbermann (A. Oh [3] 87, 461). The following values are given for the heat required to convert 1 g. of water at t° completely into water vapour; 606.5 when $t=0^{\circ}$, 637 when $t=100^{\circ}$, 676.6 when $t=230^{\circ}$ (Regnault, Acad. 21, 635); Dieteriei (W. 38, 1) gives 596.8 when $t=0^{\circ}$; Regnault (Le.) gives the formula $\lambda = A + Bt$ for the total heat of vaporisation of water at different temperatures, and gives the values A = 606.5. B =

According to Sakhrai (C. J. 61, 495 [1892]), the temperature of the steam escaping from a beiling salt solution is exactly the same as that of the solution."

The heat of fusion of ice, i.e. the quantity of heat required to convert 1 g. of ice at to into 1 g. of water at to is given as follows by different observers (the values are in gram-units different observers that values are in grant-state of heat):--79:24 and 79:06 when $t^2 = 0$; (Regnallt, A. Ch. [3] 8, 19); 79:25 when $t = 0^\circ$, 74:2 when $t = -10^\circ$, 80:22 when t varies from -2° to -21° Te = -10°, 80°22 when t varies from = 2° to = 21° (Person, A. Che [3] 21, 295; 30, 73); 77°85 at = 2°8°, 76°75 at = 4°935°, 76°11 at = 6°28°, 76°0 at = 6°6° (Petterson, J. pr. [2] 24, 129).

The thermal conductivity of water, from 10° to 18°, was determined by Winkelmann (P. 153, 481) to be 154; Bottomley (Pr.31,300) obtained nearly the same value; this figure means that heat sufficient to raise 154 mgm, water from 0° to 1° passes per second through a layer of water 1 mm. thick and 1 sq. mm. area, when the difference between the temperatures of the two surfaces of the layer is maintained at 1°. For electrical conductivity of water v. Reactions, No. 2.

The refractive indices of water at different temperatures, and for different lights of determinate wave-lengths, have been measured by many observers. The following values have been found for μ_{He} : 133120 at 19.9°, 133091 a. Börnstein's Physikalisch-Chemische Tubellen [Berlin, 1883] 205; cf. also Perkin (C. J. 61, 293), who gives values for μ for the lines A C D and F, at 15° and 83.7°.

Observations have been made on the absorption spectrum of water and water-gas, but the matter has not been thoroughly investigated (v.

Yogel, P. 156, 326; Jansen, B. A. 1866, 11).
Water crystallises, as ice, in rhombohedral forms; snow is generally found crystallised in

water, Regnance tween -75° and 0°; the determinance tween -75° and 0°; the determinance tween -75° and 0°; the determinance tween -20° and 0°; Ramsay a. Young (T. 1884, 475) give the value 5 as the mean of various experiments. Sh. of water gas at 100° is given by Strecker (W. 7, 85) as 37 referred to an equal weight of water -1, and 1·36 referred to an equal volume of air -1; the ratio S.H.p. given by S. is 1.4, Jaeger (W. 36, 165 [1889] gave the value 1·33 to this ratio, and Cohen (W. 37, 628 [1889]) gave that the mol. w. of liquid water is probably 36, and this conclusion was strengthened by Walker's experiments on the connection between heats of 1 columbility (Z. P. C. 5, 194). From six-sided stars derived from six-sided prisms.

Molecular weight of liquid water. Several observations have been made which tend to measurements of the surface tension of water Ramsay and Shields (C. J. 68, 1069 [1893]) conclude that the mol. w. of liquid water is pro-

bably 72 at the ordinary temperature.

Reactions.—1. In 1847 Grove (T. 1847. 1)
showed that water was decomposed into H and O by heat. Grove formed a little ball on the end of a Pt wire, by fusing the Pt, heated the globule of Pt to whiteness by an electric current, and plunged it into alittle air-free water, nearly and plunged is into sentile air-free water, nearly boiling, in a small basin, with a test tube full of air-free water arranged to collect any gas that might come off. Deville (C. R. 56, 195, 322 [1863]) found that H and O were given off in considerable quantities when molter ePt was plunged under water. D. noticed no decompcstition when steam was passed through t. Pt tube heated to bright redness, but by passing a cur-rent of an indifferent gas, such as CO₂, through the hot tube, and thus sweeping away the products of decomposition, H and O were obtained .-2. Water is scarcely decomposed by an electric current. Kohlrausch found the electrical conductivity of the purest water he could obtain by distillation in vacuo to be 2.5 x 10-8 in C.G.S. units, or c. 72 billionths of the conductivity of Hg (P. M. [5] 18, 542). By calculations based on this result, Ostwald concluded that in a litre of pure water the weight of water dissociated into H and OH ions, expressed in gram-molecules, is $\cdot 6 \times 10^{-6}$ (Z. F. C. 11, 521). By other methods of calculation, based on other data, Ostwald arrived at the Value 2 to 9 x 10-6 for what has been called the dissociation constant of water (Z. P. C. 11, 521); Wijs, by calculations based on the hydrolysis of methyl acctate, obtained the values 1×10^{-7} (Z. P. C. 11, 492), and 14×10^{-6} (bid. 12, 514); Arrhenius obtained the value '1125 × 10⁻⁶ (bid. 11, 827); and Bredig, the value '6 × 10⁻⁶ (bid. 11, 829). Later experiments on the conductivity of water by Kohlrausch a. Heydweiller (Z. P. C. 14, 316 [1894]) with water that had been distilled in vacuo ten years ago, had then stood in a vessel filled with water, and been again distilled in vacuo, gave the following results:—conductivity (Hg = 1) 014 at 0°, 04 at 18°, 058 at 25°, 089 at 34°, 170; all these to be multiplied by 10 10. K. a. H. say that 1 mm. of this water at 0° had a resistance = that of 40 million kilometres of Cu wire of the same area. K. a. H. calculate that in 1 litre of the purest water at 18° there is 00008 mgm. H as free ions, and 000105 mgm. at 25°.—8. Steam is decomposed by stectric sparks; for condition, and details of results v. Thomson (Pr. 53, 90).

The reactions of water are so many that an approximate classification of them into groups is all that come be attempted here. - 1. Many metals react with water, at temperatures varying from the ordinary to a full red heat, forming oxides or hydroxides and giving off H. The following metals decompose cold water : Bay & , Ca, (Ce?), (La?), Li K, Rb, Na St. Al, Fe, Pb, Mg, (? Mn), Mo, Hi react at c. 100°; and most of the other metals at temperatures from c. 100° to a full red heat .- 5. Many non-metals react, generally slowly, with water, forming acids and giving. nary ter herature; Cl reacts slowly at the ordinary temperature, and somewhat more rapidly at a red heat; Br resuts more slowly than Cl; I has probably a very slight (?any) action. S' and P react slowly at 100°; Se is said not to

decompose water at 160°. Carbon gives off H at a red heat. Boron acts like a metal, giving off Hat a red heat .- 6. Many haloid compounds react with water, giving oxyhaloid compounds or oxides, and haloid soids.—7. Some metallic sul. phides react with steam to form oxides and H.S. 8. A few of the lower oxides decompose water; e.g. CrO.xH2O at the ordinary temperature, and CO at c. 600° .- 9. Water reacts with many oxides to form hydroxides which are either basic acidic: in some cases hydrates are formed. Hydrates of various salts are also produced by combining the salts with water (v. HYDRATES, vol. ii. p. 703; cf. Hydroxides, vol. ii. p. 783) .-10. Water dissolves very many compounds of the most different properties (v. Solutions, vol. iv. p. 484).

Small quantities of water often bring about chemical changes that do not occur when the substances are perfectly dry; for instance, a mixture of dry CO and O is not exploded by sparks, but a trace of water suffices to start the change (v. Baker, C. J. 65, 611 [1894]).

The acidic and basic characters of water are so nearly balanced that the compound cannot be classed among either acids or basic bodies. The chemical relations of water to the compounds formed by reactions between it and other substances are determined chiefly by the chemical characters of the substances that react with it; thus the relations of HOH to $M_x(OH)_y$, formed by the interaction of water and metals, are those of an acid to its salts, whereas the relations of HOH to HX, formed by the interactions of water and non-metals, are those of a basic hydroxide to salts derived therefrom. The relations between both classes of derivatives of water and the parent compound are sometimes expressed by saying that the compounds belong to the water

type (v. Types, vol. iv. p. 811). M. M. P. M. WAX. A term applied to various natural solids more or less resembling bees'-wax. They are compound ethers, but differ from fats in yielding monovalent alcohols and not glycerin on saponification. They melt below 100°, are insol. water, sl. sol. or insol. alcohol, and sol. ether. They are not volatile.

Bees'-wax. [64°]. S.G. 965. Consists of a portion (about 5 p.c.) soluble in alcohol (cerin) and as portion insoluble in alcohol (myricin). Myrion is myrioyl palmitate (Brodie, A. 87, 180; 71, 144). Cerin is chiefly composed of cercticacid; but it contains small quantities of meliusic acid C₂₀H₈₀O₂ [90°], and an acid melting at 73° (Schalfejeff, B. 9, 278, 1688; Natzger, A. 224, 246). There is also present one or more acids whose lead salts dissolve in ether and whose less sales dissolve in easer and which therefore probably belong to the cleic series. Myricin may be saponified by alcoholic pot.sh, and the myricyl alcohol separated from potassium palmitate by extraction with ligroin. Crude myricin yields CCl, and C.Cl, when heated with I and excess of SbCl, at 400° (Hartmann, B. 24, 1022). Bees'-we contains two hydrocarbons, one of which [60°] (c. 275° at 11 mm.) is probably n-beptaicosane C_s.H_{set}, and the other [68°] (c. 360° at 11 mm.) n-hentriacontaine C_s.H_{set} (Schwalb, A. 235, 106). According to Schwalb, the myricyl alcohol of bees'-wax has the formula C_{st}H_{st}Q [85°], and is converted by heating with

soda-lime into an acid CalHatO, [89°], which forms a methyl ether [71°] and an ethyl ether [70]. Among the products of saponification of bees'-wax, ceryl alcohol C₂,H₂₀O or C₂,H₃₀O or C₂,H₃₀O. The lastmentioned alcohol when heated with soda-lime gives an acid C₂₅H₃₆O₂ or C₂₄H₄₈O₂ [75.5°].

Carnaüba wax v. vol. i. p. 710. Chinese wax, which is produced by an insect, is almost entirely composed of ceryl carquates (C₂, H₃₅)C₂, H₃₅O₂ (Brodie, A. 67, 199). Cork wax v. Cerin.,

Pine wax v. CEROPIC ACID.

Sugar-cane wax v. CERQSIN.

Japan wax. [42°-55°]. Obtained in the East from Rhus succedanea. It appears to be really a fat, since palmitin is its chief com-It also contains the ether of a fatty acid of higher melting-point than stearic acid (Sthamer, A. 43, 343; Buri, Ar. Ph. [3] 14,

(Sthamer, A. 45, 545; Buri, A. 403).

Wax of Ficus gummiflua of Java contains an alcohol C₁H₂₀O [73°], v. sol. ether, and a small quantity (5 p.c.) of isoceryl alcohol C₂H₂₀O, sl. sol. ether (Kessel, B. 11, 2112).

Myrtle wax. [49°]. Got by boiling the berries of Myrica cerifera of North America with water (Moore, J. 1862, 506). Consists of palmitic and some lauric acid and (20 p.c. of) ralmitin. palmitin.

Opium wax. Contains ceryl cerotate and ceryl palmitate (Hosse, B. 3, 637).

Tobacco wax. Contains $C_{10}H_{140}O_{2}$ [63°], insol. cold alcohol, sol. ether and a small quantity of $C_{40}H_{120}O_{2}$ [64·5°], rd. sol. cold ether (Kissling, B_{1} , 16, 2433).

Coca leaf wax (Hesse, A. 271, 214). The wax from Trujillo coca is palmityl-(β)-amyrin wax from Trullio coca is paintivy. (6)-ally in $C_0H_{\infty}O_2$ (75°) [α]_p = 54.5°. On saponification it yields palmitic acid and (β)-amyrin $C_0H_{\infty}O$ [196°] [α]_p = 94.2°, which yields an acetyl derivative [286°] and a benzoyl derivative [228°]. The wax from the broad-leaved coca of Peru and Bolivia melts at 70°; contains palmityl-(8)-amyrin and a ketone, (8)-cerotinone C₃H₁₀₀O [66°], m. sol. alcohol, ether, and ligroïn. The wax from Java coca contains the same substances, and also some ceryl cerotate and ethers of myristic acid and of ovycerotic acid G,H,4O, [82°], which is v. e. sol. hot alcohol and ligroin, v. sl. sol. ether, and is converted by Ac₂O at 100° into cerotolic acid C₂H₃₂O₂ [70°].

WHEY PROTEID v. MLE.
WINE CIL. Light oil of wine. An oil obtained in the preparation of ether by distilling alcohol with H.SO.. The ether is shaken with a contract of the con milk of lime and fractionally distilled, the successive fractions being ether, alcohol, and wet cessive fractions being ether, absonot, and well alcohol. Light oil of wine (25 to 5 p.c. of the alcohol etherified) rises to the surface when the last fraction (90°-120°) is allowed to stand. When dried over CaCl, it has S.G. 17.5 903, Water. Wrightin It contains O₁₈H₂₈ (157°), EtOC₂H₁₁ (112°), conessine (g.v.).

Et.CO.C,H,1 (1549), and CH,.CO.C,H,2 (1649)

(Hartwig, J. pr. [2] 23, 449).

Heavy oil of wine, which passes over when the temperature is raised after the preparation of ether, consists of Et.SO, mixed with olefines (Claesson, J. pr. [2] 19, 259; Serullas, 4. Ch. [2]

WINTERGREEN OIB contains methyl o oxy-

benzoate. winterene C₁H₁, (260°-265°) S.G. 1934. [a], 11·2° at 16°. A destrorotatory sesquiterpene obtained by distilling winterbark (from Dryskis Winter-Forster) with water (Arata a. Canzoneri, G. 18, 527). Coloured green by Br in CHCl.. in CHCl.. WOOD v. LIGNONE.

WOOD GUM v. XYLAN.
WOOD NAPHIHA v. METHYL ALCOHOL.

WOOD OIL. Gurjun Balsam. Flows from incisions in the stem of Dipterocarpus costatus. It contains an essential oil, which gives a splendid violet coloff when its solftion in CS, (20 pts.) is treated with a drop of a cold mixture of HNO. and H.SO.. The same reaction is exhibited by the balsam itself, and also, in a more transient manner, by cod-liver oil and copaïba balsam (Flückiger, Ph. [3] 7, 2). The essential oil con-(Guibourt, J. 1876, 907). The essential of consists chiefly of a terpene (255°) (Werner, J. 1862, 461), which composes 65 h.o. of the balsam (Guibourt, J. 1876, 907). The resin contains a neutral substance, C₂₁II₄₀O₂, which brystalliase from light petroleum in triclinic prisms [1296–1200]. 130°]; it dissolves in conc. H, SO,, and is reppd. from the resulting reddish solution by adding water, It is not affected by potasil-fusion (Flückiger, Ar. Ph. [3] 12, 58). A substance $C_{20}H_{20}O_2$ [129°] is described by siding (M. 2, 510)as ppd. by adding water to an alcoholic extract of wood oil. It is neutral and insol. alkalis, and yields a diacetyl derivative [75°]. It is perhaps identical with the compound C. H. O. Wood oil also contains gurjunic acid C. H. O. [220°]. which crystallises from alcohol, distils with decomposition at 260°, and forms Ag,A".

WOOD SPIRIT v. METHYL ALCOHOL. WORMSEED OIL. Oleum Cina Oleum Cina. tained by steam-distillation from wormseed, the flower-buds of Artemisia Vahliana, A. Sieberi, and A. incalla (Trommsdorff, Tr. N. J. 8, 812; and A. incatta (Frommasorii, 17. 18. 3., 32.) Võickel, A. 38, 110; 87, 312; Hirzel, J. 1854, 591; 1855, 655; Kraut a. Wahlforss, A. 128, 293; Faust a. Homeyer, B. 7, 1429; Hell a. Ritter, B. 17, 2609; Wallach c. Brass, A. 220, 291). It consists chiefly of cincol C. H. O.

291). It consists chiefly of cineol C₁₈H₁₀O. Wormseed (A. Gallica) also co-tains betaine and choline (Jahns, B. 26, 1493).

WRIGHTINE C₁, H₁₈N. [1222]. Occurs in the juice of Wrightia antidysenterica (Stenhouse, Ph. [2] 5, 493; Warnecke, B. 19, 60). Needed with bitter taste, sl. sol. water, v. sol. alcohol and ether. Cohd. H₂SO, at 100° givgs a dark-green colour, turned dark blue by adding water. Wrightine, is probably identical with consessing (g. 2).

XARTHALINE C.,H.,N.O. [506°]. Occurs in opium (T. a. H. Smith, Ph. [8] 23, 793). White crystalline powder, insol. water and alkalis, sl. sol. hot alcohol, m. sol. benzete, v. e. sol. chloroform. Weak base, forming yellow salts from which it is, ppd. by hot water. Conc. H.SO, forms a deep-orange solution, from which water pots. the sulphate as yellow needles. Hot reduce it to hydroxanthaline O.,H.,N.O., which forms white crystals [137°], nearly insol. water, w. sol. alcohol and benzene, and forms easily soluble crystalline salts. Hydroxanthaline is coloured deep-violet by H_sSO₄ (even free from HNO,), the colour being destroyed by water, but reproduced by H₂SO₄.—B'H₂Cl₂4aq : yellow needles. Gives off all its acid at 150°.

XANTHAMIDE v. Ethyl ether of (β)-Thio-

CARBAMIC ACID.

XANTHATES. The salts RS.CS.OEt where R is a metal; v. ETHYL DITHIOCARBONATE.

XANTHIC ACID v. ETHYL DITHIOCARBONATE.

XANTHINE C.H.N.O. i.e.

NH.CH: C.NH
CO.NH. CHN
CO. Xanthic oxide. Mol. w.
152. S. 007 in the cold; 08 at 100°. Occasionally found in urinary calculi (Marcet, Essay on Calculi, London, 1819; Liebig a. Wöhler, A. 26, 840; Lebon, C. R. 73, 47) and in urinary deposits (Bence Jones, C. J. 15, 78). Occurs in small quantity in the urine of man, in the pancreas, sples, and liver of oxen, in the thymus gland of the calf, in muscle of mammalia and fishes (Scherer, A. 107, 314; 112, 257; Städeler, A. 111, 28; 116, 102; Dürr, A. 184, 45; Kossel, H. 6, 422), in some kinds of guano (Ungor a. Phipson, C. N. 6, 16), and in guano (Ungar a. Phipson, C. N. o., 10), and in yeast (Schindler, H. 18, 432). Occurs a'so in lupith seeds (Salomon, J. 1881, 1012; Schulze a. Barbieri, J. pr. [2] 27, 358), in pumpkin-seeds (E. Schulze, J. pr. [2] 32, 457), and in tea (Baginsky, H. 8, 996).

Formation.—1. By the action of nitrous acid

on guanine (Strecker, A. 108, 141; 118, 151; 181, 121; Balke, J. pr. [2] 47, 542).—2. In small

181, 121; Balke, J. pr. [2] 47, 542].—2. In small quantity by, heating a mixture of HOAc and aqueous HCy (Gautier, Bl. [2] 42, 141).

Preparation.—1. Separates as a crystalline powder when NaNO, (8 g.) is added slowly to a solution of guantine (10 g.) in H₂SO, (20 g.) and water (150 g.) at 75° (Fischer, A. 215):309).—

3. The aqueous extract of sprouting lupin seeds is evaporated, the residue treated with alcohol, and the alcoholi, filtrate avanorated. The and the alcoholic filtrate evaporated. The residue is dissolved in water and AgNO and NH, added. The gelatinous pp. is dissolved in hot HNO, (S.G. 1-1), which yields on cooling a crystalline compound of hypoxanthine and silver nitrate, and on adding NH, to the filtrate silvermanthine is ppd. (S. a. B.).—8. Urine is ppd. with bary'a-water; the filtrate is evaporated to a small bulk and boiled with cupric acetate. as small's bulk and boiled with cupric acetate.

The pp. is dissolved in warm nitric acid and spd. with AgNO; the pp. is crystallised from the diluted HNO, treated with ammeniacal in AgNO, elecomposed by H₂S, and the solution

HNO; it leaves a residue coloured orange by

evaporated.-4. A solution containing ranthine is treated with Fehling's solution and hydroxylamine hydrochloride, and the ppd. copper com-pound decomposed by H.S. The xanthine may the further purified by preparing its lead salt and decomposing this with H₂S (Balke, J. pr. [2] 47,

Properties.—Small scales (by evaporation) or powder composed of minute globules, nearly insol. cold water, insol. alcohol and ether. V. e. sol. KOHAq and reppd. by CO₂ and other acids. Weak base. Does not form an acetate. A cold saturated aqueous solution of xanthine gives white pps. with HgCl₂ and AgNO₃, and a yellowish-green, floculent pp. with hot cupric acetate. An a numerical solution of xanthine is ppd. by HgCl₂, ZnCl₂, CdCl₂, and AgNO₃. Xanthine HgCl₂, ZnCl₂, CdCl₂, and AgNO₃. Xanthine reduces ammoniacal cupric chloride (Drechsel. B. 25, 2454). Xanthine evaporated with nitrie acid leaves a yellow residue turned orange by KOH (but not by NH₃), the colour becoming violet-red on warming. Solid xanthine added to a mixture of bleaching-powder and NaOHAq on a watch-glass forms a dark-green spot, chan-ging to brown and finally disappearing. Xanthine warmed with chlorine-water and a trace of HNO, as long as gases escape, and then evapo-

HNO, as long as gases escape, and then evaporated to dryness, yields a residue which is soloured rose-red by gaseous NH₂ (Weidel, A. 158, 365; Kossel, H. 6, 420).

**Reactions.—1. Decomposed above 150°, giving off HCy, NH₂, cyanogen, and CO₂—2. KClO₂ and HClAq at 60° form urea and alloxan.—3. Conc. HClAq at 230° forms glycocoll, formic acid, NH₂, and CO₂ (E. Schmidt, A. 217, 311).—4. NaOH (2 mols.) and Pb(OAc), form a lead salt which, if dried and heated with MeI at 130°, yields theolyromine (Fischer).—5. Slowly

salt which, if dried and heated with MeI at 130°, yields theobromine (Fischer).—5. Slowly attacked by pure HNO₂, the gas evolved consisting of nitrogen (1 vol.), CO₂ (4 vols.), and N₂O (11 vols.) (Franchimont, R. T. C. 6, 223). Salts.—B'H.Cl. Nodular groups of silky needles.—B'H.SO₄ aq. Scales, decomposed by water.—B'BaH₂O₂. Sl. sol. water.—B'₂Cu₂O₃. Formed by the action of Fehling's solution and hydroxylamine hydroelfloride (Balke).—B'Ag₂O. Vallowish white flocculent pp., got by adding Yellowish-white flocculent pp., got by adding AgNO, to ar ammoniacal solution of xanthine. Blackens on boiling.—NaC.H.N.O.ag. Migute needles.

Brome-zanthine C.H.BrN.O. Formed by heating xanthine with bromine at 100°, and slso by the action of nitrous seid on bromeguanine (Fischer a. Reese, A. 221, 349). Crystalline powder, sol. conc. HClAq and H₂SO₄, but reppd. by water; sl. sol. hot water and flot alcohol; sol. alkalis.

Isoxanthine C.H.N.O. i.e.

NH.CO.C.NH N. Formed by reducing diazo-

KOHAq. Yields C,H,BrN,O, aq, crystallising from water in six-sided tables.

Pseudo-xanthine C₂H₁N₄O₂. A product of the action of H₂SO₄ (2 pts.) on uric soid (1 pt.) at 120° (Schultzen a. Filehne, B. 1, 150). Formed also by the action of nitrous soid on adenius (Kossel, H. 10, 258). Powder, al. sol. water? HClAq, and NH, Aq, v. sol. KOHAq. Its aqueous solution is acid in reaction, and on evaporation with HNO leaves a lemon-vellow residue, which is turned orange on warming with KOHAq.

The name pseudo-xanthine is also given by Gautier (Bi. [2] 48, 19) to a substance C,H,N,O occurring in muscular tissue. This is a yellow powder, which forms a very soluble hydro-chloride. Its aqueous solution is ppd. by HgCl₂, AgNO,, and ammoniacar Pb(OAc), but not by Pb(OAc). This pseudo-xanthine also gives an orange colour when the residue, after evaporation with HNO, is treated with potash.

Parazanthine O,H,N,O, [0.284°]. Occurs in human urine (Salomon, B. 16, 195; 18, 3406; H. 13, 187; Thydichum, H. 11, 415; Kosšel, H. 13, 302). Silky needles or monoclinic tables. insol. alcohol and ether, sl. sol. cold water, v. sol. hot water. Sol. NH, Aq and HClAq. Poisonous, acting like caffeine and theobromine. AgNO, added to its solution in HNO, or NH, Aq gives a gelatinous or flocoulent pp. Picric acid forms a yellow crystalline pp. when added to its solution in HCIAq. Gives a red colour (like xanthine) when the residue after evaporation with children water in exposed to gaseous NH. Does not, give an orange colour when KOHAq is added to the residue after evaporation with HNO. Cond. NaOHAq forms a crystalline salt. KOHAq does the same. A solution of paraxanthine is ppd. by Cu(OAc), phosphotungstic acid, HgCl, and ammoniacal lead subacetate, but not by mercuric nitrate.

Heteroxanthine C.H.N.O. Occurs in urine of men and dogs (Salomon, B. 18, 3407; H. 11, 412). Amorphous powder, v. sl. sol. cold water, sol. NH,Aq, insol. alcohol and ether. Its solution in HClAq is not ppd. by picric acid. AgNO, HgCl₂, Cu(OAc)₂, and ammoniacal lead sub-acetate give pps. When evaporated with chlorineacetate give pps. When evaporated with chlorine-water and HNO, it leaves a residue which is coloured red by gaseous NH, the colour changing to blue on addition of NaOHAq. NaOHAq forms a salt crystallising in tables, v. sol. water, al. sol. NaOHAq. The hydrochloride forms sparingly soluble crystalline aggregates, which lose HCl on treatment with water.

Hyperanthine v. vol. ii. p. 745.

Experanthine v. vol. ii. p. 745.

Example v. vol. ii. p. 745.

Exampl Get also by heating pseudo-uric acid with H.SC. st 150° (Grimaux, Bl. [2] 81, 535). White powder, nearly insol. water, sol. NH, Aq, forming solution with blue fluorescence. Its sorution a solution with blue fluorescence. Its sorution gives a white pp. with HgCl, and a yellow pp. with AgNO, Not attacked by HNO, Sol. KOHAq and reppd by CO, Sol. conc. H.SO., torming a laminar sulphate, decomposed by water with separation of xanthinine.—I'Ag.O. Bulky yellow pp., got by pouring an ammonifacal solution of xanthinine into excess of aqueous AgNO.

AENO_

XANTHOCHELIDONIC ACID & CHRESTONIO

MANTHOCREATININE of CREATININE and LEUCOMAÏNES

XANTHOGALLOL C., H.Br., O. i.e.

C₆H₂Br₄O < O₀C₆HBr₂O > O (?). [122°]. Formed by adding pyrogallol (1 st.) to bromine (10 pts.), leaving the mixture to stand for two hours, and then shaking with water and heating (Stenhouse a. Groves, C. J. 28, 1; A. 177, 191; 179, 287; Theurer, A. 245, 334). Tri-bromo-pyrogallol is an intermediate body in its preparation. Yellow blaming (Fram CS and lignoid) and the conditions of the conditions lamins (from CS, and ligroin), v. sol. ether and *slamins (from CS, and hgroif), v. sol. ether and CS, m. sol. *ligroin. Decomposed by boiling with water or alcohol. Very stable towards oxidising agents, eyen crystallising unaltered from conc. HNO.. Not reduced by sodium-amagam or by sine and dilute H,SO. Aniline in HOAo yields an anilide [205°], to which Theurer assigns the impossible formula C,H,Br,(NHPh),O, Toluiding forms a concasponding activities. p-Toluiding forms a corresponding p-toluide. Reacts with phenyl-hydrazine acetate.

Reactions .- 1. NaOHAq forms hexa-bromobenzene dihydride C.H.Br. [189°], sl. sol. alcohol, which crystallises in prisms, while the mother-liquor contains a sodium salt of an acid C₃H₁Br₂O₂ [124°], which forms BaA", crystallis-ing from dilute alcohol in large white plates (Theurer). By the action of dilute NaOHAq on xanthogallol, Hantzsch a schmiter (B. 20, 2033) obtained O₁H₂Br₁,(OH)₂O₂, which yields Ba₂(C₁H₃Br₁,O₂)₂ and crystalline C₁H₃Br₁Ac₂O₂ 2. Na₂CO₂Aq converts xanthogallol in the cold into G₁H₃Br₁O₂, crystallising from benzene in needles [72°] and prisms [131°], yielding the crystalline derivatives C₁H₃R₁CO₂RPhH₃ and C₁H₃Br₁O₃RNI₂CH₃Me.—3. HBr passed into a cooled solution of xanthogallol in MeOH forms C₁H₃Br₁O₃(OMe), crystallising from MeOH in prisms [113°], and converted by boiling dilute NaOHAq into an acid O₂H₁Br₁O₃(OMe), which crystallises in prisms, while the motherdilute NaOHAq into an acid C.H.Br.O.(OMe), [105°], and by MeOH and hydrochloris acid into C.H.Br.O.(OMe), [77°]. The brominated acid C.H.Br.O.(OMe), reacts with aniline, forming crystalline C.H.Br.O.(OMe), the Conc. H.Br.O.(OMe), the C.H.Br.O.(OMe), the Conc. H.Br.O.(OMe), the C.H.Br.O.(OMe), the C.H.Br.O [65°].—4. Hydrochloric acid gas passed into a cooled solution of xanthogallol in MeOH forms C₁₈H₄Br₁₁Cl₂O₂(OMe)₄[86°], which is insol. water, v. tol. alcohol, does not react with aniline, and is decomposed by dilute alkalis. -5. HCl passed into an alcoholic solution of xanthogallol forms The an account solution of Espinosistic terms of the Heri, Cl.O. (OE), crystallising from alcohol in colourless prisms [75], canyetted by NaOHAq into a product [92]. Cl. H.Br. 1, 2,9 [104] is bye-product in the action of alcohol and HO] on xanthogaliol. 'It forms large yellow crystals,

v. sol. alcohol.

PANTHOGENIC ACID v. ETHYL DITHIOGRA-

XANTHOWETHYLIC ACID v. LISTERL TRIO-

XANTHONE is DIPHENTIANE ERTONE OXIDE. KANTHOPURPURIN is m-DI-OXY-ARTERA-QUINONE.

KANTHOQUINIC ACID e. Ozy-burnouma

CARBOXYLIQ ACID.

XANTHORNAMMIN.C., H., O., (?). Obtained from Persian barries (the fruit of Rhammus factoria) by extracting with three times their

weight of 85 p.e. alcohol; the yield being 12 p.e. (Liebermann a. Hörmann, B. 11, 952, 1618; A. 196, 807; cf. Kane, P. M. [3] 28, 8; Gellatly, N. E. P. J. 7, 252; C. N. 3, 196; Hasiwetz, A. 111, 108; Bolley, A. 115, 55; Ü. J. 13, 328; Stein, Z. [2] 5, 183, 568; Behrends R. 11, 1353). Yellow heedles (containing 2aq), v. sol. water and alcohol, insed, ether. Hes little timetoxial Yellow heedles (containing 2aq), v. sol. water and alcohol, insol. ether. Has little tinctorial power. Reduces Fehling's solution and ammoniacal AgNO₃, forming a mirror. Feell, gives a dark-brown pp. Ppd: by ammoniacal lead acctate. Boiling dilute H₂SO₄ splits it up into rhamnetin (2 mols.) and isodulcite (4 mols.). Salts.—C₄₈H_{ex}K_{O20}. Yellow powder, v. e. tol. water.—PbA. v. Yellow pp.

**Acetyl derivatives C₄₈H_{ex}A<sub>C₁O₂₀.

**Cohistonerous X [SI] A 669. CH HAC.O.</sub>

Acetyl derivatives C₄₈H₄₄Ac₁₇O₂₈ (Schützenberger, Z. [2] 4, 668), C₄₄H₄₄Ac₁₇O₂₈. Powder, v. e. sol. alcohol (Liebermann a. Bergami, B. 20, 2245)

XANTHOBOCCELIN v. PICRO-ROCCELIN.

XANTHORRHEA RESIN is ACAROID RESIN. **EANTHOXYLIN** C₁₀H₁₂O₄. [80⁴]. Occurs, together with zenthoxylene C₁₀H₁₆ (162°) in the essential oil from japan-peaper (Xanthoxylon piperitum) (Stenhouse, Ph. [2] 13, 423; 17, 19; 4104, 297). Silly menopolity and the control of the co 4. 104, 237). Silky monoclinic crystals, insol. water, v. sol. alcohol and ether. Its alcoholic solution is not ppd. by AgNO₃ or lead acetate, even on addition of NH,Aq.

XENYLAMINE v. p-Amido-diphenyl. XENYBENE-DIAMINE v. p-p-Di-amido-di-

XERONIC ACID v. DI-ETHYL-MALEÏC ACID.

XYLAN C.H., O. Tree gum. Wood gum. S. 2 at 100°. [a]_D = 69°6° (Tollens); —84° (Thomsen). Obtained from the bark of trees (T. Thomsen, J., Tr. [2] 19, 146; Poumarède a. Figuier, A. 64, 388). Obtained to the crient of 1.78 p.c., by extracting jute with dilute (5 p.c.) NaCHAq; and got also by extracting beechwood or pine-wood sawdust with 5 p.c. NaOHAq (Tollens, A., 254, 307, 320, 324, 326; Bl. [3] 1, 1102; Winterstein, H. 17, 381). Obtained also be extracting wheat straw first with 2 p.e. by extracting wheat-straw, first with 2 p.c. NH,Aq, and then with 5 p.c. NaOHAq (Tollens, A. 260, 291). The alkaline extract is ppd. with alcohol and HCl.

Properties. - Porous mass, insol. cold, sol. hot, water; sol. NaOHAq. The hot agreeus solu-tion becomes opalescent on cooling. Insol. alcohol, but the aqueous solution is not ppds by alcohol unless an acid or the salt of an alkali is

alcohol unless an acid or the salt of an alkli is added. Insol. NH,Aq, lime and baryta-water. Its aqueous solution is levorotatory. Gives furfuraldehyde when boiled with H,SO, or HCl, and xylose when boiled with dilute H,SO, Gives no colour with ioding. HNO, oxidises aylan to saccharic acid, but gives no mucic acid. c-XYLENE C₂H, i.e. C₄H,Me,[1:2]. Dimethyl-bensene. Mol. w. 106, [-28°] (Verson, A. Ch. [6] 6, 128). (1182)* S.G.* 8932 (Pinette, A. 243, 50); 13° 865 (Gladstone, C. J. 300). Mal 14928, Mal 15328. C.E. (0°-10°) 100968. S.V. 1839 (Schiff); 137°6 (Pinette). McL. 1,084,274 [(1,0,=94,000; H,0=69,000] (Stohmann, J. pr. [2] 35, 41). M.M. 18-31 (Schönföck, Z. P. C. 11, 758). Critical temperature: 846° (A.). Occurs in coal-tar. The S.G.*of crude xylene varies in coal-tar. The S.G.*of orude xylene varies between 857 and 866; it contains 70 to 87 p.c. the syllane, 9 to 10 p.c. p-xylene, 2 to 15 p.c.

orylene, and 8 to 10 p.e. fatty hydrocarbons (Levinstein, B. 17, 444; of. Fittig, A. 148, 10). If 100 c.e. of the mixture are boiled for 45 minutes with 40 c.c. of HNO, (S.G. 1-42) diluted with 60 c.q. of water, the p- and o-xylene are oxidised, leaving the m-xylene and fatty hydrocarbons. If the residual hydrocarbons, after washing with NaOHAq followed by steam distillation, be shaken for 80 minutes with 11 volumes of H.SO, the m-xylene will be sul-phonated and dissolved, while the fatty hydro-carbons remain. If 100,c.c. of crude xylene be shaken with 120 c.c. of H2SO4, the o- and mxylene dissolve, leaving the p-xylene and fatty hydrocarbons. On crystallising the sodium salts of the dissolved sulphonic acids, sodium o-rylene sulphonate separates first, and may be converted into o-rylene by heating in a sealed tube with HClAq at 190° (Jacobsen, B. 10, 1009), or by heating with diluted sulphuric acid. Nölting, Witt, and Forel (B. 18, 2668) found 25 p.c. of p-xylene in commercial xylene. According to Nölting and Palmer (B. 24, 1955), crude xylene may contain 10 p.c. of ethyl-benzene. When a mixture of o-xylene and ethyl-benzene. is treated with Br (20 pts.) and I, tetra-bromoxylene is formed, together with a less highly brominated ethyl-benzene (Crafts, C. R. 114, 1110).

Formation.—1. By distilling its carboxylic acids with lime.—2. From o-bromo-toluene, MeI, and Na (Jannasch a. Hübner, A. 170, 117; Reymann, Bl. [2] 26, 532).—3. By heating cantharidin with P₂S₅ (Piccard, B. 12, 580).—4. By passing MeI through a mixture of toluene and AlCl, at 85° (Jacobsen, B. 14, 2628).

Properties.—Oil, solidifying in a freezing-mixture at -28°. Unlike m- and p- xylene it does not yield a solid nitro- derivative with a cold mixture of H.SO, and HNO. It is com-

Becommission of H₂SU₂ and finU₃. It is completely oxidised by chronic said mixture.

Reactions.—1. Dilute HNO₂ forms o-toluic soid.—2. Boiling squeous KMnO₄ oxidises it to phthalic scid.—3. PCl₁ at 200° reacts, forming O₂H₁(CCl₂), CHCl₂ (Colson s. Gautier, Bl. [2] 45, 507) .- 4. Bromine in the dark forms bromo-oxylene C.H.Me.Br [1:2:4]. In direct sunshine the products are C.H.Me.CH.Br and C.H.(CH.Br), (Schramm, B. 18, 1278).—5. AlCl, and gaseous HCl at*100° yield behizene, m. and a little p. xylene, ψ -cumene and mesitylene (Hesse a. Töhl, A. 270, 168).

Properties.—Liquid. Not attacked by dilute INO. Conc. HNO, on warming forms tri-

HNO. Conc. HNO. on warming forms trinitro-xylene [176°], sl. sol. alcohol.

Reactions.—1. Oxidised by chromic acid
micture to isophthalic acid.—2. ECl., at 200°
forms a hexachloride (Colson a. Gautier, Bl. [2]
45, 566).—3. Bromine in the dark forms
C.H.Me.Br [1:3:4], while in direct sunshine
C.H.Me(OH.Br) and C.H.(CH.Br), are produced
(Sohramm, B. 18, 1277°, M. 8, 305).—4. AlCl.e
and gaseous HCl at 100° form became, mestyleng. and some p.xylene and becamene (Heise a and gaseous prevene and ψ -cumene (Heise a. Töhl, A. 270, 168). On boiling with AlCl, the products are benzene, toluene, a little p-xylene, v-cumene, mesitylene, and durene (Anschütz, A. ψ-cumene, mesitylene, and durene (Ahschütz, A. 235, 182).—5. On heating with Mel and I at 250° it yields ψ-cumene, mesitylene, and C₁₈H₁₄ (Rayman a. Preis, A. 223, 320).—6. Ethyl-malonyl chloride at 60° in presence of AlCl₂ forms the ketone C₁₈H₁₄O₂ [63°] (Béhal a. Auger, Bl. [3] 3, 122).—7. Benzoyl peroxide forms dixylylene C₁₈H₁₈ (265°), S.G. 21° 9984 (Lippmann, M. 7, 528).—8. CrO₂Cl₂ added to its solution in CS₂ ppts. chocolate brown C.H.Mc.2CrO.Cl.. which is ppts. chocolate brown C,H,Me,2CrO,Cl, which is converted by water into m-toluic aldehyde and converted by water into m-toluic aldehyde and at 200° yields C₂H₄Me.CH(GrO₂Cl)₂(Étard, A. Ch. [5] 22, 244).—9. CH₂Cl₂ and AlCl₄ form tetramethyl-anthracene [163°] (Friedel a. Crafts, A. Ch. [6] 11, 268).—10. PHJ forms C₂H₄, on heating (Bayer, Z₂ [2] \(\frac{2}{4}, 455 \)). HIAq and P at 280° form m-xylene hexahydride.

at 280° 10rm m-xylene hexahydride.
p-Xylene C.H.Me. [1:4]. [13°] (Reissert, B.
23, 2242); [15°] (Jannasch). (138°). S.G. §
8801 (R); 27 860 (Gladstone, C. J. 59, 290).
C.E. (0°-10°) 00098 (Pinette, A. 243, 51).
p. 14864. \(\mu_1 \cdot \cdot 2525 \). S.V. 140 (Schiff). H.G.
1,084,274 (Stohmann, J. pr. [2] 35, 41). M.M.
12·79 at 20°-30° (Schönrock, Z. P. C. 11, 753).
Critical temperature: 344°. Occurs in coal-tar Critical temperature: 344°. Occurs in coal-tar (v. supra) and in Galician petroleum (Pawlewski, B. 18, 1915). Formed by the action of MeI and sodium on p-bromo-toluene (Fittig, A. 136, 303; Jannasch, A. 171, 73) and on p-di-bromo-benzene (V. Meyer, B. 3, 753). Monoclinic prisms; a:b:c=2'32:1:2'34; β=69'5° (Baeyer, A. 245,

Reactions .- 1. Dilute HNO, forms p-toluic acid.—2. Chromic acid mixture yields 'terephthalic acid.—3. PCl, at 190° gives C,H,(CH₂Cl)₂ and at 200° C,H,(CCl₃)₂ (Colson a. Gathier, Bl. [2] 45, 6, 507).—4. Bromine in the dark forms C.H.BrMe, while in direct sunshine the products are C.H.Mc.OH.Br and C.H.(OH.Br). (Schramm, B. 18, 1276).—5. AlCl, and HCl at 100°cact in the same way as with o-xylene.

References .- Bromo-, Bromo-nitro-, Chloro-, DICHLOBO-NITBO, DI-10DO-, NITBO-, and OXY,

XYLENE-AZO- compounds v. Azo- com-POTNOS. * XYLENE CARBOXYLIC ACID v. DI-METEYL-

BENZOIC ACID and MESITYLENIC ACID.

M-XYLENE DICARBOXYLIC ACID C.H.Q 6.e. C,H,Me,(CO,H), [1:8:4:6]. Dimethyl-iso phthalic acid.

thalic acid.
(a).Cumidic acid. Mol. w. 194. [above \$20°]. (a) Cumide acts. Mol. w. 193. [2009 220].
Formed by heating di-bromo-m-xylens dissolved in ether under pressure with ClCO_Et and Equium-amalgam. Formed also, together with (8)-cumidic acid, by oxidation of durene with dilute HNO_s or of durglic acid with KMnO_s (Schnapauff,

B. 19, 2508). Minute prisms (from water) or plates (by sublimation).—BaA" 1 aq : crystals, v. sol. water. Yields m-xylene on distilling with lime.

Methylether Me.A". [76°]. Crystals. m-Xylene dicarboxylic acid

C.H.Me.(CO.H), [1:3:4:5]. Dimethyl phthalic acid. Isocumidic acid. [280°]. Formed by oxidaacia. isocumiate acia. [250-]. Formed by Orlaction of ω(β)- and (γ)-isodurylic acid (Jacobsen, B. 15, 1857). «Small crystals. May be sublimed. Yields m-xylene on distillation with lime. The Ca salt crystallises in small plates. The Ba salt & amorphous.

p Xylene dicapoxylic acid C_aH₁Me₄(Co₂H)g[1:4:2:5]. Di-methyl-terephthalic acid. (β)-Cumidic acid. Formed, together with (a)-cumidic acid, by oxidation of s-durene with dilute HNO, or, of durylic acid with KMnO, (S.). dilute HNO, or of duryne acid with Minute six-sided prisms (from alcohol). Sublimes in small plates without melting. Nearly insol. hot water. Yields p-xylene on distilling with lime. **BaA" 2 aq. tables, v. sol. water. Methyl ether McA". [114°]. (c. 297° cor.).

Kylone diesebasylic soid
C_sH₂Me(CO,H)CH,CO_sH[3:2:1]. [178°]. Formed
by oxidation of C_sH₃Me(CO,Et)CH,CO_sH [Béhal a. Auger, C. R. 109, 972). Gives off CO, on fusion.

Xylene di-ω-carboxylic ackl v. Phenylene-DIACETIC ACID.

Reference.—Oxy-xylene carboxymo acm. XYLENE GLYCOL v. Di-oxy-xylene.

O-XYLENE DIHYDRIDE v. CANTHARENE. m. Xylene dihydride C₁H₁₂. (133°). S.G. 22 ·828. V.D. 3·74 (calc. 3·88). μ₁ 1·4675. Formed, together with a polymeride C₁₆H₁₄. (280°–285°) S.G. 22 ·832, by heating the ketone C.H. O with ZnCl., a The ketone itself is obtained by distilling the school of the control tilling the anhydride C10H14O, which is got by the action of Ac.O on cineolic acid, formed by oxidation of eucalyptol (Wallach, A. 258, 827).

Liquid, smelling like xylene. Yields on nitration $C_0H_2Me_2(NO_2)$ [1:3:4].

p-Xylene dihydride CMe<CH..CH>CMe. (134°) at 720 mm. Formed by heating di-methylquinite dibromide C.H.,Br, with quinoline (Baeyer, B. 25, 2122). Smells like turpentine. Forms a crystalline compound with HBr.

m-Xylene tetrahydride C.H.Me.. S.O. 2 814; 14 794.

Formation .- 1. By heating oxycamphoric anhydride C, H, O, with waten at 180° or with IPI at 150° (Wreden, A. 163, 386).—2. By heating camphoric acid with sympy phosphoric acid at 200%—3. By distilling camphoric acid with 210%, [Ballo, A. 197, 322].—4 By heating camphoric acid with 211Aq at 200° (Wreden, A. 187,

171), Properties — Oil. Oxidised by chromic said mixture to accide fiscoluic, isophthalic, and terophthalic acids. HNO, forms tri-nitro-m-

xylene. xylene.

Zylene tettahydride C.H.; (181°). S.G.
22 816. Occurs among the products of the distillation of colophony (Renard, A. Oh. [6] 1,
236). Slightly dextrorotatory liquid. Yields oily di- and tri- bronno- derivatives. Sulphurie acid forms an oily polymeride O.H., which is oxidised by fuming HNO, to succinic and oxalic Absorbs oxygen. Does not reduce

ammoniacal Agillo. In ethereal solution it combines with Br, forming Q,H,Br.,
m-Xylene tetrahydride (?) C,H,e. (120°).
Octomaphthylene. Formed by the action of moist Ag,0 on C,H,e,I, which is got by the action of Cal, at 60° on Q,H,C (175°), a product of the shlorination of octonaphthene (Jskowkin, J. R. 16, ii. 294). Oil, smelling like turpentine. Combines with Br (2 atoms). An isomeric ootenaphines with Br (2 atoms). 10, ii. 294). Oil, smelling like turpentine. Combines with Br (2 atoms). An isomeric octonaphthylene (123–129°) is got by distilling $\mathcal{O}_{i}H_{i,j}$ Obtained by chlorination of iso-octonaphthene (Putochin, J. R. 16, ii. 295).

m. Xylene hexabydride C.H., i.e.
C.H., Me, [1:3]. Octonaphthene. (118°). S.G.
2 7814 (Lossen, A. 225, 110); 2 7706 (A.).
C.E. (0° 26°) 001072. V.D. 3-87. S.V. 164 8. $\mu_{\rm b}=1^{\circ}419$ at 22° (Wallach, B. 25, 923). Occurs in Baku petroleum (Beilstein a. Kurbatoff, B. 13, 1820; Markownikoff a. Spady, B. 20, 1850), and among the products of the distillation of colophony (Renard, A. Ch. [6] 1, 229). Formed by heating heptang hthene carboxylic acid with HIAq and P (Aschan, B. 24, 2718). Prepared by heating camphorie acid or mexylene with HIAq at 200° (Wreden, A. 187, 757). Liquid. Not oxidised by aqueous KMnO., H.SO, and HNO, form tri-nitro-m-xylene. Sulphur at 220° forms m-xylene.

Isomeride C, His. Iso-octonaphthene. (122°). S.G. 3 .7767 17 .7637. Occurs in Caucasian petroleum (Putochin, J. R. 16, ii. 295). Liquid.

p-Kylene hexahydride C_sH₁₀Me₂[1:4]. (138° cor.), V.D. 4·01 (obs.). S.G. ‡ ·7956. Formed by heating bromo-camphor with ZnCl₂(R. Schiff, B. 18, 1407; G. 10, 320). Liquid, yielding tribits, and the complex control of the contr nitro-p-xylene [127°] on nitration.

m-XYLENE PHOSPHINIC ACID

Chloride C,H,Me,PCl, [1:3:4]. (257°).

Goffrom mercuric dixylyl Hg(C,H,Me, [4:1:3]), and PCl, at 235° (Weller, B. 20, 1720). Liquid, converted by water into the acid C, H, Me, P(OH).

Chlorine forms the compound C, H, Me, P(OH),

which is converted by water into C, H, Me, P(OH),

which is converted by water into C_sH₃Me_sPO(OH)₂ [194°].

m.Xylene-phosphinic acid C_sH₃Me_sPO(OH)₂ [98°] (Michaelis, A. 212, 237). Formed by the action of water on the chloride. Needles (from alcohol). Probably a mixture.

Chloride C_sH₃Me_sPOl₂ (256°). S.G. ¹²
1.24. Formed from m.Yclene, PCl₃ and AcCl₄ (Weller, B. 20, 1720). It is a mixture of the receding bedy and the 1.2 Siconomical Readily. preceding body and the 1,3,5 isomeride. Readily

preceding body and the 1,5,5 shorted. Evently absorbs chlorine, forming C₂H₂Me₂PCl₄, whence SO₂ forms C₂H₂Me₂PCl₄ (280°–300°).

p. Xylene phosphinous acid. Formed by treating the chloride with hot water. (Weller, B. 21,

1694). Crystallises with difficulty.

Chloride C₄H₄Me₂PCl₄. [-30°]. (254°).

S.G. 11 1.25. Formed by beating p-xylene (159g) with falCl₄ (30 g.) and PCl₄ (200 g.) for 36 hours with inverted condenser (Michaelis a. Paneck, A. 212, 286). Strongly refracting

m-XYLENE (-PHOSPHONIC ACID

CH.Ms. 4-PRIMER INTERIOR LAND (C. M. Ms. 42) (OH), m. Zylene (a)-phosphinic acid. [194°]. S. 1.5 at 20°; 6.9 at 100°. Formed by boiling the caloride C.H.Ms. PCl. (c. supra) with water (Weller, B. 20, 1721). Reedles, S. a. sol. alcohol. Decomposed into m-xylene

and phosphoric acid on heating with alkalia. Br added to dilute solutions forms brome- and di-bromo-m-xylene. Yields two nitro- derivatives [182°] and [100°].

[1827] and [1007].

Salts. 7 Bah" aq. Plates. — CdH,h", aq.

Plates, more sol. cold than hot water. —

NiH,h", aq. — Ag,h": white pp.

m. Xylene s. phosphonic acid

C,H,Me,PO(OH), m-Xylene (B)-phosphinic
acid, [1617]. S. 1.8 at 15°; 117.8 at 100°.

'Prepared by boiling with water the mixture of chlorides C,H,Me,POCI, (280°—800°) which is

not by the action, SO on the mixture of tetra. onlordes C.H.Me.P.Cl. (250°-300°) which is got by the action of SO₂ on the mixture of tetra-chlorides C.H.Me.P.Cl. formed by combination of chlorine with the mixture of chlorides C.H.Me.P.Cl. obtained by heating m-xylene with P.Cl. and AlCl. (W.). Plates or needles, v. e. sol. alcohol and ether. Decomposed by alkalis

into m-xylene and phosphoric acid.

p-Xylene phosphoric acid C₆H₈Me_pPO(OH)₂.

[180°]. Formed by the action of water on C₆H₈Me_pPCl₄ [c. 60°] which is got by passing Cl C₈H₈Me₂.PCI₈ (c. 60°) which is got by passing Cithrough the product of the action of PCI₈ on pxylene in presence of AlCI₈ (Weller, B. 21, 1494). Needles, m. sol. water, v. sol. alcohol, sl. sol. ether. Conc. HHO₈ forms the compound C₈H₁(NO₂)Me₂PO(OH)₂ [224°]. KMnO₄ yields C₈H₃Me(CO₂H).PO₂H₂ [278°]. Salts.—KHA".—BaA". Pearly plates, more sol. cold then but water.

sol. cold than hot wafer.

Chloride C.H.Me. POUl. (281°). S.G. 18 1. Oil. Formed by the action of SO, on C.H.Me.PCl.

Reference.—NITRO-XYLENE PHOSPHONIC ACID. XYLENE PHTHALOYLIC ACID v. PHENYL MYLYL KETONE CARBOXYLIC ACID.

o-XYLENE SULPHINIC ACID C.H. SO. i.e.

* o.XYLENE SULPHINIC ACID C.H., SO; i.e. C.s.H., Me., SO, H[1:2:4]. [83°]. Formed by the action of zinc-dust on o.xylene sulphochloride (Jacobsen, B. 10, 1011). Plates (from water).

**m-Xylene sulphinic acid C.H.Me., (SO, H)
[1:3:4]. [6. 50°]. Formed by reducing the sulphonic chloride C.H.Me., SO, Cl (Jacobsen; cf. Lindoff a. Otto, A. 140; 233). Crystalline.

*p-Xylene sulphinic acid C.H.Me., (SO, H)
[1:4:2]. [85°]. Groups of needles (Jacobsen, R 11 29)

[1:4:2]. [8 B. 11, 22).

C'AYLENE SULPHONIC ACID C.H. SO. i.e. C.H.Me.(SC.H.) [1:2:4]. Formed by warming o-xylene with H.SO. (Sacobsen, B. 10, 1011; 11, 22). Tables (containing 2aq) (from dilute H.SO.).—NaA' 5aq.—BaA', 2aq. S. 5·8 at 0°; 33.6 at 100°

33 Gat 100°, Chloria: C.H.Me. SO.Cl. [52°]. Prisms. Amids C.H.Me. SO.NH. [144°]. Yilds two_acids C.H.Me(CO.H). SO.NH, on oxidation

o-Kylene o sulphonic acid C.H.Me. SO.R. [1:2:3]. Formed by the action of sodium-amalgam on C.H.Me. Cl.(SO.H) [1:2:6:3] (Krüger, eB. 18. 1760).

18° 1760).

An ide C.H.Me., SO.NH.. Granules.

m'Eylene c. sulphonic acid. C.H.Me. (SO.H.)
[1:3:2]. m-Eylene (B) sulphonic acid. Formed, together with a larger quantity of the (1,3,4)-isomeride, by dissolving m'Eylene in fuming K.SO. (Jacobsen, A. 184, 188; B. 11, 18). It remains in the said liquor after prgs. the (1,3,4)-isomeride by the proper quantity of water. Potash-fusion yields p-zylenol [74:5°] (Jacobsen, B. 21, 3828). Its K salt heated with sodium

formate forms an soid C.H.O. [99°].-KA'. BaA's: minute needles.—CuA'saq.

Ghloride C.H.Me. SO.Cl. Oil. Amide C.H.Me. SO.NH. [96°]. Needles. Manae U. 12 mer. SU. Mar. [10°]. Needles. m. Xylene sulphonic acid. C.H. Me. (SO.H.) [1:3:4]. m. Xylene (a) sulphonic acid. Formed as abore. Long flat prisms (containing 2aq). Its Ke salt heated with sodium formate yields xylylic acid.—NaA.'—BaA'. Small plates.—"nA'. 9aq.—CuA'. 6aq. Chloride C.H.Me. SO.Cl. [34°]. *A mide [137°]. Needles (from water). 3zCl at 160° forms C.H.Me. SO.MHBz [151°] Mahon, Am. 4. 194). which yields crystalline

Mahon, Am. 4, 194), which yields crystalline la(C₁₈H₁₄NSO₃)₂aq and BaA'₂, sl. sol. water.

p-Xylene sulphonic acid C_eH₃Me₂(SO₂H)
[1:4:2]. Formed by sulphonating n-volume [1:4:2]. Formed by sulphonating p-xylene (Beilstein a. Wahlforss, A. 133, 38; Fittig a. Glinzer, A. 136, 305; Jacobsen, B. 10, 1009; 11,22; Remsen a. Emerson, Am. 8, 265). Plates or prisms (containing 2aq). Oxidised by alkaline KMnO, to sulpho-terephthalic and two sulpho-panilo, w supino-terepititate and two supino-p-toluic acids.—NaA'aq. [148°]. Trimetric plates; a:b:c=1.077:1:1:498 (Moody a. Nicholson, C. J. 57, 978).—KA'aq.—BaA'₂. S. 2·27 at 0°; 5·53 at 100°.—CuA'₂8aq. Light - blue triclinio

prisms.—ZnA'₂10aq.

Chloride C.H₁Me₂SO₂Cl. [26°]. Prisms. Amide [148°]. Needles, m. sol. hot water. o-Xyleng disulphonic acid C,H,Me,(SO,H), o-Ayien, alkalpaonie acia U.H.Me.(SU.H.).
Formed by hesting (1,2,4)-xylene sulphonie acid
with CISO.3H at 150° (Pfannenstill, J. pr. [2] 46,
155).—K.A"aq.—BaA"3aq.—PbA"3aq. Prisms.
Chloride C.H.Me.(SOCI). (79°). Prisms.
Amide C.H.Me.(SO,NH.). [230°].

m-Xylene disulphonic acid C.H.Mc.(SO.H) [1:3:4:2]. Formed by heating m-xylene with fuming H₂SO₄ at 150° (Wischin, B. 23, 2113), and by heating (1,3,4)-xylene sulphonic acid with SO, at 1500 (P.). Deliquescent needles, with SU, at 100° (r.). Designescent seedies, converted by potash-fusion into C,H,Me.(OH), [146°].— (NH,),2A".—NaHA" 3aq.—K,A" 2aq.—BaA" 3aq. Needles, v. sol. water.—PbA" 3aq.—CuA". Gummy mass.

Ethyl ether Et,A". Plates. Chtoride C,H,Me,(SO,Cl), [129°]. Converted by PCl, at 180° (2,4,1,3)-di-chloro-xylene

Needles. [249°]. Amide CaH N2S2O4 Amide C, H, 2N, 2S, V, CO NH) [225°].
Oxidised by KMnO, to C, H, (CO NH) [225°].

Ethylamide C.H.Me.(SO., HHEt). [135]. m.Xylene disulphonic acid C.X.Me.(SO.H). [1:8:2:6?]. Formed in small quantity, together [1:8:2:67]. Formed in small quantry, together with the preceding isomeride, by heating (1.3,2). The sulphonic acid with CISO, H at 150 (Pfannenstill, J. pr. [2] 46, 154). Needles. Chloride C.H.Me₂(SO₂Cl)₂. Oil. A mids. [210°]. More sol. water than its

isomeride.

isomeride.

p-Xylene disulphonic acid C,H,Me,(SC,H),
[1:4:2:6?]. Formed by heating (1,4.2).
C,H,Me,(SO,Ci) with fuming H,SO, (Holmes,
Am. 18, 372; Piannenstill, J. pr. [2] 46, 156).
Needles, v. e. sol. water.—BaA" 38q.—CaA" 48q.
—MgA" 78q.—PbA" 38q.—AgA" 48q.
C & Lorent e C,H,Me,(SC,Ci), [75°].
A mide C,H,Me,(SO,NH), [295°].

References.—Baomo., Brono.nitro., Nitro.,
and MitaCambo., XILEME SULPHOMIC Acid.

XYLENE THIOSULPHONIO ACID. Xylyl ether C.H., SO, S.C.H., Xylyl disulphoside. Formed by heating xylene sulphinic soid with water at 150°-160° (Otto s. Lindoff, A. 146, 239). Oil, v. sol. alcohol and other.

XYLENIC, ALCOHOL is TOLYL-CARBINOL. XYLENIC DIBROMIDE v. Di-m-BROMO-

TVI.ENE.

XTLENIC GLYCOL v. DI-w-OXY-XYLENE.

O.XTLENOL C. H., O t.e. C. H., Me, OH [1:2:4].

Mol. w. 122. [623]. (225° i.V.). H.F.p. 61,566

(Stolmann, J. pr. [2] 84, 816). Obtained by potash-fusion from the sulphenic acid (Jacobsen, B. 11,23) and bethe discovered potash-fusion from the sulphenic acid (Jacobsen, B. 11, 28), and by the diazo-reaction from (1,2,4)-xylidine (Jacobsen, B. 17, 161). Long needles (from water). SiCl, yields Si(OC₂H₂), crystallising in prisms (350°-360° at 120 mm.) (Herkorn, B. 18, 1691). Ammoniacal ZnBr, at 300° from xylidine and dixylylamine. — NaOC₄H₂-Flat needles, v. sl. sol. NaOHAq.

Benzoul derivativa [57°]. H.F. 77,768 (Stohmann, J. pr. [2] 36, 8).

o-Xylenol C.H.Mc₂(OH) [1:2:3]. [75°]. (218° i.V.). Occurs in coal-tar (Schulze, B. 20, 410). Formed by the action of nitrous acid on

410). Formed by the action of nitrous acid on c-o-xylidine (Tohl, B. 18, 2562; Nolting a. Forel, B. 18, 2673). Slender needles. Its aqueous

15, 18, 20,3). Siender needles. Its aqueous solution gives a blue colour with FeCl.

c.m. Xylenol C.H., Mc., (OH) [1:8:2]. [49°].

Obtained from the crude xylidine, or by the action of HCl on p. oxy. mesitylenic acid (Nölting; Jucobsen, B. 21, 2829). p-Xylenol is got instead of m-xylenol by potash-fusion from (1,3,2)-xyleno sulphonic acid (Jacobsen, B. 11, 26; 21, 2828

2828; (Jacobsen, B. 18, 3463); (28°) (Staedel a. Hölz, B. 18, 2919). (211.5° i.V.). S.G. 2 10862. H.F.p. 59,501 (Stomann, J. pr. [2] 34, 316). Formation.—1. From m-xylene sulphonic acid by potash-fusion (Jacobsen, B. 11, 24, 375; cf. Wroblewsky, Bl. [2] 10, 286; Wartz, J. 1868, 459). 2. By heating oxy-mesitylenic acid with conc. HClAq at 200° (Jacobsen, B. 11, 2052).—2. By reduction of uitro-m-xylene and treatment 3. By reduction of nitro-m-xylene and treatment of the resulting xylidine with nitrous acid (Harmsen, B. 13, 1558; S. a. S.; Hodgkinson a.

Limpach, O. J. 63, 104). Properties.—Needles, Properties.—Needles, v. sl. sol. water, miscible with alcohol and ether. Volatile with steem. FeCl, colours its aqueous solution blue and its alcoholic solution green, being changed to bright blue on dilution with water. Yields the corresponding xylidine, and di-xylyl-amine when heated with ZnBr, and English, and NH,Br at 315° (Müller, B. 20, 1041). Potash-fusion forms (4,1,3)-caretoluic acid. Yields city P) (OC,H-), (Kreysler, B. 18, 1703). SiCl, forms S (OC,H-), (455°) (Hertkorn, B. 16, 1990). Salt,—NaCC,H-, V. sol. water and cone. NaOHAq (duliké va salts of ther xylenols).

Methyl ether MeOC,H, (192° i.V.) (J.); (186°) (S.). H.F.2. 46,356 (Stohmann, J. pr. [2] 35, 24). and its alcoholic solution green, being changed

Acetyl derivative C. M. OAc. (226° LV.). *Xylenol C,H,Me₄(OH) [1:8:5]. [649 (T.); [689] (N. a. F.) (220°). Occurs in coal-tar (Schulze, B. 20, 410). Formed by the action of nitrous acid on s-xylidine (Thol., B. 18, 862; Nölting a. Forel, B. 18, 2679). Slender needles (from

Not coloured by FeCl,-NaOC,H. Plates, sl. sol. NaOHAq.

Plates, 81. 801. NAUTIAQ.

p. Mylenol C.H., Me. (OH) [1:4:2]. [74:5°].

(211:5° i.V.). H.F. of 1,862 (Stohmann, J. pr.

[2] 84, 316). S.G. 24 971. Formed by potash. fusion from m and from p-xylene sulphonic acid and from oxy-mesitylenic acid (Wurtz, A. 147, 878; Jacobsen, B. 11, 26). Formed also from p-xylidine by diazotisation followed by boiling with water (Nolting, Witt, a. Forel, B. 18, 2666). Long flat needles (from dilute flechol). Volatile with steam. Its aqueous solution is not coloured by FeCl.

Potash-fusion 'gives (3,4,1)-oxy-toluic and oxy-terephthalic acidt. KNO, and HOAO yield a nitroso-derivative C,H,2Me,(OH)(NO)[1:4:3:6] [163°], which is the exim of p-xyloquinone (Oliveri, G. 12, 162; Goldschmidt a. Schmid, B. 18, 568).

Salt.-NaOC.H. Large plates, sl. sol. cold NaOHAq.

Mathyl ether McOC, H., (1942 i.V.). Oil.

Ethyl ether EtOC, H., (1999) (S.); (205°)

(N. W. a. F.). Oil. H.F.p. 54, 150.

Acetyl derivative C, H., OAc. (237° iV.).

S.G. V 10264. Oil, not solid at -20°.

Talant (2902). Occurs in beechwood to.

Xylenol. (220°). Occurs in beechwood-tar (Marasse, A. 152, 75; Tiemann a. Mendelssohn, B. 10, 57). Oil. Yields C,H,OMe (220°). On boiling with aqueous KMnO, it yields an acid which is converted by potash-fusion into u-oxyisophthalic acid [300°].

References .- BROMO- and NITRO- XYLENOLS. XYLENOLIC ACID v. OXY-DI-METHYL-BEN-

ZOIC ACID.

O-XYLENOL SULPHONIC ACID C.H. St. i.e. C.H.Me. (OH). SO.H. Formed by sulphonation of (1,2,4)-xylenol (Jacobsen, B. 11, 24). F&Cl. gives a violet colour in neutral solutions.—NaA'. Slender prisms or small lamine.—BaA'. Nodular groups of minute lamine, sl. sol. cold water.

m-Xylenol (a) sulphonic acid. Formed, together with the (β)-isomeride, by dissolving 1,8,4) xylenol in H₂SO₄ (J.). FeCl₃ gives a violet-blue colour.—NaA'. Tables.—KA'. Plates.—

blue colour.—NAA. Tables.—NA. Flates.—BAA's. Leaflets.

m-Xylenol (3).sulphonic acid

O.H.Me.(OH).SO.H [1:3:4:2] (Jacobsen, A. 195, 283). Forfind as above. Coloured riolet-blue

by FeCl. Converted by potash-fusion into (2,5,1)-oxy-toluic acid.—NAA'4aq. Lamigo.

—BaA's. Mithute needles, less soluble than the

BaA', Minute needles, less soluble than the Ba salt of the (a) acid. By sulphonating (1,3,4)-xylenol by ClSO₂H, Hodgkinson (C. J. 62, 110) obtained a xylenol sulphonic acid yielding BaA', aq.

***Tylenol sulphonic ucid
C.H.Me. (OH). SO. H 1:3:6:4). Formed from C.H.Me. (OH). SO. H by the diazo-reaction (Sartig, A. 230, 336). Slender needles, v. sol. water and alcohol. The acid and its ualts give with FeCl. a bluish-violet colour turned green by alcohol.—

RA'.—BaA', aq. Needles, v. e. sol. water.—
PbA', 2aq.

PbA', 2aq.

Ethyl derivative C.H.Mc. (OEt).SO.H.
Formed by heating diazo-m-xylene sulphonic acid with a cohol under pressure. Minute tables, v. sol. water and alcohol.—BaA', 3aq. Minute

plates, v. sol. water.

tes, v. sol. water.

p-Xylenol sulphonic acid. Formed by dissolving p-xylenol in warm H.SO. Hydrated losfiets.—NaA'5aq. Tables.—BaA'2 needles.

Reference.—NITRO-XYLENGL SULPHONIC ACID.
XYLENYL-AMIDOXIM v. DI-METHYL-BEN-ZOIC ACID.

XYLEN'IL ALCOHOL v. DI-OXY-XYLENE. XYLENYL CHLORIDE v. Tetra-co-chloro-

XYLENE. XYLETIC ACID is Oxy-DI-METHYL-BENZOIC ACID.

XILIC ACID is DI-METHYL-BENZOIC ACID. XYLIDIC ACID is TOLUENE DICARBOXMAC

c-o-XYLIDINE C.H.Me.(NH.) [1:2:8].—
Di.methyl-zhenyl-anine. Amido-xylene. Mol.
w. 121. (223° i.V.) at 739 mm. S.G. 12 991,
Obtained by reducing di*-bromo-o-xylidine
C.HMe.Br.(NH.) [1:2:45:3] with sodium-amalgam in the cold (Töhl, B. 18, 2562). Got also
by heating (1,2,4)-xylenol with NH.Br and ammonio-zine bromide at 300° (Müller, B. 20, 1039). Prepared from o-xylene by nitration and reduction (Nölting a. Forel, B. 18, 2671; Wroblewski, B. 18, 2904). Oil. When oxidised by K₂Cr₂O₇ and H₂SO, it yields a small quantity of o-xylo-quinone [55°]. Converted by the diazo-reaction into o-xylenol [73°]. H₂SO₄ and HNO₄ give (4,1,2,3)-nitro-xylidine [114°] and (6,1,2,3)-nitro-xylidine [114° xylidine [65°] (Nölting a. Stoecklin, B. 24, 567).
—Salts: B'HClaq. Plates. Begins to sublime at 100°.—B'HNO, Needles:—B'_H_SO. Large plates, sl. sol. water.

Acetyl derivative C₂H₂Me₂NHAc. [134°] (N. a. F.); [131°] (T.; W.). Slender needles. i-o-Xylidine O₂H₂Me₂(NH₂) [12:4]. [49°]. (226°). S.G. U* 1.0755. Frepared from owhene by nitration and reduction (Jacobsen, B. 17, 159). Got also by heating m-toluidine hydrochloride with MeOH at 300° (Limpach, B. 21, 643). Monoclinic crystals, not coloured by exposure to light and air. Gives no colour with bleaching powder. Its solutions colour pinewood yellow. On nitration it yields (6,1,2,4)nitro-xylidine [137°] and an isomeride [80°] (N. a. S.). Yields a saffranine on oxidation together

a. S.). Yields a saffranine on oxidation together with di-amido-di-phenyl-amine (Nietzki, B. 19, 3163).—Salt: B'HClaq. Prisms, v. sol. water. Yields \(\psi \)-cumidine when heated with MeOH at 310° (N. a. F.).

Acetyl derivative C.H.,Mc.(NHAc). [99°].

c.m. Xylidine C.H.,Mc.(NH₂) [1.3:2]. (\$).

Xylidine (214° 1.7) at 739 mm. (N. a. F.).

S.G., 22, 9942 (W.). Formed by distilling pamidognesity.enic acid with lime (Schmitz, A. 193. 179) and by reducing c-nitc-m-xylene. 193, 179) and by reducing c-nitro-m-xylene (Grevingk, B. 17, 2430). Obtained from commercial sylidine by crystallisation of the sulphate; the last mother-liquor depositing cryst tals which are converted into the acetyl derivative by distillation with HOAc. The acetyl derivative is saponified by treatment with diluse dertyative is saponified by treatment with diluge (25 p.c.) H₂SO₄ (Nölting a. Pick, B. 21, 3150; cf. Wróblewsky, B. 12, 1226). Gives m-xyloquinone (73°) on oxidation (Nölting a. Forel, B. 18, 2676). Yields (4,1,8,2)-nitro-xylidine [83°] on nitration (Nölting a. Stoecklin, Bl. [3] 5₄ 381).—Salts: B'HCl.—B'HCl aq. S. 9.7 at 18° a. Monoclinto plates. Yields mesidine on heating with MeOH at 310°.—B'HNO. S. 9.2. Needles.—B'_HRO. Very soluble needles.—B'H₁SO₄, 2½ aq. S. 60. Acetyl derivative [1740] (G.); [176-5]

(N. a. F.). Needles.

Bensoyl derivative [140°]. Needles. Yields benzoyl-nitro-xylidine [178°] on nitration

Helds benzoyi-into-xyndine [176] on nitration (Hühner, 4. 208, 318).

s.m-Xylidine C,H.Me.(NH.) [1:3:5]. (222°
I.V.). \$\frac{3}{2}\$. If 972. Formed by reduction of s-nitre-m-xylene [710] (Thöl. \$\frac{1}{2}\$. R5 (362; Nöltting a. Forel, \$\frac{1}{2}\$. 18, 2678). On exidation by ting a. Forel, B. 18, 2678). On oxidation by K₂Cr₂O, and H₂SO, it gives m-xyloquinone [73°], By boiling the diazo-compound with water xylonol [68°] is formed. ClCO_Et forms C₆H₂Me₂NH.CO₂Et [77·5°] (Frentzel, C. C. 1883, 1361).—B'HCl. MeOH at 250°-300° yields iso-cumidine C₆H₂Me₂(NH₂) [54:3:1] (Lhapach, B. 21, 643).—B'H₂SO₄ aq.—B'HNO₂. S. 4·66 at 13°. Acetyl derivdtive [140·5°] (N. a. E.); [138°] (T.); [144·5°] (W.). Colourless plates (from alcohol or ether).

i-m-Xylidine C₆H₃Me₂(NH₂) [1:3:4]. (a)-Xylidine. (215°) at 745 mm. (G.). S.G. 12° 9184 (H.). S.V. 148·3.

Formation.—1. By reducing i-nitro-m-

Formation.—1. By reducing i-nitro-m-xylene (Deumelandt, A. 144, 273; Tavildaroff, B. 2, 553; Wroblewsky, A. 192, 215; 207, 91; Grevingk, B. 17, 2430; Wallach, A. 258, 331). It may be isolated from commercial xylidine by conversion into hydrochloride and several crystallisations from water; the yield being about 40 p.o. (Nölting a Forel, B. 18, 2677).—2. By heating o and p-toluidine hydrochloride with MeOH at 300° (Hofmann, B. 9, 1295; Limpach, B. 21, 640). -3. By distilling (4,3,1,5)-amidomesitylepic acid with lime. (Schmitz, A. 193, 177).—4. By heating i-m-xylenol with anmonium-zinc bromide and NH, Br (Müller, B. 20,

Reactions.—1. When dissolved in H₂SO₄ (10 pts.) it yields C₆H₂Me₂(NH₂)(NO₂) [1:3:4:6] [123°] on nitration (Nölting a. Collin, B. 17, 265).-2. The hydrochloride heated with MeOH at 310° yields mesidine.—3. ClCO_Et forms C₄H_Me_NH.CO_Et [57°] (Frentzel, C. C. 1888, 1361).—4. When mixed with di-amido-di-phenylamine it yields a saffranine on oxidation (Nietzki, amine it yields a sairrainie on oxidation (Netzer, B. 19, 3163).—5. When m-xylidine (4 pts.) is heated with S (1 pt.) at 190° it gives off H₂S and forms a base C_xH_xN_xS [107°] (285° at 14 mm.) which crystallises from alcohol in yellowish white prisms and yields C₁₄H_xAcN_xS [227°] (Anschütz a. Scaultz, B. 22, 582). By further heating with sulphur a homologue of

turther heating with sulphur a homologue of primuline is formed.—6. **CEnanthol forms, oily C.,H.,NO (Leeds, B. 16, 288).—7. **Erolein-yields C.,H.,NO (Leeds, B. 16, 288).—8. **Erolein-yields cryptidine O.,H.,IN (270°) (Leeds, A. C. J. 5, 1).

Salts.—B'HCl. Monoclaide prisms.—B'HCl. Monoclaide prisms.—B'HCl. Monoclaide prisms.—B'HCl.,—B'HBC. Monoclaide prisms.—B'HCl.,—B'HBC. Monoclaide prisms.—B'HCl.,—B'HBC.—Trimetric plates,—B'HNO,—B',H,PCl.,—B'HBC.—B'HBR.—Trimetric plates,—B'HNO,—B',H,PCl.,—B'HBC. (Staedel a., Hölz, B. 18, 18, 1911; Bloomeracetyl derivative oxidine [192°].

**Eromo-acetyl derivative oxidine in benseen (Abenius, J. pr. [2] 49, 435). Needles (from broan-acetyl bromde and p-xylidine in benseen (Abenius, J. pr. [2] 49, 435). Needles (from dilute alcohol). Boiling alcoholic potash converts it into an azine and the compound oxidine prisms.—B'HCl., Oxidine potash converts it into an azine and the compound oxidine prisms.—B'HCl., Oxidine potash converts it into an azine and the compound oxidine potash converts it into an azine and the compound oxidine prisms.—B'HCl., Oxidine

B. 21, 2549). Crystals (from water). Converted by P.S. at 100° into the thioformyl derivative [105].

Mono-acetyl derivative

C_sH₃Me_s(NHAcf). (129°]. Needles or plates (from dilute alcohol). P_sS, forms the compound C_sH₃Me_sNH.CSMe [95°] (Jacobsen a. Ney, B. 22,

Diacetyl derivative C.H.Me.NAc. [60]. Formed, together with the mono-acetyl derivative, by boiling the base with Ac.O (Wallach, A. 258, 801).

Benzoyl derivative C.H.Me.NHBs.

**COUNTY OF THE PROPERTY O

[192°]. Needles (Hübner, A. 208, 818). Converted by HNO, into the hitro-benzoyi derivative [184°] which is reduced by tin and HOAo to C_eH₂Me₂ NH CPh [195°].

Phthalyl derivative [158°].

Prisms (from alcohol).

p. Kylidine C.H.Me.(NH.) [1:4:2]. [15:5°] (Michael, D. 26, 39). (215° i.V.) at 789 mm. (N. a. F.); (213:5° uncor.) (M.); (220°) (S.). S.G. 18 1980. 4btained from m-xylene by nitration and reduction (Schaumann, B. 11, 1537; Nölting a. Forel, B. 18, 2664; 19, 2680). Occurs to the extent of about 25 p.c. in commercial xylidine, from which it may be isolated by dissolving in warm H.SO, and pouring inter hot water. sparingly soluble m-xylidine sulphonic acid crystallises out, and the mother-lauor, after successive treatment with CaCO, and Na,CO,, yields on evaporation sparingly soluble, pearly

yields on evaporation sparingly soluble, pearly plates of sodium p-xylidine sulphonate, which on distillation with lime give p-xylidine almost without loss. May also be got from crude xylidine by means of its benzylidine derivative. Teagtions.—1. Oxidised by K.Cr.O. and H.2SO. to p-xyloquinone [123°], the yield being 70 p.c.—2. Converted by the diazo-reaction into p-xylenol [75°] (210°).—8. On heating with sulphur it yields C_{1s}H_{1s}N₂S [144°], which crystallises from alcohol in yellowish needles, and vields an acetyl derivative [212°] (Anschütz &. yields an acetyl derivative [212°] (Anschütz a. Schultz, B. 22, 585).—4. The hydrochloride heated with MeOH at 290° under pressure forms ψ-cumidine (Limpach, B. 21, 646).—5. Bensoic aldehyde forms C,H,Mc,N:CHPh [1027] (Pflug, A. 255, 16%). The same body [96°] is got by adding benzoic aldehyde to an alcoholic solution

of thionyl-p-xylidine (Michaelis, A. 274, 287).

Balts.—B'HCl aq. Leaflets, subliming at 125-130° in needles.—B'HNO, Needles.—B'H₂SO₄. Plates, 8l. sol. water.—B'₂H_CCo₄.

Bensoul derivative C.H.Me.NHBz. [140°]. Needles.

References .- BROMO , CHLORO , and Nyrro ETLIDINE.

XYLIDINE SULPHONIC AUD v. AMIDO-EYLENE SULPHONIC ACID and BROMO- and NITRO-XYLIDINE SULPHONIC ACIDS.

XYLIDINIC ACID &. TOLUENE DICARBOXYLIC

XYLINDEIN. C, 65.5 p.c.; H, 4.7 p.c.; N, 1.0 p.c. A green colouring matter in green decayed wood (Rommier, C. R. 66, 103; Liebermann, B. 7, 1102). Extracted by phenoi and ppd. by alcohol or other. Four-sided blue plates, with coppery lustre. H.SO, forms a green solu-tion. Rideal (C. N. 53, 277) finds that the blue substance in decayed birch-wood is soluble in chloroform, while the blue resin obtained from coniferin by successive treatment with H2SO,

Edinterin by successive treatment with H₂SO₄ and water is insol. chloroform. **XYLITONE** C₁₂H₁₀O. Xylite oil. (252°) (Pinner, B. 15, 589; 16, 1729) (c. 240°) (Claisen a. Ehrhardt, B. 22, 1013). S.G. 935. A product of the action of HCl en acetoce (P.). Formed also by the action of NaOEt on mesityl oxide in ether, and in the preparation of acetylacetone by the action of boiling EtOAc and NaOAc on acetone (C. a. E.). Oil, easily resini-

fied by strong acit's.

Dixylitone C₁₂H₂₀O₂. (310°-320°). A pr duct of the action of HCl on acetone (Pinner). ·XYLOHYDROQUINONE HYDROXYLO-

XYLOYC ACID v. DI-METHYL-BENZOIC ACID.

XYLONIC ACID $C_3H_{10}O_6$. $[a]_D=17\cdot48^\circ$. Formed by oxidising xylose with bromine (Tollens, A. 260, 367). Dextrorotatory. Its . Ca. Zn, and Ag salts are amorphous.—SrA',.

[a]n = +12·14°.

XYLONITRILE v. Nitrile of DI-METHYL-

BENZOIC ACID.

BENZOIG ACID.

6. XYLOQUINONE C.H.O., i.e.

6. H.Me.O. (1:2:3:6). [55"]. Formed by oxidation of c-o-xylidine by K.Cr.O., and H.SO., the yield being about 10 p.c. (Nölting a. Forel, B. 18, 2678). Yellow needles (by sublimation), v. sl. sol. water, m. sol. alcohol and ether.

7. Xyloquinone C.H.Me. (2:1:3:2:5).

m. X loquinone C₀H₂Me₂C₂ [1:3:2:5]. [78°]. Formed by oxidation either of c-m- or s-m-xylidine with K₂Cr₂O, and H₂SO₄ (Nölsing a. Forel, B. 18, 2679). Got also by oxidation of mesidine (Nölting a. Baumann, B. 18, 1151). Yellow needles.

p-Xyloquinone (1.H.Me.O. [1:4:2:5]. Phlorone. Metaph profile. Mol. w. 136. [124].

Formation.—1. Occurs, together with toluquinone and other bodies, alrang the products. of the action of MnO, and H.SO, on coal-tar of the action of MnU₂ and H₂SU₄ on coal-tar and beechwood-tar (Rommier a. Bouilhor, \$U. R. \$5, 214; Gorup Besanez a. von Rad. Z. [2] 4, 560; Carstarjen, J. pr. [2] 23, 425).—2. cBy oxidation of p. xylylene-diamine (Nietzki, B. 13, 472; A. 215, 168).—5. By oxidation of ψ-cumenol (Carstanjen, J. pr. [2] 23, 430?.—4. By oxidation of ψ-cumidine by CrO, (Nölting a. Th. Baumana B. 18, 1151; Sutkowski, B. 20, 977). S. By distilling xylidine (2182) with H 50 card. Bathanagy B. 10, 1101; Suksowsai, D. 20, 311). 5. By distilling xylidine (218°) with H.SO, and MnO₃; the yield being 5 p.o. (C.).—6. By oxida-tion of p-xylidine with K.Cr.O, and H.SO, the yield being over 70 p.c. (Nölting, Witt, a. Forel,

H. 18, 2667).—7. By heating diacetyl with dilute NaOHAq (Van Pechmann, B. 21, 1420).

Preparation.—1. Commercial xylene (130°—140°) is heated with H.SO, at 100° for six days; the product poured into water; neutralised by CaCO,; treated with K.CO,; and the K salts of the sulphonic acids fused with potass. The product is dissolved in water, acidified, and extracted with ether; and the mixture of xylenois 450 obtained is dissolved in warm H.SO., and rso obtained is dissolved in warm H₂80, and then diluted with water and distilled with MnO. Crystals of p-xyloquinone appear in the conorystats of p-xyloquinous appear in the condenser and receiver (Carstanjen, J. pr. [2] 23, 427).—2. 'Yellow carbolic acid' or 'creosote,' the mothef-liquor from which phenol has crystallised, is dissolved in H.SO, diluted with water, and then distilled with MnO. The solid found in the receiver is crystallised from alcohol when the first crop of crystals is xyloquinone (E. Carstanjen, J. pr. [2] 23, 423).

Properties.—Long yellow needles (from benzene), sl. sol. water and cold alcohol, v. sol. ether.

May be sublimed. Volatile with steam.

**Reactions.—1. Distilled with zinc-dust gives a hydrocarbon that oxidises to terephthalic acid.—2. Reduced by aqueous SO, to hydroxyloquinone.—3. Conc. HCl converts it into a mix-

quinone.—3. Cone. HCl converts it into a mixture of mono- and di-chloro-hydro-xyloquinones, C₂HClMe₂(OH)₂ [147°] and C₂ClMe₂(OH)₂ [175°].

Mono-oxim C₂R₂Me₂Q(NOH), Nitroso-p-xylonol. [168°]. Formed by heating p-xyloquinone (2 pts.) with an alcoholic solution of hydroxylamine hydrochloride (1 pt.) (Gold-schmidt a. Schmidt B. 18, 568; Sutkewski, B. 20, 978). Obtained also by adding KNO₂ and excess of HOAo to an alkaline solution of \$\beta\$-xylonol (Oliveri, G. 12, 162). Yellowish needles (from alcohol). v. sol. alcohol. ether. and henzene. (from alcohol), v. sol. alcohol, ether, and benzene. insol. cold water. Alkalis form a deep orangered solution. Reduced by SnCl, to amido-p-xylenol. Oxidised by alkaline K₃FeCy₆ to nitrop-xylenol.

Di-oxim C_eH₂Me₂(NOH)₂. [272°]. Formed by boiling the quinone (1 mol.) with an alcoholic solution of hydroxylamine hydrochloride (2 mols.) (Sutkowski, B. 20, 977). V. sl. sol. alcohol, acetic acid, and benzene, insol. water. Dissolves in alkalis with a yellow colour. By tin and HCl it is reduced to xylylene-p-diamine. Its di-acetyl derivative C₄H₂Me₄(NOAe), crystallises from acetic acide in small yellow prisms,

[170°], v. sol. alcohol and benzene.

References .- DI-BROMO- and CHLORO-TYLO-QUINOFE.

EYLORCIN v. DI-OXY-XYLENE. XYLQSE v. p. 538.

XYLOSTEIN, A glucoside in the berries of Bonicera Xylosleum (Hübschmann, J. 1856, 691; Enz. C. C. 1856, 393). Crystalline, insol. water, sol alcohol and ether.

"MYLOYL-BENZOIC ACID v. PHENYL XYLYL KETOME CARBOXYLIC ACID.

XYLOYL-FORMIC ACID v. XYLYL-GLYOXYLIG

ACID.

#p-DIXYLYL C. H. s.e.

[4:1:3] C.H.Me., C.H.Me., [3:4:1]. [125°]. Prepared by distilling mercury di-p-xyyl (Jacobsen, B. 14°21:2). Loug needles (from alcohol).

Dixylyl. (290°-295°). Formed from brome-m (?)-xylane and Na (Fittig, 4. 147, 38). Liquid.

Di-xylyl (so-called). (295°) (Oliveri, G. 12, 153). Is got by warming commercial xylene with H₂SO₄, but never from xylene which has been made from xylene sulphonic acid. Hence it is probably not a benzene derivative Armstrong, C. J. 45, 150). It is a colourless, fluorescent liquid, smelling like copaiba balsam.

XYLYL-ACETAMINE v. Acetyl derivative of

XYLIDINE and Amide of XYLYL-ACETIC ACID.

RYLYL-ACETIC ACED [102°]. Formed from its amide, which is got by the action of yellow ammonium sulphide on xylyl methyl ketone (Willgerodt, B. 21, 534). Slender needles. XYLYL-ACETIC ACID

Reference.— OXYXXIVILACETIC ACID.

XYLYL ALGOHOL is TOLYL-CABBINOL.

XYLYL-AMIDO-ACETIC ACID C₁₀H₁₈NO₂i.e.

[1:8:4] O₂H₂Me₂NH.CH₂CO₂H. [134*]. Formed by boiling m-xylidine (2 mols.) with water and the state of chloro-acetic acid (1 mol.) (Ehrlich, B. 16, 205). Prisms (from dilute alcohol). Insol. water, v. sol. acids.

Xylide C.H., NH.CH., CO.NHC, H., [128]. Formed by boiling xylidine (2 mols.) with chlory-acetic ether (1 mol.). Thick needles (from alcohol), insol. water and HClAq.

KYLYL-AMIDO-CROTONIC ETHER

[1:3:4] C₆H₂M₉₂.NH.CMe:CH.CO₂Et. from m-xylidine and acetoacetic ether (Conrad a. Limpach, B. 21, 526). Decomposed on heating into (Py. 1, 8; B. 2, 4)-oxy-tri-methyl-quinoline, di-xylyl-urea, and alcohol.

XYL7L-AMIDO-ETHYL-PHTHALIMIDE [1:3:4] C.H.Me., N.H.C.H., N.C., H.O. [123°], Formed by heating brome-ethyl-phthalimids with m-xylidine at 140° (Newman, B. 21, 2197). Small needles, v. e. sol. benzene, al. sol. cold

DI-m-XYLYL-DI-AMIDO-OIAZTHIOLE

C₁₈H₂₈N₄S i.e. S<C(NHC₈H₄):N. [79°]. Formed V₁₈H₂₈N₄S v.e. S C(NHC, H₂); N· Iro J. Former by oxidising (1,3,4)·xylyl-thio-urea with aqueous H₂O₄ (Hector, B. 23, 368). Insol. water. Forms a very soluble hydrochloride.—B'₂H₂PtCl₂. Decomposes at 214°-217°.—B'₂AgNO₃. Explodes on heating. Blackened by sunlight.—B'₂C₄H₃N₄O₅ (218°). Yellow crystals, v. sol. alcohol. Cyanogen passed into its alcoholic solutions forms C₁₈H₃N₄SCy₂ [103°].

Acetyl derivative C₁₈H₁₈AcN₄S. Needles, Bensoyl derivative C₁₈H₁₈AcN₄S. [212°].

Nitrosamine C₁₈H₁₉(NO)N₃S. [246°].

YYLYLMENIE v. XYLDINE and METYYL-

TYLYLAMINE v. XYLIDINE and METHYL-Benzyl-Amine.

Dio-xylyl-amine (C₁H₂)₂NH. (330°-345°). Formed, together with xylidine, by heating (1,2,4)-xylenol with ammonic-zipe bromide and NH, Br at 300° (Müller, B. 20, 1039). Liquid.

NIS, BY at 800° (Müller, B. 20, 1039). Liquid, solidified at a very low temperature.

10.m.xylyl-amine. "(305°-810°). Formed in like manner from m.xylidine. Oil.

10.xylyl-amine. [162°]. Formed, together with a liquid isomeride, by seating xylidine with its hydrochloride (Girard a. Vogt).

TRITYL-BENEYIL-AMINE C₁₁H₁₁N. 6.6.

C.H.Me. NH. CH.Ph. (c. 205° at 15 'gmm.).

Formed by hasting m-xylicine with benzyl elderide at 160° (Joblin-Gonnet, Bl. [8] 6, 21).

Tellowish cil, agl. alcohol and bensens.

p-Xylyl-bensyl-amine [1:4:2]C.H.Me. NH.CH.Ph. (822°) (Pflug. 4. 255 A168

255 A168).

C.-XYLYL BENZYL KETONE C., H., O i.e.

C.H., Me., CO.CH.Ph. [95°]. (210°-220° at 25° mm.). Found from o-xylene, phenyl-acetic chloride, and AlCl. (Wege, B. 24, 8540). Plates, sol. alcohol, v. sol. ether. Yields a crystalline acime. N.O.C. and honoryl chloride, xield will oxim. • NaOEt and benzyl chloride yield C.H.Me. COCH(CH.Ph)Ph [75°].

C.H., Ma. COCCH(CH., Ph)Ph [75°].

n. Xylyl bensyl ketone
[1:3:4] C., H., Ma., CO.CH., Ph. (350°). Formed, together with a smaller quantity of an isomeride
[93°], by the action of A.Cl., on a mixture of n. xylene and phenyl-acetic chloride (Süllscher, B. 15, 1681). Yields C., H., Mc(CO., H.), [3:4:1] on oxidation. NaQEt and benzyl chloride form oily C., H., CO.CH., Ph. (305°–375°).

p. Xylyl benzyl ketone C., H., CO.CH., Ph. (2010°–378°) at 26 mm. Econed in like manner

(220°-230° at 26 mm.). Formed in like manner from p-xylene (Wege). Yields an oxim [99°] and a phenyl-hydrazide [96°]. NaOEt and benzyl chloride yield C.H.,CO.CHPh.CH,Ph [60·5°].

2. XYLYL-BEIZYL-THIO-UREA C.H.,NH.CS.NHCH,Ph. [85°]. Formed from benzyl-thiocarbimide and m-xylidine in alcohol (Dixon, C. J. 59, 558). Monoclinic prisms, v. sol, boiling alcohol and chloroform.

XYLYL BROMIDE v. BROMO-XYLENE.

XYLYL-tert-BUTANE C.H.Me. OMe. (201°) Formed from m-xylene, isobutyl bromide, and AlCl₄ (Baur, B. 24, 2840). Got also from isobutyl alcohol, m-xylene, and H₂SO, or ZnCl₂ (Nölting, B. 25, 791). Oil, yields mesitylenic and trimesic acids on oxidation.

XYLYL.BUTYL ALCOHOL... [2:3:1] C.H.Me.CHPr.OII. (above 270°). Got by reducing xylyl propyl ketone with zinc-dust

by reducing xyly propyr account with 2m-account and KOHAq, or with sodium-amalgam (Chaus, J. pr. [2] 46,474). Oil, v. sol. alcohol and ether. Tri.xylyl-butyl alcohol (C.H., C.CMe, OH. (aboye 300"). Formed from xylene, tri-chlorotert-butyl alcohol, and AlCl. (Willgereat a. Genieser, J. pr. [2] 37, 361). Oil, smelling like mushrooms.

m-XYLYL-n-BUTYRIC ACID

[1:3:4]C,H,Mo,CH,CH,CH,CO,H. [70°]. Formed by saponifying the amide (Claus, J. pr. [2] 46, 476). Needles, v. sol. hot water. May be subtimed.—BaA', 4nq.—CaA', 4nq. Prisma, v. sol. water and alcohol.

water and alcohol. Amids C,H,Mer,C,H,CO,NH, [124°]. Got by heating xylyl propyl ketone with S and ammonium sulphide in world tubes at 250°. Flat siky needles. May be subfined. p-xylyl.n-butylic field [1:4:2]C,H,Mer,CH,CH,CH,CO,H. [70°]. Needles, sl. sol. cold water.— BaA', 4aq.— CAA', 2aq. Needles, sol. water and alcohol. Amids C,H,CH,CO,NH, (125°]. Formed from p-xylyl propyl ketone (C.). Fat needles, v. sol. hot water.

sol, hot water.

m.-Kylyl.isohutyric acid
m.-Kylyl.isohutyric acid
[1:8:4] C.H.Me.,CH.,CHMe.,CO.,H. [70°]. Flat
pearly needles, sol. hot water, alcohol, and ether.
May be sublimed.

Amide C.H., C.H., CO.NH. [120°]. Got by heating xylyl isopropel ketone with 8 and ammogium sulphide at 235° (Claus, J. pr. [2] 46. 483). Needles, sol. hot water.

XYLYL-CARBAMIC ACID

[1:8:4] C.H.Me.NH.CO.H. Ethyl ether EtA'. [58°]. Formed from m-xylidine and chlorotormic ether (Hofmann, B. 3, 657; Frentzel, C. C. 1888, 1861). Needles.

Xylyl-carbamic acid [1:8:5]C,H,Me,NH.CO,H. Ethyl ether EtA'. [77-5] (Frentzel).

DI-p-XYLYL-CARBINOL ([2:5:1] C.H.Me2),CH.OH. [131°]. Formed by KOH (Elbs. J. pr. [2] 35, 484; B. 19, 408). White needles (from alcohol), nearly insol. Aq.

XYLYL CYANATE [1:3:4] C.H.Me. N:CO. (205°) (Frentzel, C. C. 1888, 1361).

Xylyl cyanate [1:3:5] C_eH₂Me₂.N:CO. (208·5°). XYLYL CYANURATE

[1:3:4] (C₆H₂Me₂)₂N₂C₃O₃. [162°] (Frentzel, C. C. 1888, 1861).

XYLYLENE ALCOHOL v. DI-OXY-XYLENE.

XYLYLENE-DI-LLLYL-DI-THIO-DI-UREA (CH₃)₂C₆H₂(NH.CS.NH.C₂H₃)₂(1:4²:6]. [112:5³.] Made from p-xylylone diamine and allyl thiocarbimide (Lellmann, A. 228, 252). Needles Needles (from alcohol). Not decomposed on melting.

m-XYLYLENE-m-DIAMINE

C.H. (CH.), (NH.), [1:3:4:6]. m. Di-amido-m-xylene [105°]. Formed by reduction of nitro-xylidine [123°] or of dicatro-xylene [93°] (Fittig, A. 147, 18; Grevingk, B. 17, 2426; Witt, B. 21, 2419). white crystals. Sublimable. Does not yield a curhodine on boiling with nitroso-dimethylaniline, NaOAc, and HOAc. — B"2HCl. — B"H_SO_C. Crystalline, v. sql. Aq.

m. Nyllene-o-diamine

C_sH_sMe_s(NH_s)_s[L-9:5:6] [78:5°]. Formed by reduction of [2:4:1] C_sH_sMe_sN_sC_sH_sMe_sNH_s(1:3:5:6] (Nölting a. Forel, B. 18, 26:3) and also by the action of tin and HClAq on di-bromo-di-nitro-mxylene [191°] (Jacobsen, B. 21, 2821), and on (5,1,3,6)-nitro-xylidine (Hofmann, B. 9, 1298). Plates (from water), sl. sol. cold benzen, sol. ether.

m-Xylylene-m-diamine

C.H.Me.(NH.)₂[1:3:4:2]. [64°]. Formed by reduction of nitro-xylidine [78°] or of di-nitro-m-xylene [82°] (Grevingk, B. 17, 2426). White needles. Gives a Bismarck brown with nitrous acid and a chrysoïdine with diazobenzene.

p-Xylylene-o-diamine

C.H.Me₄(NH₂), [1:4:2:3]. [75°]. Formed by reduction of c-di-nitro-p-xylene (Lellmann, A. 228, 251; Nölting, B. 19, 145). White needles (by sublimation). Eves a deep-red colour with

FeU1, p-Xylylene-m-diamine C.H.Me₁(NH₂), [1:4:2:6]. [102°]. Formed by reducing (2,6,1,4)-di-nitro-xylene (L.; N.). Needles (by sublimation), Behaves like a m.

diamine.

p. Xylylefte-p-diamine
C.H.Me.(NH.), [142°] (S.); [147°]
(N. a. F.); [150°] (N.). Formation.—1. By reduction of xylene-azoxylidine (amido-azo-xylene)
[2:5:1] C.H.Me., N.C.H.Me., N.H. [12:5:4] by zine and HCRA (Nietzki, B. 18, 471; Nölting a. Forel, B. 18, 2685).—2. By reduction of nitro-pxylidine [142°] (Nölting, Witt, a. Forel, B. 18, 2685).—2. By reduction of nitro-pxylidine [142°] (Nölting, Witt, a. Forel, B. 18, 2685).—3. By reduction of the di-oxim of DixYLYL-ETHYLENE C. 12. 4. 2866; yon Kostanecki, B. 19, 2818; Margkwald, B. 28, 1021).—3. By reduction of the di-oxim of [106°]. c (325°—340°). Formed by distilling

p-xyloquinone C.H.Me.(NOH), with tin and HCl (Sutkowski, B. 20, 979).

*Properties. — Colourless needles, sol. hot

water and alcohol, m. sol. benzene and ether.
Yields xylequinone [123°] on oxidation. Not
oxidised by exposure to air. May be sublimed.
Salts.—B°2HCl. Colourless leaflets.—

Salve.—B'zhci. Colouriess leaness.—
B'H₂SO₄. Crystalline meal.
o-Xylylene exo-diamine
[1:?]_to_cH₄(CH₂NH₂)₂. Formed by heating the phthalimide C_cH₄(CH₂N:C₂O₂:C_cH₄)₂ with conc.
HClaq at 200° (Strassmann, B. 21, 579). Alkaline liquid, smelling strongly like ammonia.

Absorbs CO₂. Gives with FeCl, a pp. of yellowish-red needles.—B"2HCl.—B"2HAuCl₄. Yellow plates.—B"2C,H₂N₂O₂. Yellow needles, decomposing above 170° without melting.

Acetyl derivative C₈H₁₀Bc₂N₂. [146°], Bensoyl derivative C₆H₁₀Bz₂N₂. [168°], m-Xylylene-exo-diamine

[1:3] C,H,(CH,NH,),. (247°). Formed by the action of conc. hydrochloric acid at 220° on the C₁H₁(CH₂N:C₂H₁O₂)₂ [237°], which is got by heating potassium phthalimide with di-ω-bromo-*t-xylene (Brömme, B. 21, 2705). Liquid, sol. water, miscible with alcohol and ether. Absorbs CO₂. — B"2HCl. Needles (from water). — B"2H_PtCl₀.—B"C₆H₃N₃O₇. Yellow spangles, decomposing at 187

A cetyl derivative C,H,(CH,NHAc). [119°]. Crystalline mass, v. sol. hot water.

Reference.—NITRO-XYLYLENE-DIAMINE.

XYLYLENE-BENZENYL-AMIDINE v. Benz-Enyl-xylylene-dialine.

XYLYLENE BROMIDE v. DI-BROMO-XYLENE. XYLYLENE-CHLORO-MALONIC ETHER v. CHLORO-XYLYLENE-MALONIC ETHER.

Xylylene-exo-di-chloro-malonic ether v. Dr-CHLORO-PHENYLENE-DI-METHYL-DI-MALONIC ETHER. XYLYLENE-ETHENYL-AMIDINE C10H12N2

i.e. CMe $\langle NH \rangle C_sH_2Me_2$. Formed by reducing C,H,Me,(NO,)(NHAc) [1:3:5:4] with tin and HOI (Hobrecker, B. 5, 922). Resinous mass.— B'HCl. Large needles.—B'₂H₂PtCl₂.—B'HNO₂ Long needles.

XYLYLENE IODIDE v. DI-IODO-XYLENE. XYLYLENE-DI-MALONIC ACID v. PHENYL-ENE-DI-METHYL-DI-MALONIC ACID.

o-XYLYLENE SULPHIDE C.H.S &c.

 $C_0H_4 < CH_2 > S$. [c. 0°]. Formed by heating dies brome zylene with KS (Leser, B. 17, 1824; Hjelt, B. 22, 2904). Oil, smelling like mercaptan. Very unstable, quickly furning into a black fesin.—B', HgCl. Long needles.

Metaylo-iodide B'Mel. [1555].

Di-xylylene disulphide Pormed by cheating xylylene-diazosulphide at 200°-250° (Jacobsen a. Ney, B. 22, 911). Conc. H₂SQ₂ forms a blue liquid, remaining blue on diazosulphide.

O.H.Me, CH, CH, Cl, which is got from di-chlord wald, B. 25, 2368). Sl. sol. water, -Aurodi-ethyl oxide, m-xylene, and H.SO, (Hepp. B. 7, 1416). Spangles (from alcohol), sol. ether and CS. Unites with bromine. Oxidised by dilute HNO, to (1,3,4)-di-methyl-benzoic acid

Di-xylyl-ethylene C,H,Me,CH;CH,C,H,Me, [157°]. Formed in like manner from p-xylene. Plates (from alcohol). Less soluble than the preceding isomeride.

Tetra-xylyl-ethylene (C₆H₄Me₂)₂C:C(C₆H₃Me₂)₄. [245°]. Formed from xylene, CHCl₂, and AlCl₂ (Schwarz, B. 14, 1528).

xylene, CHCl., and AlCl. (Schwarz, B. 14, 1528). Yellow plates.

m.XYLYL.ETHYLENE.DIAMIND

C.H.Me.NH.C.H.NH... (274°). Formed from

m.xylyl.amido-ethyl-phthalimide and HCl (Newman, B. 24, 2197).—B'HCl. [173°].—B',H.PtCl...

—B'C.H.N.O... [141°]. Reddish-yellow needles,
v. e. sol. alcohol.

DI.-m.XYLYL.ETHYLENE DIKETONE DI-m-XYLYL-ETHYLENE DIKETONE

C.H. (CO.C. H.Me. [4:3:1]). [129°]. Formed from m.xylene, succinyl chloride, AlCl, and CS. (Claus, B. 20, 1375). Needles, insol. water, v. sol. alcohol and ether. Dilute HNO, oxidises is to (1,3,4)-di-methyl-benzoic acid. Oxim C,H,(C(NOH).C,H,)2. [140°].

C.L., (C(A)CH). (LACH). [140].

Phenyl-hydrazide

C.H., (C(N, LPh). C, H₂). [189]. Crystals.

Di-p-xylyl thylene diketone

C.H., (CO.C, H, Me., [2:4:1]). [123]. Formed from p-xylene, succinyl chloride, AlCl., and CS., (Clays). Moddler.

(Claus). Needles.

m-XYLYL ETHYL KETONE

[1:3:4] C.H.Me.CO.C.H., (239°). Light oil, with aromatic ododr, not solid at -10° (Claus, 140°).

[1:3:4] C.H.Me.CO.C.H., Violag (1:3:4).di-methyl. J. pr. [2] 43, 140). Yie benzoic acid on oxidation. Yields (1,3,4)-di-methyl.

Phenyl-hydrazide [126°]. Plates, v. sol. hot water, alcohol, and ether.

hot water, alcohol, and enter.

p.Xylyl ethyl ketone

[4:1:2] O₂H₂Mo₂CO.O₂H₃. (238° uncor.). Formed
from p-xylene, AlCl₁, and propionyl chloride
(Claus a. Fickert, B. 19, 3182). Oil. Oxidised
by KMnO, to C₂H₂Mo₂CO.CH₂CO₂H [132°] and
some (4,1,2)-di-methyl-benzoic acid.

mxylyl ETHYL KETONE CARBOXYLIC

ACRE (4,2)1.C H Mc CO CH CH-CO H.

ACID [4:2:1] C.H.Me, CO.CH, CH, CO, H.

Di-methyl-benzoyl-propienic acid. [108°].

Formed from m-xylene, succinyl chloride, Formed from m-xylene, succinyl chloride, AlCl., and CS. (Claus, B. 20, 1376). Needles, v. sol. hot water, insol. cold.—NH, A'.—KA' 4aq. V. sol. water.—NaA' 4aq. Needles.—BaA', 3aq. Needles.—BaA'; white pp.—AgA': Thite crystalline pp.
p-Xylyl ethyl ketone carboxylic acid
[4:1:2] C,H,Me,CO.CH,CH,CO.H. (84°).
Formed from p-xylene in like manner (C.),
Colourless needles.

ZYLYL-DI-ETHYL-PHOSPHINE OH, Me.PEt. (260°). Formed by the action of ZnEt on O.H.Me.PCl. (Czimatis, B. 15, 2016). Thick colourless oil. Yields B'Mef [90°], B', Me, PtCl, [202°], and B'EtI [186°]. me,rtol, [202], and 2 Hit [104], CH;CH;m-XYLYL-GLEOXALINZ C,H,N CH;CH

,[32°]. (279°). Formed by the action of HNQs on C,H,N<0H= CH [192°], which is get by the action of HCl on the product of the action (N. amido-actal on m-zylyl-thio-urea Marck-hol.

wald, B. 25, 2368). Bl. sol. water,—Aurochloride [165°].—Picrate. [159°]. Yellow
needles, m. sol. chloroform.

-XYLYL-GLYOXYLIC ACID
[4:3:1] C.H.Me., CO:OO, H. [92°]. Formed by
oxidising o-xylyl methyl ketone with alkaline
K.FeCy. (Buckka a. Irish, B. 20, 1766).—BaA'.

K₁FeCy₄ (Buchka a. Irish, B. 20, 1766).—BaA'₂—

"Xylyl-glyoxylic acid

[4:2:1] S₆H₂Me₂CO.CO₂H. [54°]. Formed by
oxidising m²xlyl methyl ketone with KMnO₄
(Claus, B. 19, 231; J. pr. [2] 43, 142). Flat
prisms, Yields (4,2,1) di-methyl-benzole acid
on böling with dilute HNQ₃. Gives rise to
C₆H₄,CH(OH).CO₂H. [119°] on reduction.—
CaA'₂Zaq. Needles.—BaA'₂Zaq.—AgA'. Needles,
sol, hot water. sol. hot water.

p-Xylyl-glyogylic acid [5:2:1] C.H.Me. CO.CO.H. [70°-80°]. Formed by oxidation of p-xylyl methyl ketone by aqueous KMnO, (Claus a. Wollner, B. 18, 1859). Crystalline, v. sol. alcohol, ether, and HOAc, v. sl. sol. water. Splits up above 200° into CO, and di methyl-benzoic aldehyde. Oxidised by HNO, to C.H.Me, CO. H. Ac,O and NaOAc yield dimethyl-cinnamic acid.—BaA', 6aq: small felted needles. - CaA', 3aq. - AgA': crystalline pp. Ethyl ether EtA'. Oil.

XYLYL GLYOXYLIC ALDEHYDE

[1:3:4] C. H., Mc., CO. CHO. Oxim [95°]. Formed from xylyl methyl ketone, NaOEls, and C. H., NO. (Söderbaum, B. 25, 3463). Needles (from benz-ene-ligroin). Acetic anhydride gives the acetyl derivatives of the syn-oxim C.H., CO.CH:NOAc C,H,.CO.CH(OH).CO.CO.C,H, [155°].

DI XYLYL GUANIDINE HN:C(NH.C.H. [1:2:4])₂. [158°]. Formed by the action of PbO and alcoholic ammonia on dixylyl-thio-urea (Hofmann, B. 9, 1295). Needles,

(from alcohol). XYLYL-HYDRAZINE [4:2:1] C₆H₁Me₂NH₁NH₂ [85°]. Formed from xylidine by diazotisation followed by reduction with Na SO,, the resulting C,H, N,H, SO,Na laq

with Na, No., the resulting U, H, N, H, SO, Na § adbeirg then treated with zinc-dust and HOAc (Klasber, M. 11, 282). Pale-yellow needles, v. sl. sol. water, v. sol. slcohol. Reduces Fehling's solution on warming. On heating with acctosic ether it yields a crystalline body [208°] reduced in alcoholic solution by Na to oxyvivlmethyllmyracols § xylyl-methyl-pyrazole. Salt:—C'HCleiq. [[183°]. Small needles.

Salt.—C'HCl&zq. [185']. Small necess. Di.o.zylyl-hydrazine, [3:2:T-C.H.Me.,NH.NHC.H.,Me., [1:2:3]. [141']. b. Hydrazo o.zyleke. Got by heating nitro-cylene (20 g.) with NaOH (20 g.), sloohol (100 c.o.) and zinc-dust (25 g.) and reducing the product with alcoholic ammonium sulphide (Nölting a. Stricker, Bl. [2] 50, 618). White needles, sol. alcohol and ther. Easily oxidised by air.

u-Di-o-xylyl-hydrazine N.H.(C.H.Me.[1:3:4]). [107°]. Formed by reducing hitro-o-xylene with sodium-amalgam ducing hitro-o-xylene with southern sol. also (N. a. S.). Yellowish white needles, sol. also

Di-m-xylyl-hydrasine . N₂H₂(C₆H₂Me₂ [1:3:5])₂. [125°]. Obtained from s-nitro-m-xylene (N. a. S.). Needles, easily oxi-

dised by air.

u-Di-m-xylyl-hydrasine u-Di-m-xylyl-hydrasine
N₂H₂(C₂H₂Me₂[1:2:4]), [122°], (Gpt by warming nitro-m-xylene (30 g.) with MaOH (30 g.), zinc-dust (40 g.), and alcohol (250 c.c.) and treating the xylene-azo-xylene so obtained with the challenge of the control of alcoholic ammonia and H2S (N. a. S.). White needles, sol. alcohol and ether.

Di.p. zylyl. hydrasine N.H. (C.N.Me. [1:2:5]). [145°]. Formed from nitro-p-xylene (N. a. S.). Needles, not affected by air.

XYLYLIC ACID v. DI-METHYL-BENZOIC ACID. a-Xylylic acid v. TOLYL-ACETIC ACID.

p-XYLYLIDENE DI-IMINI

o.H.(CH:NH)₂[1:4]. Formed by the action of alcoholic NH, or dry NH, gas upon terephthalic aldehyde (Oppenheimer, B. 19, 576). Glassy brittle crystals. V. Sl. sol. alcohol and ether.

DI-XYLYL-KETONE CO(CoH, Me.)2. (c. 340°) Obtained from (m?)-xylene, GOCl₂, and AlCl₃ (Ador a. Rilliet, B. 11, 399). Liquid, not solid at -60°. Split up by long boiling into H₂O and

C,,H,,.

U1-p-xylyl ketone [2:5:1] C₆H₁Me₂(2).C₆H₁Me₂ [1:2:5]. (327° uncor.). Formed from p-xylene, CS₂, and COCl₂ in closed vessels; the yield being 55 p.c. (Elbs, J-pr. [2] 35, 481). Oil. Quickly decomposed by distillation into H₂O and (B. 2, 1',4')-trimethyl-anthracene [227°]. Reduced by zincdust and alcoholic KOH to di-p-xylyl-carbinol [131°].

Di-xylyl-tat-a-batca-Di-p-xylyl ketone

Di-xylyl-tetasketone
C₂H₂.CO.CO.CO.CO.CO.H₂Me₂[4:3:1]. [180°].
Formed by the action of cold HNO₃ (S.G. 1·4)
on C₁H₂.CO.CH(OH).CO.CO.C.H₂.(Söderbaum, B. 25, 3475). Scarlet needles (from CS2). On dissolving in HOAc and ppg. by water it yields a dihydrate [100°] C.H...O.

**YYLYL MERCAPTAN C.H.Me.SH. (214°).

TRI. p. XYLYL-METHANE CH{C,H,Me₂}; [188°]. (above 360°). From di-p-xylyl-carbinol, p-xylene, and P₂O₅ by boiling for four hours (Eibs, J. pr. [2] 35, 484). Crystalline grains (from alcohol), v. bl-ether and benzene. o.XYLYL METHYL RETONE
[4:3:1] C₆H₈Me₂CO.CH. (2460)

o-XYLYA METHYL KETONE

(3:1] C.H.Me., CO.CH., (246°). Formed from
o-xylene, AcCl, and AlCl, (Ukus, B. 18, 1856;
19, 232; J. pr. 1890, 410). Oil, smelling like
commarin (Armstrong a. Kipping, C. J. Ch. 81).
Yields (4,3,1)-di-methyl-benzolo acid on oxida:
tion. Conce CllAq forms C.H., O[114°]. P.O.
gives a body melting av 165°. Zino-dust reduces.
the ketone to C.H., CH(OH), CH. (257°).

Oxim C.H., C(NOH), CH., [85°]. Prisms
(from. dilute alcohol), converted by AcCl into
C.H., C(NOA), CH., [72°].

(from dilute alconol), converted by Acc. Into C.H., C(N.O.A.), C.H., [72°].

Phenyl-hydrasids. Colourless prisms.

m-Xylyl methyl ketene
[4:2:1] C.H.Me., CO.C.H., (228°). Formed from m-xylene, AcCl, and AlCl, (Claus, B. 19, 280).

Obtained also by boiling m-xylene with HOAL ZuCl_m and POCl_a (Frey, J. pr. [2] 48, 120). Oi smelling like peppermint. Not condensed b HClAq. Yields C_{1.}H₂Br₂O [69°]. Reduction b HI yields C_{2.}H₃Me_{2.}OH₂OH₃OH₄ (184°) (Claus, J. pr. [2] 45, 830). HNO, gives C_{2.}H₁₂N₂O₄ [108° (Claus, J. pr. [2] 41, 492).

p-xylyl methyl ketone
[5:2:1] C_{4.}H₂Me_{2.}CO.OH₂. (225° uncor.). S.C
12° 9962. V.D. 4°93. Formed from p-xylene AcCl, and AlCl₃ (Claus a. Wollner, B. 18, 1856;
Oil, v. sol. alcohol and gther. Oxidised by 801 aqueous KMnO, to p-xylyl-glyoxylio acid. Dilut

aqueous KMnO, to p-xylyl-glyoxyliz acid. Dilut HNO, forms di-methyl-benzoic and methyl phthalic suids.

Oxim C.H. C(NOH) .CH. [58°]. AYLYL METHYL KETONE CARBOXYLICACID.

ACID v. METHYL-BENZOYL-ACETIC ACID.

XYLYL-DI-METHYL-PHOSPHINE C.H.Me., PMe. (230). Formed from ZnMe and C.H.Me., PCl. (Czimatis, B. 15, 2016). Oil Unites with CS., forming a compound [115°].

. XYLYL-METHYL-THIOHYDANTOÏN

[1:3:4] C₄H₂Me₂.N<CO.CH₂. [165°]. Formed from xylyl-thiocarbimide and alanine (Marckwald, B. 24, 3282). Needles, v. sol. alcohol.

XYLYL PENTADECYL KETONE C_oH₃Me_xCO.C₁₃H₃₁, [87°]. (269° at 15 mm.). Formed from m-xylene, pulmityl thloride, and AlCl₃ (Krafft, B. 21, 2269). Small plates, yielding di-methyl-benzoic acid [126°] on oxidation.

XYLYL PHENYLAMYL KETONE C.H.Me. CO.CHPh.C.H. [91.5°]. Formed by Friedel and Craft's method (Wege, B. 24, 3541). XYLYL-PHENYL- v. PHENYL-XYLYL

TRI-XYLYL PHOSPHATE PO(OC,H,Me,),. The o- and p- compounds are formed by heating o- and p-xylenol with POCl, (Kreysler, B. 18, 1702). They are oils, v. sol. ether, alcohol, and

m-XYLYL-PHTHALIDE

 $C_eH_4 < CO \xrightarrow{CH(C_eH_sMe_s)} O$. [84°]. Got by heating C₆H₂Me₂.CO.C₆H₄.CO₂H with zine and HCl (Gresly, A. 234, 237). Needles (from alcohol), sl. stl. benzene.

XYLYL-PROPIONIC ACID

XXIXI.-PROPIONIC ACID

[1:3:4] 6.4 Me., CH., CH., CO., H. [105°]. Formed by saponifying the amide. Silky needles, v. sol. hot water.—BaA', 6aq. Plates, m. sol. water.—CaA', 4aq.—AgA'. White powder.

Agnide & H., Me., C.H., CO.NH., [107°]. Got by heating the oxim of m. xylyl ethyr zetone with yellow ammonium sulphide under pressure (Claus, V. pr. [2] 46, 477). Needles, sol. hot water. water.

m-XYLYL PROPYL KETONE C12H10O i.e. [4:2:1]C.H.Me.CO.Pr. (251°). Formed from m*xylene, butyryl chloride and AlCl, (Class, (J. pr. [2] 46, 474). Oil, v. sol. alcohol and ether? Yields mxylyl-glyoxylic acid [54°] on Saldation with YM-2. Exidation with KMnO.

exication with KMnO_s.

Oxim. Crystal₁, v. e. sol. alcohol.

b-Xylyl propyl ketone [5:3:1] O_sH₁Me₂CO.Pr.

(240). Formed in like mather from p-xylene.

Lightwil.

Oxim (47°]. • Colourless needles.

o-Xylyl isopropyl ketone

[4:3:1] Q_sH₁Me₂CO.Pr. (258°). Oil, melling like

tarpentine (Claus, J. pr. [2] 45, 484). Y di-methyl-benkoic acid [163°] on oxidation. Oxim [68°]. Large prisms. Yield

m. Tylyl isopropyl ketone
[4:2:1] C.H.Me. CO.Fr. (245°). Oil yielding
m-tylyl-glyoxylic acid on oxidation by KMnO.
Osim [97°]. Prisms (from sicohol).

Phinyl-hydraside [129°]. Crystals. p-Xylyl isopropyl ketone

[5:2:1] C.H.Me. CO.Fr. (240°). Formed from p-xylene, isobutyryl chloride, and AlCl. (Claus, J. pr. [2] 46, 484). Oil, smelling like mush-

Oxim [76°]. Plates and prisms...
TETRA-0-XYLYL SILICATE Si(OC,H,Me.),. (c. 460°). Formed by heating o-xylenol with SiCl, the yield being 85 p.c. of the theoretical amount (Hertkorn, B. 18, 1691). Large prisms. Tetra-m-xylyl silicate Si(OC₂H₃Me₂). (453°-

457°). Formed, in like manner, from m-xylenol.

Oil.

77. XYLYL THIOCARBIMIDE C,H,NS i.e. [4:2:1] C,H,Me,,N:CS. Formed from di-xylyl-thio-urea and P,Q, (Hofmann, B. 9, 1295). Crystals. Converted by PhOEt and AlCl, into C.H.NH.CS.C.H.OEt [140°] (Gattermann, B. 25, 8530). XYLYL ETHYL DITHIOCARBONATE

CS(OEt).SC:H.Me. Formed from potassium

xanthate and m-diazo-xylene chloride (Leuckart, J. pr. [2] 41, 192). Oil, converted by heating with alcoholic potash into xylyl mercaptan

DI-XYLYL-THIO URBA

CS(NH.C.H.Me.[1:2:4]),. [158°]. Formed by digesting xylichine with CS, as long as H.S escapes (Hofmann, B. 9, 7295). Crystals (from

[186°]. Formed from crude xylidine sulphate and potassium cyanate (Genz, B. 8, 226). Needles (from alcohol).

receies (from alcohol).

s.Xylyl ures NH, CO,NH,O,H,Me,[1:3:5].
[162°] (Frontzel, C. C. 1888, 1361).
Di-s.xylyl-ures CO(NHC,H,Me,[1:3:5]),
[275°] (F.); [251°] (G. a. C.). Formed from s.xylidine and GOCl, (F.). Formed also from m.xylyl cyanate and xylidine (Gattermann a. Cantzler, B. 25, 1089). Needles

m-xylyl cyanate and xylotine (caterman a: Cantzler, B. 25, 1089). Needles.

Di.m.xylyl-area CO(NH.C₃H₃Me₂(1:2:4)).

[263°]: A product of the distillation of m-xylylamido-crotonic acid (Conrad a. Limpach, B. 21, .

527). Sublimes when mereng.
Di-xylyl-urea CO(NHC, H, Me.). Formed by heating urea (1 pt.) with crude xylidine (8 pts.). Felted needles (from hot alcohol), not melted at 250° (Genz, B. 3, 226).

Reference. - METHYL-BENZYLAIREA.

YTTERBIUM. Yb. At. w. c. 173. This name is given to the metal, not yet isolated, of an earth separated by Marignac, in 1878, from crude erbia obtained from gadolinite or euxenite. The claim of ytterbia to rank as a definite homogeneous compound is not yet satisfactorily established.

The discovery of a new earth in a mineral from Ytterby in Sweden was announced in 1788 by Gadolin; in 1797 Eckeberg confirmed the disthe mineral from which it was obtained was called gadolinite. Researches into the nature of called gadolinite. Researches into the nature of yttria were conducted by Berzelius in 1819 (v. Lehrbuch [5th ed.] 2), Mosander in 1839 and KHSO, fused over a powerful burner, pulverised 1848 (J. pr. 30, 27), Scheerer in 1849, Cleve and others. In 1879 Marignao made 4 careful examination of erbia (M. Ch. [5] 14, 247); he fractionally decomposed erbium nitrate by heat fractionally decomposed erbium nitrate by heat, and obtained an earth which he called ytterbia. The erbia used by Marignac was fink, and gave, rne erous used by marigina was plus, and gave, in solution, an absorption spectrum; the new earth was white and showed no absorption spectrum. Nilson (B. 12, 554; 13, 1439 [1879-89]) prepared ytterbia, but found a reacting weight for the earth different from that assigned to it by for the earth different from that assigned to it by Marignac. By repeated fractional decomposition by heat of the gitrate of ytterbium, Nilson separated another aerth which he called scandia (cf. Scandium, this, vol., p. 431). Nilson 45: 13, 1430) in 1873 made a fuller examination of ytterbia, and defermined the at. w. of the metal of this earth, and the properties of several salts of the metal. In this memoir Nilson asserted

that erbia was separable into seven distinct earths: erbia proper, scandia, terbia, thulia, ytterbia, yttria, and Soret's X (afterwards called holmia). (cf. Erbium, vol. ii. p. 456; and Metals, RARE, vol. iii. p. 245).

Ocquirence. - Along with orbia, scandia, yttria, &c., in very small quantities in a few rare Scandingvian minerals, chiefly in gadolinite and euxenite. Nilson (l.c.) obtained c. 20 g. ytterbia from 6-7 kilos, of the crude earths prepared from c. 15 kilos. gadolinite.

the fused mass, and thoroughly exhausted with cold water; he ppd. the aqueous solution by ammonia, washed the ppd. in the solution for some time, and filtering, he ppd. by oxalic acid, washed the pp. dried it, and heated strongly until it was decomposed. The crude garths thus obtained were freed from K.CO. by boiling with water, and were than dissolved in HNO,Aq; the solution was evaporited to dry-ness, and the residue was lused until red vapours began to come off. The reddish-yellow, opaque solid was then treated with boiling water, wheresond was then treased with boung water, where by a reddish-yellow pp. was formed, which was filtered off by means of a suction-pump! (This pp. contained oxide of Th, along with oxides of Ce, Fe, and U.) The reddish filtrate was evaporated to dryness, and the solid nitrates thus obtained In this memoir Nilson asserted were partly decomposed by heating, the soluble

(undecomposed) portion removed by solution in water, the residue dissolved in HNO2Aq, the solution evaporated to dryness, the residue partly decomposed by heating, the unde-composed nitrates were removed, by washing with water, the residue was dissolved in HNO, Aq, and so on. After thirty repetitions of this process a solution was obtained that showed merely a trace of red colour after thirty-five repetitions the solution was quite colourless, and showed only two faint absorption bands, one in the green and the other in the red; after forty repetitions a solution was obtained which gave only the red band; and when the process of partial decomposi-tion by heat had been repeated skity-eight times a solution in HNO.Aq was obtained which showed no trace of an absorption spectrum. This solution was saturated with H,S, the small yellowish-brown pp. of PtS, was filtered off, the filtrate was ppd. by oure exalic acid, the pp. was washed, dried, and decomposed by heating strongly, and pure ytterbia was thus obtained. For a modification of this method of separating ytterbia from accompanying earths v. Auer ven Welsbach (M. **4,** 630).

Atomic weight of ytterbium.—The metal has not been isolated; the at. w. was determined by Nilson (B. 13, 1433) by dissolving pure Yb,O₃ (v. supra) in HNO₃Aq, adding a suitable quantity of H.SO, Aq, exaporating on a water-bath to drive off HNO, then on a sand-bath, and finally over as flame until all free H.SO, was removed, weighing the Yb,(SO), thus obtained, and analysing it. Nilson dissolved pure Yb,O, in HNO,Aq, evaporated to dryness, partially decomposed the nitrate by heat, treated with water, co., as described supra, and in this way obtained seven fractions, each of which was converted into sulphate. The results are presented in the following table :-

Weight of	Weight of sulphate	Pctge. composition of sulphate		Atomic W.
taken	formed	Yb,O,	80,	bf Yb.
1.0063	1.6186	62-171	37.829	173-21
1.0139	1.6314	62.149	37.851	173.03
·8509 ·	1.3690	62.155	37.845	173.08
·7371	1.1861	62.145	37.855	173.00
1.0005	1.6099	62.147	● 37.853	178.01
-8090	₹.3022	62.126	37.874	172.84
1.0059	1.6189	62.134	37.866	172.91
Mean .	ہے۔ ۔ .	,,62·147	87.853	173.01

Chemical relations of ytterbium.—If Yb is really a homogeneous substance, it must be placed in Series 10 of Group III. in the periodic classification of the elements. This group contains the following elements:

ought to be decidedly more metallic than B, and somewhat more metallic than Al, Ga, or In; the data, however, are too meagre to allow a detailed comparison to be made. Little is known of the properties, of compounds of Yb; but what is known broadly confirms the conclusions drawn from the position of the element in the periodic scheme of classification (cf. Easths, METALS OF

THE, vol. ii. p. 424).

Ytterblum oxide Yb₂O₂. (Ytterbia.) A very heavy, white, infusible powder; slowly acted on by acids when cold or gently warmed, but resdily dissolved by dilute acid solutions when boiling. Solutions in acids are colourless, and show no absorption spectra. The emission spectrum of as solution in HClAq, obtained by help of the spark, shows several lines, the most conspicuous of which have the wave-lengths 6221, 5556, 5476, 5352, and 5334 (v. Lecog de Boisbaudran, TR, 5352, and 5334 (v. Lecog de Boisbaudran, CR, 5352, and 5354, and 53 C. R. 88, 1342). S.G. 9.175. S.H. (0°-100°)

·0646 (Nilson, I.c.).

Hydrated ytterbium oxide. A white, gelatinous, but heavy pp. obtained by adding NH,Aq to a solution of a salt of Yb; shrinks much when dried, and absorbs CO₂ from the air.

Easily soluble in acids (Nilson, l.c.).
Ytterbium salts. Nilson (l.c.) prepared an oxalate, an acid selenite, and a sulphate; and

oxalate, an acid sciente, and a suppate; and Marignac (C. R. 87, 578) prepared a formate. Ytterbium ozalate Yb_(\(\infty\)_0\), \(\bar{1}\), \(\bar{ changed in air; gives up part of its water at 100°. Prepared by adding oxalic acid to a warm solution of the sulphate.

Ytterbium selenite Yb, 0,4SeO, 5aq.

tained by adding Na₂SeO₃Aq to a solution of Yb₂(SO₄)₃, washing the ppd normal selenite, dissolving in water containing a large excess of H2SeO2, evaporating nearly to dryness, and washing the residue with water. A white crystalline

salt, insoluble in water. Loses 4H₂O at 100°.

Ytterbium sulphate Yb₁(SO₁), Prepared by dissolving Yb₂O₂ in HNO₂Aq, adding H₂SO₂Aq, evaporating on a water-bath to drive off HNO₂, then on a sand-bath, and finally over a flame at low redness till all H₂SO₄ is removed. An opaque, white solid. Dissolves in water when a large quantity is added at once; if a little is added much heat is produced, the salt combines with the water, and then dissolves very slowly when more water is added. Decomposed at a red heat, fully et a white heat. S.G. 8.793. S.H. 1039 at 0° to 100°.

A hydrated sulphate Wb, (SO,). Saq was obtained by Nilson in large, white, lustrous prisms by evaporating a solution of Yb. (SO.), in water at a gentle heat. M. M. P. M.

at a gentle heat. M. M. P. M. YTTRIUM: Y. At. w. c. 89 6. The name of trium is given to the metal of an earth-obtained from a few fare Swedish minerals. The tains the following elements:

Even series—

2 4 6 2 10

B (11) So (14) Y (89) La (139) Yb (173)

Odd series—

3 5 7 9 11

Al (27) Ga (70) In (114) — T1 (204)

A comparison of the position of Yb with the positions of elements placed in Series 10 (c. that is a position of the positions of positions of positions of elements placed in Series 10 (c. that is a position of the position of Yb with the position of you have that Yb oxides 4cf. Erroum, vol. ii. p. 456; Scampton, vol. i wars von p. 879; and

infrq, Homogeneity of Yttria).

Occurrence.—About 30 to 35 p.c. of yttria, in combination with SiO2, is found in the exceedingly rare Swedish mineral gadobnite; some specimens of orthite also contain yttria, and the earth has also been found, in combination with Nb₂O, and Ta₂O₅, in specimens of curenite. The exides that generally accompany yttria in these rare minerals are ceria, didymia, erbia, lantana

lime, magnesia, soda, and oxide of iron.

Preparation of yttria.—The crude oxides of yttrium, erbium, &c., are separated from gadolinite by the method of Bahr, a. Bunsen described under Erbuum (vol. ii. p. 457). Madistrial of the contract of the oxides of the contract of the critical of the crit rignac (A. Ch. [5] 14, 247) converted the oxides into nitrates, heated the nitrates in a Pt basin until red fumes came off freely; treated the residue with water, and separated the solution, which contained much Yt nitrate, from insoluble basic nitrates of Er, &c. He then evaporated the solution to dryness, heated again until partial decomposition was effected, again treated with water, poured off the solution, evaporated it to dryness, partially decomposed the solid nitrates by heat, and so on. After some hundred repetitions of these processes, approximately pure yttria was obtained. Auer von Welsbach (M.4, 630) sengrated approximately pure yttria from the crude earths obtained from gadolinite by a long-continued series of operations based on the facts (1) that yttrium nitrate is less readily decomposed to basic salts than erbium sitrate when a fairly conc. solution of these nitrates is beated with the oxides of the metals finade into a paste with water, and (2) that basic yttrium nitrates dissolve in a solution of the normal nitrates of Y and Er more readily than basic erbium nitrates.

References.—Gadolin (Crell's Annal. 1796 [1] 313); Eckeberg (Scher. J. 3, 187); Klaprotti (Scher. J. 5, 531); Vauquelin (Scher. J. 5, 552); Berzelius (Scher. J. 16, 250, 404; and Lehrbuch (Scher. J. 18, 281); Lehr 24, 1051; Scher. J. 1801; Lehr 24, 1051; Scher. J. 1801; Lehr 24, 1051; Scher. J. 1801; Lehr 25, 1051; Lehr 25 [5th ed.], 2, 177); Berlin (P. 43, 105); Schoerer (P. 56, 483); Mosander (P. M. 23, 251); Popp (A. 131, 179); Delafontaine (Ar. Sc. [2] 21, 97; 22, 30; 25, 112; 51, 48; 61, 273); Bahr. (A. 135, 376); Bahr a. Bunsen (A. 137, 1); Cleve a. Höglund (Bl. [2] 16, 193, 279); Cleve [Bl. [2]

porated, separated and dried the double chloride of yttrium and ammonium thus formed, mixed this with Na, the double salt and the Na being arranged in alternate layers, heated the mixture in selected except the salt and the Na being arranged arraphit till extinct heated the mixture arranged in accrume inyers, nearest the introduction of closed crucible till action began and ther allowed the reaction to proceed; washed the fused mass with water, separated unreduced yttria by levigation, washed the dark grey powden that remained with water and then with alcohol. yttria by levigation, washed the dark-grey powden that remained with water, and then with alcohol, and dried it over H.SO. In 1890 Winbler (B. 23, 787) obtained a black powder that decomposed water by heating utria and finely divided Mg in the ratio Y.O.; 3Mg (cf. Yagara, p. 882). Popp describes yttriam as a dark-grey powder resembling ferrum reductum, decomposing cold-water slowly and hot water rapidly, Yoz. IV.

easily dissolved by dilute acids, including acetic acid, decomposing boiling KOHAq, and NH, ClAq at the ordinary temperature, with evolution of H and NH₁; we metal burns brilliantly when heated on Pt foil; when heated in O it burns with a very dazzling light.

with a very dazzing igut.

An examination of the emission spectrum of yttrium was made by Thalén: the most prominent lines observed had the wave-lengths 6191, 6331, 5387, 5971, 5662, 5496, 5402, 5205, 5202, 5203, 5203, 53030, 53030, 5303, 5303, 5303, 5303, 5303, 5303, 5303, 5303, 5303, 5303, 5 5200, 5088, 4900, 4881, 4854, 4874, and 4809

(Kongl. Sie. Vetens. Acad. Hundl. 12).

The atomic weight of attrium was determined by Berzelius, Delafontaine, Popp, Bunsen a. Bahr (v. supra, References) by analyses of the sulphate, or by transforming yttria into the sulphate; the values varied from 92.2 to 102.3. În 1873 Cleve a. Höglund (v. B. 6, 1467) made more accurate determinations by analysing purer specimens of Yt2(SO4)3, and obtained the value

Chemical relations of yttrium. - Assuming yttrium to be a homogeneous element with at w. c. 89, it must be placed in Series 6 of Group III. in the periodic arrangement of the elements. This group contains the earth metals; yttrium is preceded in the even series family by B and Sc, and as succeeded by La and Yb. A consideration of the position given to Y in the periodic classification shows that the element bught to dosely resemble the other metals of the earths. little is known of the properties of many of the earth metals to allow of a detailed comparison of them one with another. A general account of the relations of these metals will be found in Electrical Metals of the (vol. ii. p. 424).

The homogeneity of uttrice. The properties

described as belonging to yttria before 1885 were the properties of a mixture of at least five, and perhaps six, different bodies, according to Crookes (C. N. 54, 13, 155). Crookes subjected 'yttria' to a prolonged process of fractionation by ammonist for a description of this method v. EARTHS. vol. ii. p. 423), and he then examined the phosphorescence spectra of various fractions. Crookes concludes that yttrium is a compound, or perhaps a very intimate mixture, of simpler bodies. For details of the phosphorescence spectra of the substances obtained by fractionating 'yttria' v. METALS, RARE (vol. iii. p. 248). By thirty-two fractionations of 'yttria' by ppn. with NH,Aq, Preparation of yttrium.—The metal has not preparation of yttrium.—The metal has not been obtained pure. Wöhler in 1828 (P. 13, followed by twenty-six fractionations by ppn. with NH, Aq. been obtained impure yttrium by reducing the chloside by sodium. In 1864 Popp (A. 131, 179) dissolved yttria in HCfAq, added NH, ClAq, evaluation of the chloside sense and add dried the double abloride with propared. Sense and which when mixed with line and which when compared with line and which when line and when mixed with lime, and which, when converted into chlorida, gave a spark spectrum,

Schowing only the lines of yttrium.

Yttrium, bromide of, YBr, 19H₂O. Colourless, gery deliquescent tablets; obtained by dissolving Y₂O₂ in HBrAq and concentrating (Cleve, Bl. 2] 18, 193). The anhydrous salvis obtained by Duboin (C. R. 107, 99, 248) by heating Y₂O₃ to redness on a sapport of gas-carben in a current of CO and Br vapour. Very soluble in water or alcohol; insoluble in ether.

Yttrium, chloride of, YCl, 6H_O. Obtained by dissolving yttria in HClAq, evaporating to dryness on a water-bath, dissolving in alcohol, and evalurating over H.SO. (Cleve, I.c.). Crystallises in large, colourless, very deliquescent,

rhombis prisms (C., I.c.). The anhydrous com-pound is formed by heating yttria to redness on a support of gas-carbon in a slow stream of CO and Cl (Duboin, l.c.). By evaporating a solution of yttria in HolAq with addition of NH₂Ol a double compound of YCl₂ and NH₄Ol is obtained; double compounds with KCl and NaOl are formed by fusing the constituent chlorides together. Popp (4.131, 179) described the double compound YOl, 3HgCl, 9H,O. Cleve (Bl. [2] \$1, 195) described YOl, 5HCl, 8H,O.

Yttrium, fluoride of, 2YF, H.O. Obtained as a gelatinous pp. by adding HFAq, or solution of

a getatious pp. by-adding HrAq, or solution of an alkali fluoride, to colution of a salt of ytrium (Cleve, Bl. [2] 18, 193). Yttrium, iodide of, (? YI₂). Deliquescent crystals, soluble in alcohol; ootsined by evaporating a solution of yttria in HKAq (Berlin, P.

43, 105; no analyses given).
Yttrium, vxides of. Besides yttria, Y₂O₃, there probably exists another oxide containing

more oxygen.

more exygen.

YTTRIA YO. (Yttrium sesquioxide.) A hydrate, probably Y.O. 6HLO (Topp, l.c.), is, obtained, as a gelatinous pp. closely resembling hydrated alumina, by ppg. the solution of a salt of yttrium by ammonia. The oxide is formed by strongly heating this hydrate; also by decomposing by heat the carbonate, nitrate, or oxafate of yttrium in presence of air. Yttria is described as a heavy, white or almost white or oxaste of yttrium in presence of air. Yttria is described as a heavy, white or almost white powder, S.G. 5-078 (Cleve, &c.); 5-046 (Nilson a. Pettersson, B. 13, 1459). S.H. (0°-100°) 1026 (N. a. P., Le.). By heating amorphous yttria with CaCl, for some hours, and warhing with warm water, Duboin (C. R. 107, 99, 243) obtained highly vertractive crystals of YaO₃, scarcely acted on by acids or by fused Na₂CO₃.
Yttria is a markedly basic oxide; it absorbs CO₂ from the air, and decomposes solutions of ammonium salts, giving off NH_s. Yttria is insoluble in water; it dissolves slowly in cold HClAq, HNO,Aq, or H,SO,Aq, but more rapidly on warning. By heating a mixture of yttria and finely-powdered Mg, in the ratio Y₂O₄:3Mg, Winkler (B. 23, 787) obtained a black powder which slowly gave off H from cold water, rapidly from hot water, and dissolved in dilute HClAq, with violent evolution of H.

YTTRIUM PEROXIDE. By adding H.O.Aq and NH₂Aq to a solution of sulphate or nitrate of yttrium, Cleve (Bl. [2] 43, 53) obtained a white gelatinous pp. to which he gave the composition Y₄O₂; but this formula cannot be regarded as final.

ttrium, salts of. The salts which are formed by replacing the H of acids by yttrium belong to the form Y₂X₂, where X = 2ClO₂, 2NO₂, SO₃, SO₄, CO₃, 4PO₃, &c. Almost all the yttrium salts of oxyncids that have been prepared are normal salts; a basic nitrate, and an acid or no-phosphate and selenate, are known. Many of the relief are stringly by discovery attacks. the salts are obtained by dissolving yttria in acids and evaporating; those salts which are fusionable, or but slightly soluble, in water are formed by ppn. from the nitrate or sulphate. The salts formed by ppn. are the arsentie, borate, carbonate, chromate, iodate and periodate, oxalate, phosphutes, selenite and sulphite; besides these salts, the following salts of oxyacids are known, and are soluble in water: bromate, chlorate and perchlorate, nitrate, selenate, sulphate, thiosulphate and tungstate. A few double salts are known; the principal

A few double salts are known; the principal are $Y_2(CO_3)_xM_2CO_3xH_2$ (Bl. [2] 18, 193, 289; 21, 344; v. also Berlin, P. 43, 105; Högbom, Bl. [2] 42, 2; Popp, A.

131, 179).
Yttrium, sulphide of. No compound of yttrium and sulphur has been isolated with certainty. Addition of (NH₄)₂SAq or NH₄HSAq to a solution of a salt of ttrium ppts. hydrated oxide. By fusing yttria, S, and an alkali carbonate, and washing the fused mass with water, a lowish-green solid is obtained that is insoluble in water, but is partly decomposed thereby to hydrated oxide and H.S; this solid dissolves in acids, giving off H.S. The same solid seems to be obtained by strongly heating yttria in H laden with CS.. No compound of yttrium and S was with CS₂. No compound of yttrium and S was obtained by heating yttria with Na₂S₂. By heating YCl₂ in a stream of H₂S, HCl is given off, and a yellow powder remains, which is decomposed by water, with evolution of much H₂S (v. Popp, A. 131, 179). According to Popp (Lo.), the composition of this substance is Y₂S₂.

By passing dry H.S. over a mixture of YCl, with excess of NaCl, heated to c. 1000° in a boat of gas-carbon, Dufoin (C. R. 107, 99, 243) "obtained a greenish, crystalline solid, which when washed with water left transparent, greenish lamilie of the double compound Y₂S₂.Na₂S. M. M. P. M.

ZANZALOÏN & Aloïn.

ZEOBLY C13HmO. [231°]. Occurs in the ethereal extract from Zeora sordida (Paterno, G. 7, 281, 508). Small pyramids with hexagonal base (from ether-alcohol), v. sl. sol. alcohol and ether, insol. water. Neutral. Not attacked by alkalis or dilute acids.

ZINC. Zn. At w. c. 65.8 (v. infra).
Mol. w. c. 65.8 at c. 1400°; probably the same
fit colution in Hg (v. infra). Melts at 419° (determined by air thermometer; V. Meyer a.
Riddle, B. 26, 2443); at 41757° (determined
by platinum thermometer, Callendar, Griffiths,
C. N. 68, 1); for older determinations, giving

m.p. from \$40° to 450°, v. Carnelley's Mellingand Boiling-point Tables (1, 14). Bolls between
930° and 954° (Deville a. Troost, C. R. 90, 773);
at 930° (Violle, C. R. 94, 720; cf. Troost, C. R.
24, 723). S.G. c. 6·9 to 7·2 (v. Schiff, A. 107,
59; Kalischer, B. 14, 2750; Quinoke, P. 135,
642; Spring, B. 16, 2724). V.D. 34°8 at c. 1400°
(Mensching a. V. Meyer, B. 19, 3295). S.H.
(0° to 100°) '0935 (Bunsen, P. 141, 1); (19° to
47°) '0932 (Kopp, T. 155, 71; cf. Schicker a.
Wartha, B. 8, 1016). C.E.; if length of bar at
0° = 1°, then length at 9° = (1 + \beta t); if volume at
0° = 1°, then volume at 1° = (1 + \beta t); if volume at
0° = 1°, then volume at 1° = (1 + \beta t); if volume at
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Historical.—That copper acquired a reddish solour, and that its properties were modified, by melting with certain ores, was known to the ancients and the alchemists; the ore with which copper was generally melted to form brass was called cadmia fossilis. The fact that a lustrous solid could be obtained by heating cadmia fossilis seems to have been known to the ancient writers on mineralogy. According to Kopp (Geschichte der Chemie, 4, 116), the earliest use of the word sinc is found in a writing of the fifteenth century attributed to Bagil Valentine. Paracelsus, in the sixteenth century, speaks of zinc as a definite metal-like substance, and assigns it to the class of bastard or semi-metals. The name 'zino' was applied during the seventeenth and eighteenth centuries alike to zinc of and of the metal-like substance obtained from these ores. Boyle speaks of zinc, and also uses the word spelter, or splauter, a term of Indian wigin according to Kopp. Tolerably pure zinc seems to have been obtained from zinc ore about 1720, probably by Henckel (v. Percy's Metallurgy, 1850).

probably by Henckel (v. Percy's Metallurgy, 1, 520).

Occurrence. — Zinc is found in small quantities; Becker (J. M. 1857, 698); and Phipon (C. R. 55, 218) noticed the occurrence of native sinc in Victoria. Considerable quantities of compounds of zinc occur in many places; the commonest ores are calamine (carbonate). Silicona calagrine suilicate), blende (fulphic), and red sinc one (oxide); aluminate, arsenate, phosphate, and sulphate of zinc are also found, but in smaller quantities. Small quantities of Od compounds occur in most zinc over. The

ash of a plant that grows on the waste heaps of the zinc works in Rhenish Prussis (Viola calameteria) is said to contain compounds of sinc (Braun; P. 927 175). Zinc compounds have been found in some springs (v. Hillebrand, U. S. Geolog. Survey Bull, No. 113 [1898]). Traces of sinc compounds have been found, according to Lechartier a. Bellamy (C. R. 84, 687), in the human liver, in calves' liver, in beef, hens' eggs, wheat, barfey, maize, beans, and vetches.

Formation.—Line ore, generally carbonate or supplied, is roasted in reverberatory calciners; the roasted ore is mixed with half its weight of powdered chargoal, cokes or anthracite, and heated in crucibles or retorts arranged so that the reduced metal distils from the impurities; the metal is condensed and collected in suitable vessels, and CO passes off. For details and descriptions of the different forms of apparatus v. Dictionary or Applied Chemistry, vol. iii. p. 1042.

p. 1042.

Preparation.—Commercial zinc generally contains from 5 to 3.3 p.c. lead, with c. 2 to 5 p.c. iron and cadmium, and small traces of arsenic.

Pure zinc was prepared by Reynolds a. Ramsay (C. J. 51, 854 [1887]) by dissolving zinc sold as free from common impurities in dilute II,SO,Aq, evaporating, crystallising the sulphate several times, electrolysing a solution of this salt, the metal being deposited on an clectrode of Pt wire, dissolving the metal in dilute HClAq, ppg. ZnO₂H₂ by NH₄Aq, dissolving the pp. in excess of NH₄Aq, and ppg. ZnS by H₂S; the ZnS was dissolved in **HClAq**. and again ppd. from an anynomical solution by H₂S; the pp. was well washed, dissolved in pure dilute H₂SO₄Aq, and the sulphate obtained on crystallisation was re-crystallised several times; an aqueous solution of this sulphate was then electrolysed, using a Pt wire as electrode, and the metal was melted in a tube of hard glass from which the air had been exhausted. By distilling this metal in vacuo in a tube of hard glass, very pure zine was obtained. Pullinger (C. J. 57, 816 [1890]) distilled zine sold as 'chemically pure' in a hard glass tube, bent slightly towards the closed end, placed in a combustion furnace, the open end being con-nected with a good water-pump. By melting By melting the distilled zinc in a tube of hard glass with a small bulb blown on the end, the part of the tube between the bulb and the wider portion containing the zinc being papillary, and the open end being connected with a water-pump, he obtained the zinc insperfectly bright, smooth. lustrous spheres ree from hollows; the pump was stopped while the zinc was molten, and the increased pressure caused the molten metal to increased pressure caused the moiten metal to filter through the capfllery tube into the bulb. For the preparation of pure zind by electrolysis of an ammoniacal solution of the sulphate, v. Myers (C. R. 74, 195).

Stolba (C. C. 1884. 4f9) says that sine can be obtained free from As and nearly free from iron by the combined interaction 3088 and

Slobs (C.C. 1834. 419) says that since an be obtained free from As and nearly free from iron by the combined interaction 358 and water vapour. He mixes burnt gypsum with one-fourth its weight of S powder, moulds the moistened mixture into spheres about 5 cm. diameter, and sinks these to the bottom of a crucible containing molten zinc; vapours of

H,S and S are given off, and the molten metal is thereby briskly agitated. When the reaction is completed, the little balls are taken out, the upper crust is removed, and the operation is

repeated if necessary. Zinc-dust is obtained either in the distil-lation of the metal, or, in not such fine division, by crushing and powdering the metal in an iron mortar at a temperature somewhat below the mp. of zinc. The ZnO₂H₂ always present in specimens of zino-dust may be removed by digesting with NH ClAq and then with NH Aq (, and drying on a porous tile in vacuo (Carnegie, C. J. 53, 471).

Properties.—Zinc is a white metal, with a slight shade of blue; it is very lustrous when polished. Commercial zinc is brittle at the ordinary temperature, but it becomes malleable between 100° and 150°; at 210° it again becomes brittle, and at that temperature it can be finely powdered in a mortac. Pure zinc is said to be malleable at the ordinary temperature. mercial zinc that has been heated to 1008-150° retains its malleability when it cools. Kahlischer (B. 14, 2747) noticed that rolled zinc ceased to give a ringing sound when struck after it was heated to c. 160°-30°, that it could then be bent easily, and that when bent it emitted a sound like the 'cry' of tin; he found that the zinc became crystalline, and the crystalline structure wac more decided the higher the temperature; the S.G. was very slightly increased, and the electrical resistance was reduced by c. 3 p.c. as softer metal than copper; its hardness is in-oreased by rolling. The tensile strength of zinc varies much with the mode of preparation. Zinc crystallises easily, especially when pure; the form is that of hexagonal plates (for references v. supra, beginning of this article). Zinc melts at c. 420° and boils somewhat below 1000° (v. supra). Molten zinc expands somewhat during solidification. The metal can be distilled at a full red heat; the vapour takes fire in the air, and burns with formation of ZnO and the production of a bright white light. Zinc exposed to the ordinary air becomes very gradually covered with a thin film of a basic carbonate which protects the mass of the metal from further corrosion; in pure dry air zinc is unchanged. Zinc dissolves in dilute acids, generally with evolution of H (v. infra, Reactions with sulphuric and nitric acids); it also dissolves in solutions of caustic potash or sods. When impure zinc is amalgamated it results the action of acids. Zinc is not acted on by mineral lubricating oils; some of the commoner animal oils attack it slightly (v. Redwood, C. S. I. 5, 362). Zinc ppts. most of the other metals from their solutions; if a piece of impure zinc is dissolved in an acid, most of the metallic impunities (As. Cd., Cu., Phy. &c.) remain Endissolved as iong as undissolved. most of the metallic impurities (As. Cd. Cu. Ph. co.) remain midissolved as long as undissolved zino is present. Zinc combines directly with O. S. Se, Te, the halogens, and P; it forms alloys with many metals. Pure zinc does not decompose boiling water, but the commercial metal reacts and gives off H. Zinc-dust usually contains some ZnO.H.; it is said also to contain H, produced by the interaction of Zn. 22. 22. 22. produced by the interaction of Zn and ZnO₂H₂ (w. Greville Williams, C. N. 52, 205, 268), Atomic and molecular weights of sone. In 1809 Gay-Lussac (Mem. S. d'A., 2, 174) deter-

mined the weight of ZnO obtained by dissolving a determinate weight of zinc in hitric acid, evaporating to dryness, and strongly heating the residue; Berzelius in 1811 repeated the experiment of Gay-Lussac (G. A. 37, 400; v. also P. 8, 184); and in 1843 Erdmann made similar experiments (v. Berzelius' Lehrbuch, 8, 1219), The values obtained for the at w. of zinc were 0539 (G.-L.), 65-41 (B.), and 64-94 and 64-98 (E.). In 8844-8 aver decomposed ZhC₂O₄ by heating in air, and determined the weights of ZhO and CO₂ produced; the value 65.85 was thus obtained for the at. w. of zinc. In the same year Favre obtained the value 65.78 by dissolving zinc in dilute H₂SO₄Aq, burning the H given off by passing it over hot CuO, and weighing the water than 25.40 and Ch₂S₃ 10 163 In 1884 thus produced (A. Cha[3] 10, 163). In 1884 Marignac determined the Cl and the Zn in ZnCl2-2KCl, and obtained the value 65.18 for the at. w. of zinc (A. Ch. [6] 1, 309; v. also Baubigny, C. R. 97, 908 [1683]). By dissolving zinc in dilute H,SO,Aq and measuring the H given off; van der Plaats concluded that the at. w. of ony van der Plaats concluded that the at. W. of zine is 65-18 (C. R. 100, 52 [1885]). Reynolds a. Ramsay, in 1887, by measuring the H given off by the interaction between very pure zine and H.SO.Aq, obtained the value 65-48 (C. J. 51, 854). By oxidising zine to ZnO, by INO.Aq, in 1888, Morse a. Burton, obtained the value 65-1 (Am. 10, 311). In 1889 Gladstone a. Hibbert (C. J. 55, 443) determined the ratio of gine displayed to gilver deposited by one and the zinc dissolved to silver deposited by one and the same electric current; taking the at. w. of silver as 107.66 (the value adopted in this Distionary) the at. w. of zinc was found to be 65.29.

In 1886 Mensching a. V. Meyer (B. 19, 8295) found the V.D. of zinc at c. 1400° to be 34.3, a number which shows that the gaseous molecule of zine is monatomic. Ramsay, in 1889, determined the lowering of the vapour pressure of Hg produced by dissolving zine therein (C. J. 55, 521); assuming that equal volumes of dilute solutions contain equal numbers of molecules, and that the molecular weight of liquid Hg is 200. Ramsay's results indicate that the molecules of zine in dilute solutions of this metal in clusion that the molecule of zinc in dilute solu-

tions in these metals is monatomic.

Chemical relations of sinc. Zinc is the second odd-series member of Group II. in the periodic classification of the elements. Zinc is periodicensisting and in the elements. Zind if preceded in the odd series of this group by Mg and is followed by Cd, —, and Hg; the members of the even series of Group II. are Be, Ca, Sr, B3, —, —. *Zinc is the second member of settles 5; it is preceded in this series by Cu, and is appropried by Ga, Ga, As, Sa, and Bs. succeeded by Ga, Ge, As, Se, and Br. The general chemical character of zinc is that of a metal; its oxide ZnO is basic, its chloride ZnOl, is volatilisable without decomposition. No acids are known containing zinc, and the molecule of the glament is monatomic. The fact that com-pourits of ZnO and K.O are obtained by dis-solving ZnO.H. in KOHAq and adding alcohol shows that the hydroxide of the metal has feebly marked acidic properties, and the isolaŽÍNO. SEE

tion of a number of oxychlorides and basic carbonates, hitrates, and sulphates illustrates the fact that zinc is less positive than Mg, which is the first member of the zinc family of Group II. For a general account of the properties of the family of which zinc forms a member v. MAGNESIUM GROUP OF ELEMENTS, vol. iii. p. 163. The atom of zinc is divalent in the gaseous

molecules of its compounds.

Reactions and Combinations .- 1. Zine wunchanged in pure dry air; in ordinary air the surface layers are slowly converted into a basic carbonate, which protects the metal beneath. Heated strongly in air or oxygen, zinc burns to ZnO .- 2. Heating zine in bromine, chlorine, or iodine produces ZnBe2, ZnCl2, or ZnI2-3. When zinc is heated in phospherus vapour, phosphete of zinc (q. v., p. 890) is formed.—4. By heating zinc with selenion vapour, a compound of Zn and Se is formed (v. Zinc selenide, p. 890). 5. Zinc combines with tellurium when the elements are heated together (v. ZINC TELLURIDE, p. 891) .- 6. Sulphur and zinc combine when a mixture of these elements is very strongly compressed (Spring, B. 16, 1000).-7. Zinc deconfposes water at a red heat. Commercial samples of zinc decompose water at 100° (L'Hôte, C. R. 101, 1153).—8. ZnSis formed by strongly heating ainc in a stream of hydrogen sulphide; when hydrogen schmide is used the product is ZnSe, and by heating the metal in hydrogen telluride ZnTe is formed (v. Margottet, C. R. 84,1293). --9. Zinc is said to reduce carbon monoxide at a 9. Zinc is said to reduce carroin monorate at a very high temperature.—10. Zinc is superficially oxidised by heating to dull redness in nitric oxide (Sabatier a. Senderens, C. R. 114, 1429). Oxidation in nitrogen dioxide (NO₂) is effected at 300° (S. a. S., C. R. 115, 236).—11. Many metallic oxides are reduced by heating with metatac oxides are reduced by heating with zinc.—12. Zinc reacts with sulphurous acid solution; according to Schweizer (v. C. N. 23, 293), the products are ZnSO₃, along with H₂S₂O₄Aq, H₂S₂O₄Aq, and S.—13. Zinc dissolves in hydrochloric acid, giving off H and forming ZnOl₂. Reynolds a. Ramsay (C. J. 51, 857) say that pure zinc scarcely reacts with boiling hydrochloric acid. For reactions of zinc with sulchloric acid. For reactions of zinc with sat-phuric and nitric acids, v. infra.—14. Zinc dis-solves slowly in hot solutions of caustic soda or potash, giving off H, and forming ZnO.xM.20 (cf. Zing hydroxide, p. 888); the reaction is much hastened by adding iron or Pt along with the zinc .- 15. Many metallic salts in solution are reduced by zinc, with pnn of the metals, e.g. salts of As, Cd, Cu, and Ph.—16. When zincdust is shaken with an aqueous solution of ferric chloride, the whole of the ferric salt is very rapidly reduced to ferrous chloride (for details of the application of this reaction in the estimation of ferric iron, ve Carnegie, C. J. 53, 468 [1888]).—17. According to Siersch (J. 1867. 468 [1888]).—17. According to Siersch (J. 1887. 257), zinc dissolves in sodium chloride schution, forming ZnCl., 2NaClAq, ZnO, and H.—18. Poumarède (J. pr. 73, 496) says that nearly all chlorides and fluorides are reduced by reacting with vapour of zins in an atmosphere of H.—19. By heating to reduces a mixture of zino filings and sodium metaphysphate, Hoslet (A. 100, 99) probably obtained phosphides of sinc (v. Zino Phosphides, p. 890).—20, Zinc reacts with sodium hydrogen sulphite solution,

forming ZnSO, Na.S.O.Aq, and Na.SO.Aq (v. Hrgosulphires, this vol. p. 593).—21. By heating sine with sine sulphide in an exhausted tube, some of the ZnS is carried forward and deposited in the front part of the tube; probably at a high temperature ZnS is decomposed, and there exist only Zn and S, and at a lower temperature these recombine to form ZnS (Morse a. White An. 11, 348). A similar phenomenon is noticed on fleating zine with zine oxide (M. a. W., l.e. p. 258).—22. ZnS is formed by strongly heating zine and mercuric sulphide or zine and potassium polysulphides (vo Zino bulphide,

When slips of zinc-foil are immersed in CuSO₄Aq, a deposit of finely-divided Cu is formed on the sine. This copper-zing couple is an energetic reducing agent; KClO₃Aq is reduced to KClAq, KNO,Aq to KNO,Aq and NH,Aq, K,FeCy,Aq to K,FeCy,Aq, SO,Aq to K, So,Aq to K, FeCy,Aq to K, FeCy,Aq to K, FeCy,Aq to K, FeCy,Aq to C, II, NH, c. (v. Gladstonea. Tribe, C. J. 33, 306).

Reactions of zine with sulphuric and nitrio acids. Commercial zine dissolves easily in

dilute H.SO, Aq, with formation of ZuSO, Aq and evolution of H. In 1830 De la Rive noticed that very little action took place between approximately pure zine and H.SO.Aq; this fact has been confirmed by other experimenters. Reynolds a. Ramsay (C. J. 51, 857 [1887]) found that zine prepared by repeated electrolysis of the sulphate and distillation in vacuo scarcely reacted with H.SO, Aq; L'Hôto (C. R. 101, 1153) also asserted that pure zinc does not react with H.SCAAq. Divers a. Shimidzu (C. J. 47, 598 [1885]) observed very great differences between the rate of action of the same 1.50,Aq on sheets of commercial zine of the same size. Pullinger in 1890 (C. J. 57, 815), and Weeren in 1891 (B. 24, 1785), made somewhat elaborate investigations into the connections between the conditions and the rate of the interaction of zinc and M2SO4Aq.

Pullinger used 'pure' sulphuric acid diluted with three times its weight of water; and zine prepared by distilling that sold as 'chemically pure' in vacuo and casting in balls under pressure to provent the formation of cracks or hollows (v. supra, Preparation of zinc, p. 885). He found that when the surface of the zinc was very smooth this was best accomplished by immersing in aqua regia for 10 or 15 seconds, and washing with water—and the acid was boiled for some hours before the experiment, there was practically no reacting at 20°-25° (spheres of zine weighing c. 2) g. lost from 5 to 6 mgns. in 20 meyers). Pullinger found that the presence of small quantities of H.S. SOg, or H.S. Aq did not affect the weight of zinc dis-solved by the boiled H.S.O. Aq; addition of some H.Q. materially increased the sale of action; and H.S.O. Aq that had been electrelysed before use dissolved from four to zen times more zinc than some of the same acid that had not been than some of the same sold that and not been electrolysed; addition of a few drops of HNO₂Aq considerably increased the action; when a few drops of HIAq were added to the H₂SO₂Aq practically ne action occurred. P. supposed that all the 'pure' acid used by him contained traces of an oxidising substance, probably H₂S₂O₅, and that the solvent action was due to this. P.

866 ZINC.

insists on the important connection between the rate of action and the amoothness or roughness of the surface of the kinc used. But he concludes that 'in all probability gure digite sulphuric acid would, at ordinary temperatures, be entirely, without action upon installic zinc, whether the surface of the latter were rough or smooth.'

Weeren used zinc which he founds to be chemically pure by analysis; he gives no account of his method of preparation nor any details of his analytical results. W. found that the weight of pure zinc dissolved by pure H₂SO₄Aq (1:20) at the ordinary temperature, and under a pressure of 10 mm., was c. ten times greater than the weight dissolved at 760 mm. pressure; but the weights of impure zinc dissolved at the two pressures were almost the solved at the two pressures were almost the same. The pure zinc used by W. dissolved fairly rapidly in beiling H_2SO_4Aq ; in one case when 2·1 mgm. dissolved at 0° after thirty minutes' action, 122 mgm. dissolved in the colling acid. W. found that the solubility of his pure zinc increased very slowly as temperature rose up to within 1° of the b.p. of the acid used, but that when ebullition actually began the solubility of the zinc suddenly increased; the weight of pure sine dissolved by H,SO,Aq at 100° and boiling, was c. sixteen tiffes greater than the weight of the same zinc dissolved by the same acid at 100° but kept from actually boiling by pressure. On the other hand, W. noticed that as much impure zinc dissolved at 100° when the acid was boiling as when it was prevented by pressure from boiling. Addition of oxidisers, CrO, or H₂O₂, enormously increased (c. 300 times) the solubility of pure Are in H₂SO₂Aq at 18°-20°, but only aligntly increased (a. six times) the solubility increased (a. six times) the solubility increased (a. six times) the solution. only slightly increased (c. six times) the solubility of impure zinc. W. supposes that when pufe zinc is immersed in pure H₂SO₄Aq a slight reaction occurs, and that the H produced is attracted to and held firmly on the surface of the zinc, and that the reaction ceases because the surface of the metal is protected by the layer of H. Increase of temperature does not appreciably affect the rate of action, because the layer of H remains fixed to the surface of the zinc, but when the acid boils the H is re-moved and rapid dissolution occurs; any conditions which remove the layer of H increase the solubility of the zinc. W. supposes that the late of dissolution of impure zinc in H2SO, Aq is not much affected by boiling, presence of oxidisers, the zinc, but at the surface of the zinc, but at the surface of the zinc, but at the surface of the more negative impurities. The rapid solution of zinc in HNO Aq is connected, according to W., with the rapid oxidation of the Hproduced at the surface of the zinc, and hence the production of a layer of water on the surface of the metal which destroys the attraction between the zinc and any H that may scape oxidation.

As regards the products of the interaction of sine and sulphuric acid, when the acid is fairly concentrated (o. H.SO., H.O. to c. H.SO.) SO. is given off, and at moderately high temperatures H.S and S are also produced (o. Calvert a. Johnson, C. J. [2] 4, 485 [1867]). A qualitative examination of the products by Pattison Muir a. Adie (C. J. 58, 47 [1898]) showed that ZaSO, is the only salt of sine produced, with any concentration.

tration of acid, and at any temperature up to the b.p. of the acid used; that with approximately pure zinc little or no SO, or H.S is formed unless the temperature be high; and that the purer the zinc the less is the quantity of S produced (cf. Ditte, A. Ok. [6] 19, 68).

of S produced (cf. Ditte, A. Ch. [8] 19, 68).

The products of the interaction of zinc and nitrio soid are Zn(NO₂)Aq, Zn(NO₂)Aq, NH,NO₂Aq and NH,NO₂Aq, and NO, N₂O, and N., Acworth found that when HNO₂Aq reacts with zinc in presence of (NH₂)NO₃ the chief gaseous product is N (along with some N₂O and NO) (C. J. 28, 828 [1875]). Acworth a. Armstrong studied the greation of HNO₂Aq and Zn more fully in 1878 (C. J. 32, 54), and found that more fully in 1878 (C. J. 32, 54), and found that the only gaseous products were N, N₂O, and NO (cf. Deville, C. R. 70, 22, 550 [1870]). According to Divers (C. J. 43, 443 [1883]), a little NH₂OH is formed when bold HNO₂Aq (3 to 4 p.c.) is poured on to granulated zinc and quickly poured off again. Divers a. Shimidzu (C. J. 47, 597 [1885]) found that considerable quantities of NH₂OH are produced by the combined reaction of HNO₂Aq and H₂SO₂Aq, sor HNO₂Aq and HClAq, on sinc (v. Hydroxylamine, Formation, vol. ii. p. 734). Divers (Le.) thought that zinc more fully in 1878 (C. J. 32, 54), and found that vol. ii. p. 734). Divers (l.c.) thought that zinc does not form Zn(NO₂), by a direct reaction with HNO, Aq, but by interacting with some of the Zn(NO₃)₂ formed by the primary action of the metal on the acid. The products of the interaction of zinc and HNO, Aq have been examined recently by Montemartini (G. 22 [1], 277 [1892]), who says that free H is not produced (he also says that no NH₂OH is formed), and that in addition to nitrate and nitrite of zinc and ammonium, hyponitrite is also produced; the gaseous products, according to M., are N.O., NO, NO₂, and N; there is no nitrous acid formed, says M., if the HNO, Aq contains more than 30 p.c. HNO₃, and no NO₂ if less than 30 p.c. HNO₃ is present. M. also gives determinations of the quantities of the various products at different temperatures, and of the rate of reaction with different concentrations of HNO₂Aq (Abstract in C. J. 62, 1279 [1892]).

Zinc, alloys of. Alloys of zinc have been formed with most metals by fusing the constituents togother; the alloys are generally hard, some of them are brittle. With antimony, two crystalline alloys are formed by melting the metals together, in the ratios 3Zn:2Sb and Zn:Sb, and allowing to cool very slowly; Cooke (Ant. S. [2]*e18, 229; 20, 222) formulates these alloys as Zn,2Sb, and Zn,2Sb, respectiyely. These alloys react with water and give off H. Alloys with argenic are formed by heating together Zn, and As, or Zn and As, 03, or by heating Zn in rapour of As and H; by the last method Descamps (C. R. 86, 1022, 1065) obtained crystals agreeing in composition with the formula Zn_As,. Spring (B. 16, 324) formed an alloyby compressing Zn and As, in the ratio 3Zn:2As, at 6,500 atmospheres. Zinc alloys with bismuth when the metals are melted together, but on cooling, two layers are fermed, the upper containing zinc with c. 2 p.c. Bi, and the lower Bi with from 5 to 12 pec. zinc. An alloy of zinc with bismuth and lead (3 pts. Zn, 5 pts. Bi, and 5 pts. Pb) melts at 945°. For descriptions of alloys with calcium v. Caron (C. R. 48, 440 e 50, 547); Wöhles (Z. 138, 253); and Norton a Twiteball

(Am. J. 10, 70). Brass is composed of alloys of sine with copper (v. vol. ii. p. 254; and for details v. Dictionary of Applied Chemistry, wol. tails v. Diotionany of Applied Chemistry, wol.
iii. p. 1052). Alloys of zinc with copper and
mickel form German silver; mast modern,
bromes are alloys of zinc with copper and tin
(v. vol. ii. p. 254; and for details v. Dictionany
of Applied Chemistry, vol. iii. p. 838). Zinc
alloys with tron (for details v. Dictionany of APPLIED CHEMISTRY, vel. iii. p. 1051). For alloys with lead v. vol. iii. p. 125 (also Krant, S. D. I. 5, 537). Alloys with lead and tin are mentioned in vol. iii. p. 126 (v. also Wright a. Thompson, Pr. 48, 25). For alloys with magnetium v. Parkinson (J. pr. 101, 375). Zinc and mercury form a number of amalgams, which are brittle when a little Hg is present and party when much Hg is present (for references v.S.C.L9, 512). For alloys with platinum v. this vol. p. 288. For alloys with silver v. Wright a. Thompson (Pr. 48, 25).

For an account of the formation of zinc

alloys by immersing zinc in various metallic solutions v. Mylius a. Fromm (B. 27, 630

[1894]).

Zinc, amide of, Zn(NH,),. This compound was obtained by Frankland (Pr. 8, 502) by passing dry NH, into an ethercal solution of

passing dry NH, into an ethercal solution of ZnEL, A white, amorphous powder; unchanged at 200°, but decomposed at a red heat to Zn,N,2 (v. Zino nitrains, p. 889) and NH,; reacts with water to form ZnO,H, and NH,. Zino, bromide of, ZnBr,. Formula probably molecular, from analogy of ZnCl,. S.G. 3-643 at 10° (Bödeker). Melts at 394° (Carnelley, C. J. 33, 277). Boils at 695° to 699° (C. a. Williams, C. J. 33, 283); at 650° (Freyer a. V. Meyer, B. 25, 622). H.F. [Zn,Br²] = 75,930 (Th. 3, 275). Preparation.—1. Zino filings are heated to

Preparation .- 1. Zinc filings are heated to dull redness in a stream of Br vapour. - 2. Zinc, or ZnO,H, is dissolved in a slight excess of HBrAq, the solution is evaporated to dryness, and the dry residue is sublimed out of contact with air.

Properties and Reactions.—White needles; y deliquescent. Easily soluble in water, very deliquescent. Easily soluble in water, alcohol, or ether (v. Berthemot, J. Ph. 14, 610). Thomsen gives $[ZnBr^2,Aq] = 15,030 (Th. 3, 275)$. Aqueous solutions of ZnBr, of different concentrations have the following specific gravities according to Kremers (P. 108, 115):—

t 19·5°.	P.c.ZnBr.
	1863
	81.7
•	43.2
	52 ·6
	59.1
	• \$8∙0
	t 19·5°.

**Combinations.—1. With ammonia to form a series of compounds. These compounds were examined by Rammelsberg (P. 55, 240), and, more recently, by André (Bl. [2] 39, 398 [3833]). By dissolving ZnBr, in NH, Aq under different conditions, A. obtained 41 ZnBr, 2NH, H.O. (2) 3ZnBr, 2NH, 2H,O, (3) 3ZnBr, 10NH, H.O., and (4) ZnBr, 5NR, by saturating hot NH, Brisq with 2DO, and obtained 3ZnBr, 5NH, 3D.—2. With casium bromids, to form ZnBr, 3CaBr and ZnBr, 2CaBr (Wells a. Campbell, Zeit. f. pacerg. Chamic. 5, 273).

Zinc, chloride of, ZnCl. Mol. w. c. 136.
Melts at 262° (Braun, P. 154, 190). Boils at
703, 719° (Carnelley a. Williams, C. J. 33, 284);
at 750° (Freyer a. V. Meyer, B. 25, 622). S.G.
2.753 at 132 (Bödeker). V.D. at 890° to 907°
66 (F. a. M. 4.c.). H.F. [Zn,Cl] = 97,210 (Th.
3, 275).

Formation.—1. By fleating zinc filings in Cl.—2. By heating a mixture of 2 pts. HgCl, and 1 pt. zinc filings in a retort.—8. By distilling a mixture of equal pts. ZnSO, and CaOl, or a mixture of 1 pt. ZnO and 2 pts. NH,Cl.—4. By dissolving zinc, or ZnO.H., in HClAq, evaporating to dryness, and heating the residue in a retort.

Preparation. -1. Zinc filings are heated in a small retort in a stream of Cl; the product is distilled.—2. Zine, or ZnO₂H₂, is dissolved in a slight excess of HClAq; the solution is evaporated to dryness, and the residue is distilled from a small retort.

Properties and Reactions .- A white, semitransparent, crystalline, very ca istic solid; very deliquescent. Encily soluble in water, also in alcohol. Thomsen gives [ZnCl²,Aq]=15,680 (Th. 3, 275). Sublimes at a red heat. An aqueous solution is partly decomposed on eva-poration, giving exychlorides (q.v.). Oxychlorides are also formed by heating assolution of ZnCl, in HClAq with ZnO, also with HgO or PhO. Kremers (P. 105, 360) gives the following data:

S.G. ZnCl., Aq	P.c. ZnCl
1.1275	13.8
1.2466	25.8
1.3869	87.5
1.5551	49.2

A conc. solution of ZnCl2 is often used as bath for maintaining fairly high constant temperatures. Dry ZnCl, is used as a caustic; also as a dehydrating agent; a dilute aqueous solu-

as a dehydrating agent; a dilute aqueous solution is employed as an antiseptic.

Combinations.—1. With water. By keeping ZnCLAq containing 70.5 p.c. ZnCl, at 9° for 24 hours, Engel (C. R. 102, 111) obtained large crystals of the tribydrate, ZnCl, 3H,O, melting at 7°. When ZnCl,Aq containing 79.9 p.c. ZnCl, at 0° is kept for a long time it solidifies; on heating to 16° a part melts and a part remains solid; the liquid part is the dihydrate ZnCl, 2H,O, and the solid part is the hydrate ZnCl, 2H,O, and the solid part is the hydrate ZnCl, 2H,O, and the solid part is the hydrate ZnCl, 2H,O, and the solid part is the hydrate ZnCl, 2H,O, and the solid part is the hydrate ZnCl, 2H,O, 3H,O (B, t.c.). By heating a syrupy solution of ZnCl, with a little ECIAq, Schindler (Mag. Pharm. 36, 45) obtained octahedral crys. solution of ZnCl., with a little gloral, Schindler (Mag. Pharm. 36, 45) obtained octahedral crystals of the monohydrate of Dl. H.O. According to Engel (L.C.), the hydrate obtained by S. was 2ZnCl., 3H.O.—2. With hydrogen chloride and water. Engel (M. 5, 432) obtained the compounds 2ZnCl., HCl. 2H.O and ZnCl., HCl. 2H.O by pissing HCl gas into ZnCl., Aq, and adding zine from time 50 times and, when the solution had the S.G. of 2.0, cooling to 6. Warious compounds of Encl., with ammonic have been described; the formula ZnCl., NH., ZnCl., 2NH., 2(ZnCl., 2NH.), H.O. ZnCl., 4NH., H.O. and ZnCl., 5NH., H.O. have been given to compounds obtained by dissolving ZnCl., in NH., All, passing in NH., and evaporating under different conditions (v. Marignac, Ann. M. 5) 12, 1; Divers, O. N. 18, 13; Priwoznik, P. 142, 467; Davis, C. N. 26, 265; André, A. Ch. [6] 3, 84, 98; Thoms, B. 29, 748).—4. Lang (B. 21, 1578) described a compound with pyridine, ZnCl₂.2C,H₃N.—5. ZnCl₂ combines with alkali chlorides. Compounds, ZnCl₂NH₄Cl.xH₂O, ZnCl₂NH₄Cl.xH₂D, and ZnCl₂SNH₄Cl.xH₂D, and ZnCl₂SNH₄Cl.xH₂D, and ZnCl₂SNH₄Cl.xH₂D, and ZnCl₂SNH₄Cl.xH₂D, ZnCl₂SNH₂Cl.xH₂D, ZnCl.XH₂D, ZnCl.X Pharm. 36, 45), Marignac (J. 1887, 217), Ram-melsberg (P. 94, 508), and Hantz (A. 68, 227). A compound ZnCl₂, 2KCz is described by R. (l.c.) A compound ZnCl₂-2KOr is described by R. (l.c.) and M. (l.c.); and a compound ZnCl₂-2NaC' 3H₂O by M. (l.c.). Wells a. Campbell (Zcit. f. anorg. Chemis, 5, 273) describe two compounds with CsCl, to which they give the formulæ ZnCl₂-2CsCl and ZnCl₂-2CsCl. –6. With sinc oxide, v. Oxychlerides, p. 891.

A solution of zinc in conc. ECAq, to which

as much NH,Cl has been added as the weight of zine dissolved, is used for cleaning the surfaces of metals that are to be soldered together; any oxide on the metallic surfaces reacts with the NH₄Cl present to form chloride which dissolves

in the ZnCl₂ solution.

Zinc, cyanide of, and double zinc cyanides; . vol. ii. p. 347. For details regarding the conditions of formation and the properties of zinc-mercuric cyanide, v. Dunstan, C. J. 61, 666 [1892].

Zinc, ferrocyanide of; v. vol. ii. p. 337.

Zinc, fluoride of, ZnF₂. Formula probably molecular, from analogy of ZnCl₂. Formed by heating zinc or ZnO to redness in a stream of dry HF; also by the interaction of fused ZnCl, and dry HF at 800° to 900°; also by heating the hydrated salt to redness in dry HF (Poulenc, C. R. 116, 581 [1893]). The tetrahydrate ZnF2.4H2O is obtained by evaporating a solution of zinc in HFAq, and crystallising. The salt ZnF, crystallises in colourless needles, probably monoclinic. S.G. 4.84 at 15°; the crystals act strongly on polarised light (P., Lc.). Clarke (Am. S. [8] 13, 291) gives S.G. of ZnF, as 4.556 at 17°, and 4.612 at 12°; and the S.G. of ZnF, 4H, O cs 2.567 at 10° and 2.535 at 12°. ZnF, is slightly soluble in cold, more soluble in hot, water; it is insoluble in alcohol at 95°; soluble in boiling HClAq, H2SO4Aq, or HNO3Aq (P., I.c.). Heated in air, or to redness in steam, it is wholly changed to ZnO; fusion with alkali carbonates, produces ZnO and alkali fluorides; heating with H.S forms ZnS, and with IICl forms ZnCl. It is reduced by H at a red heat (P., Lc.). ZuF, forms double salts with Air, and with alkali fluorides. Berzelius (P. 1t 20) described the saits ZnF, 2AlF, and ZnF, 2KF; described the saits ZnF_x.2AlF, and ZnF_x.2KF; and Wagner (B_x 19, 896) the saits ZnF_x.2MH, F. 2aq. ZnT_x.4KF, and ZnF_x.NaF. The compound ZnF_x.ZrF, 6aq = ZnZrF, 6aq is described by Marignac (A. Ch. 13, 60, 257). S.G. 2.255 at 12° (Topsöe, C. C. 4, 76). For ZnF_x.SiF, v. Zinc silicofiluoride, p. 890. Zinc, hydrophosphide cf. ZnPH, A white, righle acid having this composition was abstracted.

friable solid hexing this composition was obtained by Drychsel a. Finkolstein (B. 4, 352) by tained by Drgohsel a. Finkolstein (B. 4, 352) by passing dry PH, into a coole! Ethereal solution of ZnEt. The compound can be kept in a closed, vessel; in air it absorbs moisture and rapidly depomposes, giving off PH.

Zine, nydrosulphide of. According to Thomsen (B. 11, 2044 [1878]), the pp. obtained by mixing NaHSAq and ZaSO, Aq, in equivalent grantities in propagate of size

quantities, is probably a hydrosulphide of zine (no analyses or formula given). Addition of

two equivalents of RaSH in solution to an equivalent of ZnSO, in solution produces no pp., but the solution gives a pp. of ZnS or hydro sulphide on standing, or on addition of scid or solphide on standing, or on addition of scal or code (T., l.v.). According to von Zotta (M. 10, 807 [1890]), the pp. supposed by Thomsen to be zinc hydrosulphide has the composition ZnS₂H₂ZznS. When four equivalents of NaSH are added to one equivalent of ZnSO, both in solution, and the clear solution is boiled, or treated with acid or alkali, a pp. of ZnS.H., 2ZnS is obtained (von Z., l.c). Linder a. Picton (O. J. 61, 130 [1892] obtained evidence in favour of the existence of compounds of Zn, S, and H, probably 7ZnS.H.S and 12ZnS.H.S, by passing H₂S into water at 0° with ZnO₂H, in suspension; they failed to isolate a definite compound with certainty.

Zinc, hydroxide of, ZnO₂H₂. (Zinc hydrate. Hydrated zinc oxide.) Obtained, as a white flocculent pp., by adding to solution of a salt of zinc rather less KOHAq than is sufficient to decompose the whole of the salt, washing thoroughly, and drying at a low temperature. According to Ville (C. R. 101, 375), 2nO₂H, is obtained in crystals by shaking very finely-powdered ZnCO₃, or basic carbonate, with twice as much KOH in 10 p.c. solution as is theoretically required for the decomposition of the carbonate; formation of crystals of ZnO,H, begins at once, and is complete after twenty to thirty minutes. ZnO,H, is said to be obtained in lustrous rhombic prisms by immersing zine in contact with iron or copper on MH₂Aq (Nicklès, A. Ch. [3] 22, 31; Carnu, Bl. 5, 64 [1863]). Bödeker (A. 94. 358) obtained the monohydrated hydroxide ZnO₂H₂H₂O in very fustrous octahedra by keeping a saturated solu-tion of the hydroxide in NaOHAq in a closed vessel for some weeks. S.G. of ZnO2H2 is given vesser for some weeks. S.G. of n_2 Li₂ is given by Nicklès (l.c.) as 2·677, and by Filhol (A. Ch. [5] 21, 415) as 3·053. Thomsen gives $[Zn,0,H^2O] = 82.680$ (Th. 3, 275). ZnO_2H_2 dissolves easily in acids, forming salts ZnX^1 .

ZnO2H2 also dissolves in caustic alkali solutions, and in (NH.).CO,Aq. By adding alcohol to a solution of ZnO,H, in KOHAq, Laux (A. 9, 183) obtained small lustrous crystals (?ZnO,K,); Fremy (C. R. 15, 1106) obtained (?) ZnO2K2.ZnO; Fremy (C. R. 15, 1106) obtained (?) ZnO₂k₂.ZnO₅ by using NaOHAq Como⁵. a. Jackson (B. 21, 1589 [1888]) obtained two compounds derived from ZnO₂H₂ by replacing H by Na. They Chook a solution of ZnO₂H₄, in cono. NaOHAq with alcohol separated the upper (alcoholic) layer 2nd allowed it to crystallise, and treated the lower (watery) layer repeatedly with alcohol until it solidified. The crystals from the lower leaves had the corrections

layer has the composition
Zn₂O₂Na₁H₂.1{E₂O(=Zn₃(OH)₂(ONa),.17H₂O),
agreeing, except in water of crystallisation, with agreeing, except in water of crystanisation, with an ammonium compound described by Malagati (C.R. 62, 413 [1866]); this compound melts at c. 70°, rapidly absorbs CO, from the air, loses $12H_0O$ at 100° , is insol in ether, and is decomposed by water, but not in presence of excess of NaOH, with formation of 2nO and a little ZnO₂H. The crystals from the upper layer had

the composition 2500 NaH.7H.0 = (2Zn(OH)(Oha).7H.0), corresponding with the compound described by Fremy (l.c.); this compound forms white radiating needles, which do not melt at 300°; it

bsorbs COafrom the air more slowly than the ther compound, is decomposed by alcohol or water, and does not lose H.O until heated above 200° (v. Am. 11, 145 [1889]). C. a. J. failed to obtain compounds derived from ZraQH, by replacing H by NH, or Mg. Compounds of ZnO with BaO, CaO, and MgO are described by Bertrand (C. R. 115, 939); these compounds are of the forms 2ZnO.MO.xH₂O.

Zinc, iodide of, Znl. Formula probably molecular, from analogy of ZnCl. Formed by heating together zinc and iodine, and subliming; also by digesting I with water and excess of zinc until the liquid is colourless and evaporating over H₂SO₄ (Rammelsberg, P. 43, 665). Crystallises in white octahedra; •S.G. 4·696 (Bödeker); melts at c. 440° (Carnelley, C. 3. 33, 278); and boils at c. 624° (C. a. Williams, v. Carnelley's Meltingand Boiling-point Tables, 1, 23). H.F. (Zn. I] = 49,230; [Zn, I], 3,0] = 60,510 (Th. 3, 275). Heated in air ZnI, gives off I, and ZnO remains. Kremers (P. 111, 61) gives the following data :-

8.G. ZnI, Aq 1.2340	P.c. ZuI. 23·1	S.G. ZnI,Aq o	P.c. ZnI, 63:5	
1.5121	42.6	2.3976	76.0	
1.7871	56.3			

Hot ZnI Aq is said to dissolve zinc in con-

Hot ZnLAq is said to dissolve zine in contact with the air, and on filtering an oxyio-lide is said to be deposited (Müller, J. pr. 20, 411). ZnI, Aq also dissolves I; Baup (J. Ph. 9, 37 [1823]) says enough I is dissolved to form ZnI, ZnI, combines with NII, By allowing a solution of ZnI, in NII, Aq to evaporate, Rungmelsberg (P. 48, 152) obtained lustrous, founded prisms of ZnI, 4NII, decomposed by water with production of ZnO. Various double companies with ather indides have been described: production of ZhO. Various adults consisted; ZhI_2MI, where, M = NH, K or Na (Rannolsberg, Le.; also P. 43, 665); ZhI_2CsI and ZhI_3CsI (Wells a. Campbell, Zeit. f. anorg. Chemic. 5, 273); ZZhI_BAI, (R., Le.); ZnI2.2BiI3. 12aq (Linau, P. 111, 240).

Zinc, nitride of, Zn₂N₂. Obtained by Frankland (Pr. 8, 502) by heating zinc amide (Zn(NH₂)₂; v. p. 887) to low redness. A grey, pulverulent solid; unchanged by heating to redness out of contact with air; reacts violently with water to give ZnO₂H₂ and NH₃.

Zinc, nitroprusside of, v. vol. ii. p. 341.

Zinc, oxides of. Besides the arornal basic oxide ZnO, there seems to be another higher (? superoxide) of zine.

ZINC ONDE ZnO. Formula not certainly

Occurrence.-With oxides of Mn, and Fe, 3 red sinc ore and franklinite.

Formation.—1. By burning zinc in air or 2. ZnCO, or another salt of zinc with a volatilisable

Preparation.—Pure ZnSO, prepared as described under Zngo, Preparation (p. 883), is disscribed under Zugo, Frequention (p. 883), is dis-solved in water, and the solution is very slowly added to a boiling solution of pure Na₂CO₂ con-taining rather loss Na₂CO₂ than suffices to de-compose all the ZuSO₄. The pp. of basic zing carbonates washed by decantation with boiling water until the washings are free from estbonates

and sulphates; it is then dried, powdered, and heated either in a Hessian crucible, or, better, in a flask of hard glass, until a portion taken from the middle dissolves, when cold, in acid without effervescence. The solid is now finely powdered, sifted through a fine sieve, again heated and then rubbed up with water, and washed and dried ZnO is prepared in crystals by heating ZnCl, to redness in steam crystage by heating ZnOl, to reduces in steam (Daubric, G. R. 39, 153); also by heating the amorphous oxide slowly in a stream of H (Regnault, A. Ch. [2] 62, 350; Devillo, A. Ch. [3] 43, 477); also by heating the amorphous oxide to whiteness in a stream of O. (Sidot, C. R. 69, 202); also by heating Zn(NO₃)₂ to roduces (Brügelmann, W. 4, 283).

(Brugemann, W. 4, 283).

Properties: Asslightly yellow, powdery solid; becomes darker yellow when heated, but recovers its original colour on cooling. S.G. 5-5 to 5-7 (b. Brügelmann, B. 13, 1741; Filbol, A. Ch. [3] 21, 415; Herapath, C. J. 1, 42; Karsten, S. 65, 394). S.Ge crystalline (at 15-) 5-782 (Brügelmann, W. 4, 286). ZhO crystallises in slightly yellow, lustrous, chemimorphous pyramids because the because when the large of the section. longing to the hexagonal system (B., Lc.). Thomsen (Th. 3, 275) gives H.F. [Zn,O] = 85,430. Richards a. Rogers (Am. 15, 567 [1893]) found that ZnO, prepared by heating Zn(NO), gave off some gas when dissolved in dilute acids; the maximum amount of gas from 10 g. ZnO was maximum amount of gas from 10 g. ZnO was 20 c.c.; the gas consisted chiefly of N, with a little O; the higher the temperature to which the Zn(NO₃), had been heated the less was the quantity of gas obtained; but some N always came off, even from ZnO which had been heated to the softening temperature of porcelain. Mota-say (C. R. 115, 1034 [1893]) states that ZnO volatilises readily when heated in an electric furnace, and condenses again in transparent crystals. ZnO is not decomposed at c. 1750° (Read, C. J. 65, 313 [1894]).

Reactions and Combinations .- 1. ZnO is a basis oxide. It interacts with most acids to form salts ZnX(X = 2NO, SO, 3PO, &a) and water .- 2. With fairly cone. caustic soda or potash, salts are formed which are most simply regarded as derived from ZnO2H2 with H replaced by Na or K (v. Zino hydroxidg, p. 888).— 3. ZnO is reduced to Zn, with explosive violence, by heating with magnesium (v. Winkler, B. 28, 123).-4. Morse a. White (Am. 11, 258) heated w mixture of ZnO and zinc in an exhausted tube, and found that a deposit of InO formed in the front part of the tube. They suppose that some of the original ZnO is decomposed by the combined action of heat and zinc, and that zinc and O exist together in the hot part of the tube, but combine in the cooler parts of the tube to form ZnO₈ 5. Oxychlorides, oxybromides, and pro-bably oxylodides of zinc are formed by heating ZnO with inc th'oride, bromide, and iodide re-spectively.—6. ZnO is reduced to zinc by heating with carbon or in cardon monoxide.—7. ZnO does not directly interact with water; ZnO.H. is produced by ppg. a zine salt solution by an as produced by ppg. a zine sait solutiff by an alkali (v. Zino hydroxides of aluminium, chromium, and iron along with B₂O, in a pottery furnace until the B₂O, was voratilised, Ebelmen (A. Ok. [3] 32, 34) obtained the compounds ZnO.Al.O. ZnO.Cr.O., and ZnO.Fe,O.

ZINC PEROXIDE. In 1818 Thénard (A. Ch. [2] 9, 55) obtained what he called 'deutoxide de 3, 00) obtained what he called 'deutoride de zinc' by the action of H₂O₂Aq on gelatificus ZnO₂H₂, and also by adding KOHAq to a solution of ZnO₂H₃ in HClAq to which H₂O₂ had been added. In 1884 Haas (B. 27, 2249) obbeen added. In 1004 Hars (B. 11, 2249) outsined a white, tasteless, neutral, felatinous pp. by adding H₁O₂Aq to softtions of zinc salts and then adding NH₂Aq; after washing and drying at 100°, the solids had approximately the compositions Zn₃O₅ and Zn₃O
5. H. thinks it probable that the substances obtained by him were compounds of ZnO and ZnO₂; the formula 2ZnO.3ZnO₂ agrees well with some of his

analyses.

Zinc, oxybromides of. Oxybromides of zinc are formed by heating solutions of ZnBr, with ZnO, and by partially ppg. ZnBr, Aq by NH, Aq. Several compounds have been described by André (Bl. [2]-89, 398 [1884]):

(1) ZnBr, 4ZnO.xH, O, x = 10, 13, and 19;

(2) ZnBr, 5ZnO.6H, O, (3) ZnBr, 6ZnO.356H, O. Zinc, oxychlorides of. These compounds are formed by adding to ZnCl, Aq a quantity of NH, Aq less than sufficient for complete npn: also by

less than sufficient for complete ppn.; also by boiling ZnCl2Aq with ZnO, or with certain other metallic oxides. Schindler (Mag. Pharm. 36, 45) obtained ZnCl, 3ZnO.4H, O by boiling and the same compound by partially pgg. 2nCl_Aq by NH_Aq. By adding to ZnCl_Aq so much NH_Aq that the pp. which formed at first partly dissolved, and also by treating ZnCl, 4NH, with water, Kane (A. Ch. 72, 296) obtained ZnCl, 6ZnCl.10H, O. André (C. R. 106, 854) obtained 2ZnCl., 3ZnO.11H O by boiling ZnCl., Aq with HgO and letting the solution cool; using Pr) he obtained another own-chloride, probably ZnCl₂.3ZnO, combined with ZnCl₂.PbO.

Zinc, oxyiodides of. According to Müller (J. pr. 26, 441 [1842]), ZnI,Aq dissolves zinc when warmed therewith in the air; on cooling,

an oxyiodide, ZnI, 3ZnO. 2aq, is ppd.

Zice. oxysulphides of. The compound Zine, oxysulphides of. 4ZnS.ZnO occurs native as voltzite, as spherical globules in some specimens of galena. A compound having the same composition was found in a furnace flue at Freiberg by Karsten (S. 57, -186). By heating dry ZnSO, to redness in H, Arrivedson obtained a yellow-coloured oxysulphide ZnS.ZnO (P. 1, 59).

Zinc, perbromoplatinocyanide of, v. vol. ii. p.

Zine, phosphides of. Zinc and P combine when heated together, forming a greyish, lustrous, somewhat malleable compound. By heating finely powdered zino in exapour of P. Schrötter obtained a compound, with S.G. 4.76, having the composition Zn.P. (W. A. B. 1859. 301). Vigier obtained the same compound by 801). Vigier obtained the same compound by heating zinc in F until distribation began, and then passing H laden with vapour of P over the zinc. The same compound was formed by Regnault (A. Ph. [4] 9, 162) by heating to wifiteness a mixture of MgHPO, ZnS and C; along with the Zp. P, were formed crystals of another phosphide, probably ZnP; and by treating Zn.P, with dilute acid, an amorphous, yellow solid remained which detonated when mixed with KClo, and struck and which was perhans with KClO, and struck, and which was pethaps EnP. The compound Zn.P. was obtained by

Housief (d. 100, 99) by strongly heating a mix-ture of ZnO, P.O., and C. By heating a mix-ture of NaPO, and zinc shavings in a retort, H. (l.c.) obtained a yellowish red, loose sublimate which contained Zn and P; and by heating the fused mass in the retort with HClAq, grey fus-trous tablets of ZnP₂, remained, Lüpke (C. O. 1890 [ii.] 642) formed zine phosphide († ZnP₂) by adding amorphous P to molten zinc covered by accurate amorphous r to molten zinc covered rithe(NH_s)₂CO_s; this phosphide was not decomposed by water, but was slowly decomposed by dilute HClAq, giving off PH_s. For the compound ZnPH v. Zinc hydrophosphina 1999

^Сри́пов, р. 888.

Zinc, platinocyanide of, v. vol. ii. p. 344.

Zinc, salts of. Many salts are obtained by replacing the H of acids by zinc. The greater number of the salts of zinc are normal salts; several basic carbonates, nitrates, and sulphates are known. The following are the chief salts of zinc derived from oxyacids:-Argenite and arsenate, borate, bromate, carbonates, chlorate and perchlorate, chromates, iodates, and per-iodates, molybdates, nitrates and nitrites, plosphates and phosphites, selenate and selenite, silicate, sulphates and sulphite, thiosulphate, tungstates, vanadates (v. CARBONATES, NITRATES, SULPHATES, &c.).

Zinc, selenide of, ZnSe. This compound, is formed, in reddish-yellow, regular crystals, S.G. 5.40, by heating zine to redness in a stream of H,Se, and then subliming in a slow stream of

of H (Margottet, C. R. 84, 1293).

Zinc, selenocyande of, v. vol. ii. p. 548.

Zinc, silicofluoride of, ZaSiF₆GH₂O. Obtained in hexagonal plates, easily sol. in water, by evaporating to a small bulk a solution of ZnO in H2SiFAq (Berzelius). S.G. 2.104 (Topsöe, C. C. 4, 76).

Zine, stannifluoride of, ZnSnF.6H2O; v.

this vol., p. 724.

Zinc, sulphocyanide of, v. vol. ii. p. 353.

Zinc, sulphide of, ZnS. This compound is not formed by heating together zinc and S, as the S volatilises before the temperature of combination is reached.

Occurrence. - As zinc blende.

Preparation.—1. By repeatedly subjecting a mixture of zinc and S, in the ratio Zn.S, to a great pressure; the product resembled zine blende (Spring, B. 16, 1,000).—2. By rapidly heating a mixture of zinc filings and cinnabar in a fetort; formation of ZnS occurs with dein a fetcht; Permation of ZnS occurs with detonation; Hg dtatils off.—3. By heating ZnO with S.—4: By heating ZnO, or ZnO,H, in a stream of H₂S; in the case of ZnO₂H, formation of ZnS takes place, very slowly (v. Wagner, D. P. J.e. 197, 334).—5. ZnS is also formed by heating dry ZnSO₄ with S and C.—6. ZnS is obtained by rassing H₂S into e neutral or alkaline soft-tion of a zine salt, or into a solution in a weak acid, such as acetic acid. washing the no. Arriver acid, such as acetic acid, washing the pp., drying that 100°, and heating in a stream of dry H.S. The pp. dried at 100° is said to be 2ZnS.H.O. (Geigor a. Reimann, Mag. Phorm. 31, 178; cf.

Souchay, Fr. 7, 78).

C. Rrogeries and Reactions.—G.G. of ZnS = 8.98 (Kars@n, S. 65, 894); S.G. of Lende = 403 to 4.07 (o. Neumann, P. 28, 1). Thomsen (Th. 8, 276) gives H.F. of ZnS.xH.O as [Z2,S.xH.O] = 41,580. ZnS prepared by ppn_ds a yellowing solid; easily sol. in acid; forming salts of an and giving off H.S. Zino blende is a grey to black crystalline solid; slowly acted on by solids. By repeatedly washing ppd. ZnS, also by passing H_SS into water containing pure ZnO₂H_S in suspendion. Winssinger (Bl. [2] 49, 452 (1888)) obtained colloidal ZnS, sol. in water; the solution could be boiled until all excess of H.S was expelled without ppn. of ZnS. ZnS prepared by adding excess of NH Aq to ZnCl Aq. ppg. all the sinc as ZnS by H_sS, washing and drying the pp., and then heating nearly to whiteness in a Hessian crucible inside a plumbago crucible, is very phosphorescent (v. Henry, C. R. 115, 503).

By heating ZnS with zinc in a vacuous tube,

Morse a. White (Am. 21, 348) found that some of the ZnS was carried forward and deposited on the cooler part of the tube; they supposed that some of the ZnS was decomposed, and that Zn and S existed in the hottest part of the tube and combined in the cooler portions. By heating blende with I and a little water some ZnSO, is formed (Filhol a. Melhies, A. Ch. [4] 22, 58;

Lasaulx, J. 1870.1272).

According to Schiff (A.115, 74), a polysulphide of sinc, probably ZnS, is formed by ppg. a neutral solution of a salt of zine by K,S,Aq, and drying the pp. over H₂SO. Spring (B. 16, 1000) thought that a polysulphide of zing was probably formed by strongly compressing a mixture of zinc with excess of S.

Zinc, telluride of, ZnTe. Obtained, in large Zino, telluride of, Zine. Obtained, in angeruby-red, regular crystals, by strongly heating zine in estream of H.To, and then subliming is a slow current of H (Margottet, C. R. 84, 1293).

Zino, titanifluoride of, ZnTiF₆; v. this vol., p. 742.

M. M. P. M.

ZINC, ORGANIC COMPOUNDS OF.

Zine methyl or Zine methide ZnC,H, i.e. ZnMe, Mol. w. 95. V.D. 3·29 (calc. 3·30). —40°] (Haase, B. 26, 1053). (46°). S.G. 195 ZnMe₂. 1.386.

Formation.—1. By heating methyl iodide with zinc in sealed tubes at 150°. The compound IZnMe is formed as an intermediate product. The reaction takes place more easily when the MeI is mixed with two-thirds of its volume of ether and heated to 100°, but it is then difficult to separate the ether from the ZnMe₂ (Frankland, A. 85, 346; 111, 62; Wanklyn, C. J. 13, 124; Butlerow, A. 144, 2; Ladenburg, A. 173, 147).—2. By heating fine granulated zine with HgMe, in a scaled tube for 24shours, at 120°, and distilling the product (Frankland a. Duppa, C. J. 17, 30).—3. IZnMe is formed in 24 hours if MeI is left in contact with a large amount of copper-zinc couple (Gladstone, C. J. 35, 109).

stone, C. J. 35, 109).

Preparation.—Zinc filings (9 pts.) are heated with reduced copper (1 pt.) till the copper-zinc fluple is produced, and the product treated with MeI (Gladstone, C. J. 35, 569).

Properties.—Colourless mobile liquid, taking:

Properties.—Colourless mobile liquid, taking fire on exposure to air. Decomposed by water into CH4 and Zn(OH). By very careful exidetion it appears to yield Zn(OMe), and crystalline Zn(Me), which is split up by water drifto Zn(OH), methal alcohol, and CH4.

Ractions.—1. Actyl chlorids (1 mol.) forms CH4. COl(@ZnMe).CH4, which is slowly converted, by further streatment with ZnMe, into

CH., CMe(OZnMe). CH. + ClZnMe. crystallising in prisms, and converted by water into tert-build alcohol, CH, zinc chloride, and Zn(OH). The compound OH, COI (OZnMe). OH, yields acctone on addition of water (Butlerow, Z. 1864, 365, 702; Privlow, N. Petersb. Acad. Bull. 22, 497; Bogomeletz, A. 209, 88).—2. Bromotacetyl bromide, followed by water, yields methyl-isopropylecarbinol (Winogradoff, A. 191, 127). 8. In ethereal solution secondary hexyl iodids has In ethercal solution secondary hexyl iodids has no action at 100°; but at 125° the products appear to be CH₁, ethyl iodide, and hexylene (Pufflie, C. J. 39, 464).—4. Chloral followed by water forms CCl₂.CHMe.OH₄ while butyric chloral yields CH₂.Cl₂.CHMe.OH₄ while butyric chloral yields CH₂.Cl₂.CHMe.OH₄ while butyric passed into ZuMe, forms OH₂N₂O₄(ZnMe), which is decomposed by water, yielding crystalline (CH₂N₁O₂).Znaq, from which the Na salt CH₃N₂O₂Na aq of 'di-nitro-methylic' acid may be obtained (Frankland, A. 99, 309).

Zinc ethyl or Zinc ethide ZuEt. Mol. w.

Zinc ethyl or Zinc ethide Zulet. Mol. w. 123. [-28°] (Haase, B. 26, 1053). (118°). S.G. 12 18182. H.F. - 31,800 (Guntz, C. R. 105, 673). V.D. 4.26 (obs. and calc.).

Formation.—1. By heating zinc or zinc.

Formation.—1. By heating zine or zinesedium alloy with EtI or a mixture of EtI and
ether (Frankland, C. J. 2, 297; 3, 44; Tr. 147,
431; 145, 259; A. 95, 28; Wanklyn, C. J. 13,
121; Pebal, A. 118, 22; 101, 105; Rieth a.
Beilstein, A. 123, 245; 126, 248; Chapman,
Laboratory, 1, 195; Alexejeff a. Beilstein, C. R.
63, 171; Rathke, A. 152, 220; Wichellaue, J. 1868, 425).-2. By heating granulated zinc with HgEt, in sealed tubes for 36 hours at 100° (Frankland a. Duppa, C. J. 17, 3).—3. From zine filings and EtBr (Wichelhaus A. 152, 321).

Preparation .- Clean zin filings (180 g.) are mixed-with copper (20 g.) reduced from the oxide at a dull-red heat by coal gas; the mixture is rapidly heated over a very large Bunsen flame, and is well shaken meanwhile. As soon as the filings begin to cake together and the copper is no longer visible, the copper-zine couple has been made. The flask is now connected with an inverted condenser, inclined slightly upwards, and when it is cold ethyl iodide (175 g.) is added. Dry CO₂ is passed through the apparatus, and the flask, heated by a water-bath; in half an hour the Eff ceases to run back from the condenser, for it has been converted into IZnEt. The apparatus is now tilted so that the condenser is inclined downwards, and heated in a bath of paraffin. reaction 2IZnEt = ZnI, + ZnEt, now takes place, and ZnEt, (60 g.) is collected in a receiver kept full of CO₂ (Gladstone a. Tribe, C. J. 26, 445; 35, 569).

35, 569).

Properties.—Colourless, mobile liquid, fuming in the air, and quickly taking fire, burning with a luminous green-sided flame, and giving off clouds of ZnG. Immfediately decomposed by water into Zn(OH), and ethans. In like manner containing a containing containing it attacks ofgenic compounds containing hydroxyl or amidogen, with elimination of ethane. It causes india-rubber to swell remark-

ably. Reactions .- 1. Gradually treated with dry oxygen it appears to produce ZnEt(OEt) and Zn(OEt), successively (Frankland). According to Demuth a. Meyer (B. 28, 394), the passage of oxygen through a solution of ZnEt in ligroin

(7 vols.) yields EtZn.O.O.Et, which is decomposed by heat, sometimes with explosive violence. The compound EtZn.O:OEt sets free I from a solution of KI and yields alcohol when distilled with dilute H.SO. —2. Sulphur forms zine mercaptide Zn(SEt).—Be appears to uct in like manner (Chabrie, Bl. [3] 2, 789).—3. Iodine forms IZnEt and ZnII successively, together with Etl. Bromine acts in like manner. Sinc ethyl takes fire in chlorine. 4. Dry ammonia forms $\text{Zn}(\text{NH}_2)_2$ and ethane (Frankland, Pr.~8, 502).—5. Nitric oxide is absorbed by an ethereal solution of ZnEt2 forming crystalline ZnEt2(NO)2 which melts below 100° and is split up by water into ethane and C.H., N.O., ZnOH. Carbon dioxide passed into an aqueous solution of this salt ppts. passed into an aqueous solution of this sure pres-tine carbonate, while zine "dinitrothylato" (C₂H₃N₂O₂)₂Zn remains in solution (Frankland, Tr. 1857, 59; A. 99, 342; C. J. 37, 570). The salt (C₂H₃N₂O₃)₂Zn aq crystallises in prisms, yields NH₂ and NH₂Et on treatment with sodium-amalgam (Zuckschwerdt, A. 174, "302), and HNO₂ and NH Et on treatment with alcoholic potash (Zorn, B. 15, 1008). The dinitroethylpotesta Zolin, B. 15, 10005. And difficulty attes NaA', BaA'₂, CaA'₂3aq, MgA'₂, CuA'₂3aq, AgA', and Ag₂A'(NO₃) were prepared by Frankland.—6. SO₂ forms zine ethane sulphinate (Hobson, C. J. 10, 455).—7. PCl₂ yields PET, (Hofmann a. Cahor.rs. Tr. 1857, 578).—8. Sicl. gives Fift,—9. Heated with Etl at 170° it forms n-butane and ZnI., Ethano and ethylene are also formed (Brodie, C. J. 3, 405). ZnEt, does not act on amyliodide.—10. Displaces halogens in organic compounds by ethyl.—11. Adds itself to a carbonyl group. Thus with di-chyl-hotone it forms Et₂C(OZnEt).Et, which is converted by water interirethyl carbinol. Di-pmpyl ketone forms, in like manner, ethyl-di-propylcarbinol. Ketones containing the group CO.CH. act differently, forming condensation-products; thus acetone yields mesityl oxide and phorone (A. Saytzeff, J. pr. [2] 31, 319). Zinc ethyl has no action on paraldehyde (Wedensky, J. pr [2] 39, 568). With acetic aldehyde it forms CH,CHEt.OZnEt, which is converted by water into sec-butyl alcohol .- 12. In some cases it can add ZnEt and H to a carbonyl group, C.H. being evolved. Thus ZnEt, converts chloral, dissolved in pure ether, into crystalline CCl2.CH2.OZnEt, which is converted by water into tri-chloro-ethyl alcohol (Delacre, Bt. [2] 48, 784). Further action of zinc ethide on chloral yields (CCl₂.CH₂O)₂Zn, s white powder. In like manner butyric chloral is converted into C₂H₁Cl₂.CH₂.OH.

In this splitting off of an olefine, ZnEt₂ differs from ZnMe, but resembles zinc propyl and zinc isobutyl (Garzarolli, A. 223, 162)—13. Can displace oxygen by two ethyl radicles; thus it converts oxalic ether into CO_Et.CEt_CO_Et (Fank-land a. Duppa, A. 142, 1; Pa 12, 396).—14. Can displace ethoxyl by ethyl. Thus iv converts formic ether into HCEt(OZnEt).OEt and then into HCEt(OZnEt). Et, which in turned by water into di-ethyl-sarbinol (Wagner & Saytzeff," A. 175, 851) .- 15. Candisplace chlorine by hydrogen. Thus with chloro-benzoic acid the first product is probably C.H. (ZnEt). CO.Et., which is converted by water into benzoic ether, C.Y., and ZnO.—16. With benzonicitie at 150°, and subsequent treatment with alcohol, cyaphenene is formed (Frankland a. Evans, C. J. 37, 568). It

polymerises phenyl-actionitrile in the same way, forming cyanbenzine.—17. Cyanbgen forms ZnO, and EtCN (Frankland a. Graham, C. J. 37, 740).—18. Azobenzene is reduced by ZnEt, collowed by water, to aniline (Frankland a. Louis. bollowed by water, to antime (Frankland a. Louis, C. J. 37, 563).—19. Acts on primary and secondary amines, giving off ethane, but has no action on tertiary amines (Frankland, Pr. 8, 502; Gal, J. Ph. [5] 7, 484). ZnEt, has no action on nicotione or quinoline, but forms with many alkaloids containing O compounds from which the alkaloids are regenerated by water.—20. Acetamide gives (AcNH).Zn, while oxamide gives C.O.(NH).Zn.—21. Acts on HgCl, forming ClHgEt and HgEt, (Buckton, A. 109, 218). Cilight and Hgret (buckton, A. 107, 210). Hg_Cl₂ yields HgEt₂, mereury, and ZnCl₂— 22. AgCl forms ZnCl₂ silver, and butane.— 23. CCl₄ forms EtCl, ethylene, and propylene (Rieth a. Beilstein, A. 124, 242).—24. Chloroform yields amylene (R. a. B.), while bromoform gives propylene and EtBr (Alexejeff a. Beilgtein, C. R. 58, 172). CHCl₃I produces ethylene, butane, and hydrogen (Borodine, A. 126, 239).

Zinc bromo-ethide ZnBret.* [62°]. Formed

by the action of the copper-zinc couple on EtBr at 100° (Gladstone a. Tribe, C. J. 27, 410).

Pearly scales, decomposed by heat partly into ZnBr, and ZnEt, and partly into Zn, ZnBr, C, II, and C, H.

Zinc iodo-ethide ZnIEt. Formed in like

manner. Crystalline. Split up by heat into

Zinc propyl ZnPr. (148°) (S.); (146°) (Glastone a. Tribe, B. 6, 1136); (150°) (Pape, B. 14, 1873). Formed by heating propyl lodide with zine and a small quantity of an alloy of zinc and sodium (Stcherbakoff, Bl. [2] 37, 345). Heavy liquid, with disagreeable odour. Reacts with aldehydes, forming propylene and such com-pounds as RCH...OZnPr, which yield secondary alcohols on addition of water.

Zinc isopropyl ZnPr... (136°) with decomposition; (96° at 40 mm.). Got by heating PrI (170 g.) with ether (100 g.), zinc (100 g.), and zinc sodium (3 g.) at 100° (Ragozin, J. R. 24, 549). Fuming liquid. Yields crystalline Zn(OFr),

549). Fuming liquid. Yields crystalline Zn(OFr), on exposure to air. Split up at 132° into Zn and hydrocarbons (Gladstone a, Tribe, C. J. 39, 6).

Zine jsobutyl Zn(C,H₀), (166°) at 734 mm.
(Garzarolli-Thurnlackh a, Popper, A. 223, 167).

Formed from zine and Fr.CH₂I. Got also from Zn and Hg(O,H₀), (Cahours, Bl. [2] 21, 357).

Zine isoamyl Zn(C,H₁), (220°). S.G. 2
1-022. V.D. 6·25 (calc. 6·87). Prepaged by heating zine with Hg(O,H₁), (Ffankland, A. 85, 860; 130. 122b. Liquid, fuming: in the air but not 130, 122). Liquid, fuming in the air but not taking fire. Takes fire in oxygen. When addedo to cooled aldehyde it yields, after addition of ice-cold water, methyl-isoamyl-carbinol, ice-cold water, and chyl and isoamyl alcohols.

(Sokoloff, C. C. 1887, 988). ZINCATES. Compou ZINCATES. Compounds derived from ZaO,H, by replacing H by positive metals; v.

ZING HYDROXIDES, p. 888.

ZINGONATES v. under ZINGONIUM HYDROXIDE.

p. 896. p. 930.

**XINCOPILA; oxide of sircontum (c. v., p. 896).

ZIXCONIUM. Zr. At. w. 0890 (v. p. 894).

Mol. w. not known. Melts above m.p. of Si (t.c. above c. 1800°) (Troost, J. 1865. 188). S.G.

4-15 (Troost, J.c.); 4-25 (Moissan, G. R. 116, 1222). S.H. (0"-100") '005 (Mixter a. Dana, M. 169, 388 [1853]).

Historical:—Klaproth in 1789 (Beiträge, 1,

203, 227) announced the discovery of a new earth, in combination with silica, in the rare mineral sircon. The same earth has been found in a few other rare minerals, such as eudialyte, polymignite, fergusonite, &c. Bright-coloured varieties of zircon are generally called hyacinth, the greyish or brown-kinds are called zirconites and a variety which is nearly colourless is known

as Jargon.

In 1845 Svanberg (A. 56, 223) stated that zirconia was a mixture of at least three oxides, but Berlin (J. pr. 58, 147), Marignac (A. Ch. [3] 60, 257), and Hermann (J. pr. 31, 75; 97, 331) failed to obtain any evidence of the composite character of zirconia. At a later time, Sorby (B. 2, 126, 193 [1869]), and also Forbes (B. 2, 337, 383), thought they had obtained spectroscopic indications of the presence of another earth in zircon; but it was shown that the abnormalities observed were due to traces of compounds of tranium (Sorby, C. N. 21, 73; Knop, A. 159, 44; cf. Hannay, C. J. 26, 703).

Occurrence.—Never uncombined. The principal naturally occurring compound of Zr is zirconite, which is more or less pure ZrSiO. This mineral is found in small quantities in the sand and alluvial deposits of certain rivers in Ceylon, and in the older rocks in many parts of the world; it has been found in the granites of Sweden, Switzerland, Tyrol, and North America (v. J. M. 1877. 97).

Formation.—1. By heating K,ZrF, with K (Berzelius, P. 4, 117 [1825]).—2. By passing vapour of ZrF, over Na in a red-hot tube (Troost, C. R. 61, 109 [1865]).—3. By heating ZrO₂ with Mg (Phipson, J. pr. 96, 353 [1865]).—4. By melting ZrO₂ in a carbon crucible in an electric furnace; or by mixing ZrO, with carbon, melting in an electric furnace, then mixing the Zr parbides thus formed (v. Carbides, p. 894) with excess of ZrO2 and again melting (Moissan,

J. R. 116, 1222 [1893]).

Preparation.—1. Finely powdered zirconite (ZrO, SiO,) is thoroughly mixed with an excess of finely powdered carbon, the mixture is compressed into small cylinders which are placed in a closed carbon crucible and heated in an electric lurnace (with a current of 30 to 35 ampères and 70 volts), while a stream of CO₂ is sent through the crucible; the greater part of the \$10₂ is thus voltilised (Troost, C. R. 116, 1428). The carbides of Zr in the crucible are now mixed with excess of ZrO. and melted in the electric furnace (Moissan, C. R. 116, 1222).—2. Finely powdered and sifted zirconite furnace (Moissan, C. R. 116, 1222).—2. Finely powdered and sifted zirconite furnation with 2 to 3 timesits weight of KHF, the mixture is heated to bight redness for c. 15 mins., and after cooling, it is boiled with water containing a little dilute HFAq; K,SiF, is removed by filtration, the filtrate deposits K,ZrF, on cooling. The K,ZrF, is re-crystallised from water, then dried, mixed with K, and heated in a vessel of glass or iron, the product is washed with water, digested for a long time with cele. HClaq at 40°, then yashed with water containing NH Cl, and finelly with alcohol (Berzenus, Lc.: Trocat, A. 136, 353). This method yields amorphous sirconium. According to Bailey (Pr. 46, 74 [1889]), the only

method that gives nearly pure amorphous Zr is to heat ZrO, with Mg foil (not powder) and treat with HClAq.—3. One part dry K,ZrF, is mixed with 11 pts. Al and the mixture is heated to the melting-point of iron in a crucible made of gas coke; the product is digested with conc. HClAq diluted with twice its volume of water, when the crystalline leatlets of A, that have formed on the surface of the Al, separate from the mass of Al before the latter is wholly dissolved. When the whole of the Al has dissolved an alloy of Zr and Al remains, besides the crystalline leaflets of Zr; if the temperature of reduction is not sufficiently high, the main product is the Zr-Al alloy (Troosa, c., cf. Franz, B. 8, 58). This method yields crystalline zirconium.

Various methods have been used for decomposing zirconic and obtaining compounds of Zr. Franz (B. 3, 58) fuses the powdered mineral with KHSO, treats the fused material with boiling water containing a little H.SO., washes the insoluble 3ZrO.SO. thus formed, and adds it, in small portions at a time, to molten NaOH; he then lixivister with cold water, dissolves the ZrO, that remains in hot conc. H2SO, dilutes, ppts. by NH,Aq, washes, dries, and decomposes the ZrO,xH,O by heat. The method of fusing the Zro...zH. to by heat. The method of reasons with KHF, used by Marignae (r. supra., No. 2) yields pure K.zrF_e very readly; Zr(SO_e), may be obtained by heating the K.zrF_e with cone. H.SO_e (v. Hiortdahl, A. 137, 34; cf. J. pr. 83, 201). For other methods v. Hermann (J. pr. 21). 201). For other methods v. Hermann (J. pr. 97, 330); Scheerer (P. 59, 48); Stromeyer (A. 113, 727); Chancel (J. pr. 74, 471); Berlin (J. pr. 58, 145); Henneberg (J. pr. 88, 508); Bailey (Pr. 46, 74 [1889]).

Properties .- Zirconium las been isolated as black amorphous powder, and also as a greyish

crystalline solid.

Amorphous zirconium (v. Preparation, No. 2) is a black powder, which is extremely porous and resembles powdered charcoal; when pressed with a burnisher it agglomerates to graphite-like lamine. After being heated strongly, and then cooled, in vacuo, it is said to glow and burn when exposed to air. The porous amorphous metal is said not to conduct electricity. Amorphous Zr is stated to be insoluble in ordinary acids, including aqua regia; but, according nary actos, including aquar regits; but, according to Bailey (Pr. 46, 74 [1889]), it dissolves in cold coac. H.SO₄; HFAq dissolves it readily, H being given off. It is oxidised by heating in the air, when it burns to ErO, with a brilliant white light; oxidation is also effected by fusion with caustic or carbonated shales, or with KNO, or KClO,

Crystalline zirtonium (v. Preparation, No. 3) is a very lustrous, greyish, brittle, solid, which resembles Sb in appearance; very hard, easily scratching glass and ruby (Moissan, C. R. 116, 1227/s. Sec. 4.15 (Troos. J. 1865. 183); 4.25 (Moissan, L.c.). S.H. (0° to 1002) 006 (Mixter a. Dana, A. 169., 388 (1873)). Crystalline Zr burns in the Q-H flame; it is not oxidised in Outli bested to whiteness at dissolves slowly O until heated to whiteness it dissolves slowly in hot conc. HClAq, and is very slightly acted on by HNO, Aq or H, SO,, even when warm; cold HFAq dissolves it readily. Molten KClO, or KNO, is said to be without action; molten KOH dissolves the metal as long as any moisture is

present.

According to Troost (J. 1865. 188), Zr melts

According to Troost (J. 1865. 188). Zr melts above the mp. of Si (i.s. above c. 1800°). The emission-spectrum of Zr has been mapped by Thalén; the chief lines are 6127 in the red, and in the blue, 4815, 4771, 4738, 4709, and 4886.

The at w. of Zr was determined, (1) by Berzelius (P. 4, 126; 8, 186 (1825)), by finding the ratio of ZrO, to SO, fit the sulphate; (2) by Hermann (J. pr. 31, 77 (1844)) by analysing ZrOl,: (8) by Marignao (A. Ch. '3) §0, 270 (1860)), by analysing K₂ZrF₂; (4) by Bailey (Pr. 46, 74 [1889]), by decomposing Zr(SO₄), by heat and weighing the ZrO₂ produced; (5) by Mixter and weighing the ZrO, produced; (5) by Maxter a. Dana (A. 169, 388 [1873]), by determining the S.H. of Zr; (6) by Deville a. Shoot (P. 108, 636; 641 [1859]), by determining the V.D. of ZrCl.. The results of Berzelias gave the at w. of Zr as 89.2; those of Hermann, 88.5 to 90.7; those of Marignac, 90.3 to 90.6; and the results obtained by Briley gave 90.4 as the at. w. of the metal.

Zirconium is the fnird member of the evenseries family of Group IV. in the periodic classification of the elements. This group contains the following elements:-

As is to be expected from its position in the classificatory system, Zr is a metal with some non-metallic properties; the oxide ZrO₂ forms corresponding salts, many of which are basic salts; the haloid compounds, ZrX₄, are propably all volatilisable without decomposition (the V.D. of ZrCl, only has been determined), but aqueous of Zru, only has u en determined, our aqueque solutions yield oxyhalides on evaporation; hydrated ZrO, reacts as a weak acid towards strong bases, forming zirconates; salts are known derived from the acid H₂ZrF₆; there is an oxide higher than ZrO₃, probably ZrO₂. For a more detailed comparison of Zr with the other evenseries elements of Group IV. v. TITANIUM GROUP OF ELEMENTS (this vol. p. 749), and cf. Tin GROOP OF ELEMENTS (this vol. p. 735). The atom of Zr is tetravalent in the gaseous mole-

cule ZrCl.

Reactions and Combinations.—1. Heated in Reactions and Combinations.—1. Heated in air, or oxygen, Zr burns to ZrO, giving out dazzlingly white light; amorphous Zr burns easily, orystalline only at a white heat, and then merely superficially.—2. Both amorphous and crystalline Zr dissolve readily in hydrofluoric acid, giving off H and forming ZrF..—3. According to Bailey (Pr. 46, 74), amorpheus Zr dissolves in cold cone. Sulphuric acid. Both forms dissolve in aqua regia.—3. Cone. hydrochloric acid reacts with Zr, when warm, forming ZfCl, solution. Crystalline Zr is said to interact chloric acid reacts with Zr, when warm, forming ZfCl, solution. Crystalline Zr is said to inveract with gaseous hydrogen chloride, &c. dull redness, forming ZrCl, =6: Amorphous Zr is exidised by molten potash or soda, also by molten mitre or potassium chlorate; the crystalline form of Zr is said not to be acted on by molten KNO, or KClO, and by molten caustic alkalis only as long as there are traces of moisture present.—6. Zr combines directly with the halogens, to form ZrX, and probably with sulphur (v. Sulphide, p. 897).

Detection and Estimation.—Addition of hot

edic. K.80.Aq to solutions of salts of Zr pptd. white basic sulphate of Zr, which is insoluble in water and nearly insoluble in much Hölaq. Turmerio paper becomes reddish-brown when immersed is a solution of a salt of Zr in Hölaq. the reaction is completely masked by the presence of boric acid (v. Brush, J. pr. 62, 7).
Bailey (C. J. 49, 481 [1886]) found that addition of H₂O₂Aq to a slightly acid solution containing salts of Zr, along with salts of Fe, Nb, and Ti, ppd. the whole of the Zr as ZrO, (or Zr,O,), but none of the other metals. Troost makes use of the comparatively small volatility of ZrO, at a very high temperature, to separate this oxide from SiO₂ (v. C. R. 116, 1428).

Zr is generally estimated as ZrO₂; salts of volatilisable acids are decomposed by heat; or solutions may be ppd. by NH₂Aq and the pp. washed, dried, and strongly heated.

Zirconium, alloys of. An alloy of Zr with aluminium is obtained in the preparation of Zr by reducing K₂ZrF₄ by Al (v. Preparation of Zirconium, No. 3). Mellis (Z. [2] 6, 296) obtained crystals having the composition ZrAl, (or perhaps Zr,Al,Si) by heating to whiteness a mix-ture of 1 pt. powdered zirconits with 5 pts. cryolite powder, 10 pts. mixed KCl and NaCl, and 1 pt. Al, treating with dilute HClAq, and separating the larger crystals of the alloy from the finer crystals of Si.

Zirconium, bromide of, Zrir. Formula probably molecular, from analogy of ZrCl. Obtained by mixing finely powdered ZrO, eugar charcoal, making into balls with starch paste, drying, and heating to bright redness in a current of dry CO₂ and dry Br (Mellis, Z. [2] 6, 296). ZrBr₄ is a white, microscopically crystalline, hygroscopic powder; it is easily volatilised; heated in H it is not reduced to a lower bromide. Contact with moist air or water paduces the oxybromide ZroBr,; evaporation of an aqueous solution gives the heptahydrate of this compound ZnoBr, TH, O in large needleshaped, transparent crystals (M., l.c.).

Zirconium, carbides of. By heating an in-

timate mixture of ZrO, and C in the electric arc, in an atmosphere of CO, Troost (C. R. 116, 1227 [1893] obtained a very hard, steel grey solid, approximating closely to the composition ZrC, By using less C, other carbides seem to be produced (cf. Moissan, C. R. 116, 1222), but analyses other compounds are not given. ZrC, dissolves easily in dible HFAq, but is not acted on by other toids. Moissan (l.c.) says that carbides of Zs containing more than 5 p.c. O (ZrC₂ contains c. 21 p.c. O) take fire fairly desily when exposed to the air; Troost says that carbides with a small proportion of O are only superficially oxidised by heating to redness, but that these with much Q burn brilliantly at that temperature.

temperature.
Zirgonium, chloride of, ZrCl., Mol. w. c. 2315. V.D. 117 at 440° (Deville a. Troost, P. 108, 636).

P. 105, 550).

Representation.—1. By heating Zr in Cl.—2. By heating an intimate mixture of ZrO, and Cl in Ch.—3.4. By passing vapour of BiOl, over heated ZrO, Troots a. Hattefeuille, C. B. 76, 1819).

Preparation.—A mixture of ZrO, with c. its own weight of lampblack is made into a paste with oil a little balls, c. the size of frazel nuits.

are rormed or ruis, and mese are covered with powdered charcoal, and heated to full redness in a closed ordeible until the oil is completely charred; the pellets are then heated to bright redness in a tube of hard glass, while, a current of dry Cl is passed through the tube, the ZrCl, which terms on the cooler parts of the tube is sublimed, in a stream of dry Cl, into a tube drawn out into bulbs, which are sealed off when

the operation is finished (v. Bailey, Pr. 46, 74).

Properties, Reactions, and Combinations. A white solid; volatilises unchanged at c. 400°. Dissolves in water, with production of heat; the solution on evaporation gives cayechorides (q.v.). Does not interact with sine ethica at 180° (Hinsberg, A. 239, 253). Combines with ammonia to form ZrCl, ANH,; with sodium chloride to form ZrCl, 2NaCl (Paykull, B. 6,

1467).

Zirconium, ferrocyanide of. According to Hornberger (A. 181, 232), the pp. formed by adding K.P.Cy.Aq to a solution of a salt of Zr, when washed and dried, has the composition Zr₃(FeCy₆)₂(?); it is a blue powder with a greenish tinge, insoluble in water, decomposed by acids, giving off HCN.

Zirconium, fluoride of, ZrF, Form bably molecular, from analogy of ZrCl, Formula pro-

Formation.—1. The hydrated compound Erf., 3aq is formed by slowly evaporating a solution of ZrO.H., or ZrF., in HFAq.—2. By heating ZrO. with twice its weight of (NH.)HF. to dull redness, till all the ammonium salt is

volatilised (Marignac, A. Ch. [3] 60, 263). Preparation.—Deville (A. Ch. [3] 49, 84) obtained ZrF, by heating to whiteness a mix, ture of finely powdered sirconite and fluorspare in a stream of HCl (? ZrSiO₄ + 2CaF₂ + 2HCl = ZrF₁ + CaCl₂ + CaSiO₃ + H₂O₃.

Properties and Reactions.—Prepared as de-

scribed, ZrF, is a colourless, transparent, crys. talline (probably hexagonal) solid; volatilisable at white heat; insoluble in water and acids.

ZrF, prepared by heating ZrO₂ with (NH₄)HF'₂
is said to be soluble in water and in dilute HFAq. The crystals of Zrf., 3aq are partially decomposed on drying. Heated to full redness in air, Zrf. gives ZrO. and HF.

Combinations.—1, With water (v. Formation, No. 1) to form Zrf., 3aq. -2. With various me-

tallic fluorides to form compounds of the form ZrF, xMF.yH.O. These salts are often calle zir, xmr.ym... these saits are often called sirono-fluorides, or fluo-sironates; they are better named sirconi-fluorides. The zirconi-fluorides have been examined chiefly by Marignac (4 Ch. [3] 50, 257); they are obtained sibbel by marignacy and solutions of solutions are either by gradual evaporation of solutions con-dining the constituent fluorides or by adding hydroxides or carbonates of the various metals to colutions of ZrF, in HFAq, and evaporating.
Ammonium zircon? fluorides. Tro

(NH.), ZrF., rhombic crystals, isomorphous with K.ZrF.; (2) SNH, F.ZrF., small octahedrs, showing simple retraction (Baker, C. J. 35,

oadmium simoni-fluorides. Two salts seem to exist: (1) 2CdF, ZrF, 6aq, monochinic crystals, isomos hous with the Mn salts? (2) CdF, 2ZrF, 6aq, laminar, fan-shaped groups of crystals.

Manganese sirconi-fluorides.

MnF, ZrF, 5aq; and (2) 2MnF, ZrF, 6aq.
Nickel zirconi-fluorides. (1)

(1) Mif-2rf, 6aq, hexagonal prisms; S.G. 2-227 (Topsös, C. C. 3, 76); and (2) 2Nif-Zrf, 12aq, monoclinic crystals. The first salt forms a double salt with K-Zrf, viz. NiZrf-K-Zrf, 8aq.

Potassium zircomi fluorides. (1) K_ZrF_a; obtained by strongly heating sirconite with two or three times its weight of KHF_a, boiling with very dilute HFAq, filtering from K.SiF, and allowing the filtrate to cool. from K.SiF., and allowing the filtrate to cool. Crystallises in rhombic crystals, terminated by six-sided pyramids; solubility. 78 at 29, 14 at 15°, 2.7 at 193, and 25 at 10°. S.G. 3.582 (Topse, Lc.); (2) KF.ZiF., aq (= KZiF., aq); obtained, in monoclinic crystals, by dissolving the preceding tall in water containing a large excess of ZiF. (3) 3KF.ZiF., [a, KZiF.]; obtained by crystallising K.ZiF., from a solution containing excess of KF; small, brilliant, regular octubedra, with simple refraction (n. Baker, C. J. 35, 762). Soluble in water; the hot come, solution deposits K.ZiF., on cooling. Sodium zirconi-fluorides. The salt 5NaF.2ZiF. is said to be always formed in

5NaF.2ZrF, is said to be always formed in whatever proportion the constituent fluorides

whatever proportion the constituent matrix are mixed. Small, monoclinic crystals; solubility at 18° = 38, and at 100° = 0. 1°6.

Zinc zirconi-fluorides. (1) ZnZrF, 6aq; isomorphous with ZnSiF, 6aq and ZnSnF, 6aq. crystallising in regular hexagonal prisms, easily crystallising in regular hoxagonal prisms, easily soluble in water. S.G. 2.255 (Topsöe, L.c.).
(2) 2ZnF₂ZrF, 12aq; deposited from a solution containing excess of ZnF₂, in monoclinic crystals, somorphous with 2NiF₂ZrF, 12aq. Zirconium, hydride of. By leating ZrO, and Mg powder, in the ratio ZrO₂2Mg, in an atmosphere of H, Winkler (B. 24, 888; of B.

23, 2666) obtained a black powder which burnt 23, 2666) obtained a black powder which obtain in O, and contained c. 73 p.o. H. On treating this with dilute HClAq, Mg and MgO dissolved, H being given off, and a black residue was left which W. regarded as ZrH., Supposing the reduction of the ZrO₂ had proceeded in accordance with the equation ZrO₂ + 2Mg + 2H = 2MgO + 2ZrH₂, the product would have contained 53·44 p.c. ZrH₂, and, therefore, would have given 1·15*p.e. H; as only '73 p.c. H was found, W. concluded that c. ½ of the ZrO₂ had been

reduced. Airconium, hydroxide of, (?) ZrO.H. Addition of NH,Aq to a solution of a salt of Zr produces a white, bulky, gelatinous pp. of ZrO...eH.O. According to Berzelius, the dry pp. has the composition ZrO.H.O. ZrO.H., Hermann (J. pr. 97, 318) gave the formula ZrO.2H.O. ZrO.H. to the pp. driedwisti7.5°; Paykull (B. 12, 1719) to the pp. dried at 17.5°; Paykull (B. 12, 1719) said that after drying in vacua, the composition was \$7.0.3H_0. and after drying at 1009 YZrO_H_0...A detailed examination of the dehydration of the pp. formed by adding NH_Aq to a cold solution of Zr(90), was made by Carnelley a. Walker (U. J. 53, 48, 82 [1888]). The loss of water by the air-dried pp. was fairly regular to c. 90°, when the pp. had approximately the composition ZrO_2H_0; the loss was then less rapid, but very regular, up to c. 385°, whereat the composition was approximately 2ZrO_H_0; the composition was approximately 2ZrO, H.O; somewhere between 385° and 415° there was a sudden increase in the percentage loss of water

for a rise of 10°, this increase being accompanied by a change of colour from grey to pure white; at 415° the composition was approximately 24ZrO₂.H₂O; water was then given off very fegu-larly, until at c. 550° dehydration was completed. C. a. W. conclude that probable to definite hydrate of ZrO, unchanged throughout a fair range of temperature, is formed by heating ZrO.xH2O ppd. from a salt of Zr; theyothink that the change of colour which accompanies the comparatively large percentage loss of water at c. 400° is an accompaniment of a condensation of molecules chiefly of the composition $n(2ZrO_2.H_2O)$ to inclosures chiefly of the composition $n(24ZrO_2.H_2O)$. There's, a distinct resemblance between the phenomena of the de-hydration of ZrO₂xH₂O and those of the dehydration of SiO₂xH₂O, SiO₂xH₂O, and TiO, xH,O.

Hydrated ZrO2 ppd. cold, and washed with cold water, dissolves easily in the ordinary acids, including oxalic acid (Bailey, C. . 49, 481), forming salts ZrX1, and ZrX11, when ppd. hot, or washed with hot water, the pp is only slowly dissolved by the ordinary acids. According to Paykull (B. 12, 1719), moist ZrO...xH.O absorbs produces basic sulphates 3ZrO_x4SO₃. 15aq and 6ZrO_x7SO₃, 19aq \(\frac{P}{L}\), \(\lambda c.\), \(\lambda c.\)
ZIRCONATES. \(\frac{ZrO_x \text{C}_1}{L}\) behaves as a weak

acid towards the stronger bases. A few salts have been prepared which are most simply rogarded as derived from $Zr(OH)_x$ by replacing II by alkali and alkaline earth metals; these y analy a reconstruction of the state of the

= Na₂O.ZrO₂); obtained by heating ZrO₂ with Na₂CO, in the ratio ZrO₂:Na₂CO₃; the crystalline mass thus formed is gradually decomposed by water with separation of amorphous ZrO₂. (2) Na₄ZrO₄ (=2Na₂O.ZrO₂); obtained by heating ZfO₂, with a considerable excess of Na₂CO₃ to whiteness for a considerable time; decomposed by water, with formation of (3) Na2O.8ZrO2. 12aq, which forms hexagonal tablets.

Zirconates of calcium and magnesium were obtained by H (l.c.) by heating to reduess mix-tures of ZrO, with SiO, and CaCl, or MgCl, Ouvrard (C. R. 112, 1444 [1891]) describes lithium zirconate, Li,ZrO, obtained by fusing ZrO, with LiCl, and cooling slowly; when Li,CO, was used, and the fused mass was treated with boiling water containing a little acetic acid, pure

ZrO, remained.
Zirconium, nitride of.. In fusing amorphous
Zr with Al, in a cracked little crucible, Mallet (Am. S. [2] 28, 346 [1858]) obtained a dark-grey, porous solid, which gave yellowish luctrous microscopic cubes wher treatel, with HClAq; the crystals wife unchanged by aqua replace alkali solutions; when fixed with KOH they gave off NH. The yellow crystals were probably a nitride of Zr.

Zirconium, oxides of. Besides zirconia, ZrO., there exists a higher oxide, probably ZrO,; and, possibly, also a lower oxide (?) ZrO.

ZIRCONIUM DIOXIDE ZrC., (Zirconia. Zirconic anhydride.) Mol. w. not known.

Proparation.—There are many methods for

preparing ZrO, from Urgonite. 1. The mineral is fleated to redness and thrown into water, and the least-coloured pieces are finely powdered and levigated; the powder is very strongly heated with four times its weight of Na₂CO₃, in a Pt orucible, and the product is heated with excess of HClAq; the whole is evaporated to dryness; of Hold; the whole is evaporated to dryness; the residue is digested with water, filtered from SiO₂, and ZrO₂xH₂O is ppd. by NH₂Aq. The pp. is washed and dissolved in Hold, and the solution is nearly saturated with Na₂O₂, and boiled with Na₂S₁O₂Aq as long as SO₂ is given off, whereby ZrO₂xH₂O is ppd. (Berzelius, P. 4, 124; 8, 186; Hermann, J. pr. 31, 77; Chancel, A. 108, 237; Stromeyer, A. 113, 127).—2. Very finely powdered sigconite is boiled with conc. High powdered successes is bosted with water and dried; 100 g. of the dried powder are added to 400 g. molten NaOH, with which 20 g. NaF have been mixed, and the whole is heated in a nickel crucible until the action ceases, when the molten mass is pouled on to a sheet of nickel, and, after solidification, is plunged into water; the portion insoluble in water is dissolved in HClAq, the solution is evaporated to dryness, and treatment with HClAq and evaporation to dryness are repeated several times to remove SiO, and HF. The solution in HClAq is then ppd. by NH, Aq; the ZrO, xH,O is thoroughly washed by decantation, dissolved in the smallest possible quantity of cone. HClAq, and the solution is evaporated to fryness: the residue is washed in a funnel with conc. HClAq mixed with 4 pts. of alcohol; the washed solid Inixed with 4 pis. 62 alcohol; the washed solid is then repeatedly orystallised from cond. HClAq. The white, lustrous crystalls of ZrOCl_xxH₂O hus obtained are dissolved in water, and ZrO_xxH₂O is ppd. by NH₂Aq (Venable, C. N. 64, 315 [1891]; cf. Bailey, Pr. 46, 74 [1889]; cf. Preparation of Zirconium, p. 893). By heating ppd. ZrO₂xH₂O to c. 150°, ZrO₂ is obtained tained.

Crystalline zirconia is obtained from the amorphous form (1) by fusing with borax at a very high temperature, and washing with HClAq (Nordenskijold, P. 114, 612; Knop, A. 157, 363); (2) by fusion with microcosmic salt (K., l.c.);
(3) by heating to dull redness in dry HCl at a pressure of three atmospheres (Hautefeuille a. Perrey, C. R. 110, 1038); (4) by melting and volatilising in an electric furnace, using a current 360 ampères and 70 volts (Moissan, C. R. 116, 1232 [4893]); (5) by heating, to dull redness, a salt of Zr with an acid that can be removed by heating, in a current of dry HCl (H. a. P., l.c.).

(H. a. P., l.c.).

Properties.—Amorphous zirconia is a white, tasteless, chodorous powder; S.G. c. 5% insoluble in adds, except in conc. H.SO, (v. Beactions, No. 7) or HFAq. Crystalline zirconia is a transparent, colourless solid; S.G. 5-1 (Moissan, Lc.), 5-42 (Knop, Lc.), 5-7 (Nordenskjold, Lc.). The crystals are desoribed by N. (l.c.) as quadratic prisms, isomorphous with SnO₂ (tinstone) and TiO₂ (rutile). The crystals are extremely hard; they soatton class easily SnO_c (tinstone) and ThO_c (ruttle). The crystals are extremely hard; they so that had see easily (Moissan, Lc.). It is generally said that when ZrO_c is heated to incipient redrises it glows brightly, and becomes denser but the experiments of Carnelley a. Walker (C. J. 58, 82 [1888]) on the action of heat on ZrO_c Eligon

make it probable that the glowing is an accompaniment of the dehydration from approximately 2ZrO₂,H₂O approximately 24ZrO₂H₂O. Zirconia reacts towards acids as a basic oxide, forming salts ZrX^{I} , and ZrX^{II} . (many of which are basic salts); it also decompose alkali care bonates and some other alkali and alkaline earth salts, when fused therewith, forming zirconates mZrO, nM, O (v. Zirconates, p. 896).

Reactions.—1. When ZrO, is heated to a very high temperature it melts, boils, and vola tilises, condensing in crystals; Moissan (C. R. 116, 1222 [1893]) effected the volatilisation in crucible heated in the electric furnace, using a current of 300 ampères and 70 volts.

2. When very strongly heated with excess of carbon, carbides are formed (v. Carbides, p. 894). Heating in a carbon crucible in the electric furnace produces Zr (M., l.c.) 3. Heating with magnesium produces Zr, perhaps also an oxide lower than ZrO₂ (Winkler, B. 23, 2642; 24, 888; Phipson, pr. 96, 353; Bailey, Pr. 46, 74; cf. Zirconium monoxide). When heated with magresium in an almosphere of hydrogen, some ZrH₂ is perhaps produced (v. Zirconium hydride, p. 895).—4. ZrCl₄ is formed by heating ZrOs mixed with carbon in a stream of chlorine; using bromine produces ZrBr, (v. Bromide and tusing oromine produces Zini, by Somme and Chloride, pp. 894). — 5. ZrF, is formed by heating ZrO? to dull redness with excess of ammonium flyoride. — 6. K.ZrF, is formed by ammonum provide.— o. R.267; is formed by slightly heating ZrO₂ with excess of polassium hydrogen fluoride, boiling with very dilute HFAq, and filtering.—7. Zr(SO₂)₂ is obtained by heating ZrO₂ with excess of a mixture of 2 pts. conc. subphuric acid and 1 pt. water.

ZIRCONIUM PEROXIDE. By adding H.O.Aq and NH2Aq to a solution of Zr(SO₁), Cleve (Bl. [2] 43, 53) obtained an oxide containing more Othan ZrO₂; to this oxide he gave the formula ZrO₃. Bailey in 1886 (C. J. 49, 149, 481) czamined the pp. obtained by adding H₂O₂Aq to solution of Zr(SO₄)₂; according to B., the moist pp. has the composition Zr,O,, and this composition is unchanged after keeping (moist) for some months. In Bailey's paper in 1889 (Pr. 46, 74) he gives the composition ZrO, 3H, O to the oxide ppd. by H₂O₂Aq, either from an acid or an alkaline solution of Zr(SO)₁, after drying over P₂O₂; and the composition ZrO, after drying at 100°. The oxide ZrO, 2H₂O was obtained (C. J₄ The oxide ZrO, 2H,O was obtained (C. J. 100°. The oxide ZrO, ZH,O was obtained (C. J. 49, 485) by preparing a solution of Zr(SO), by heating K,ZrF, with H,SO,, and at once adding H,QAq. Zr peroxide is insol. in very dilute (1 p.c.) H,SO, Aq or HC,H,O,Aq (B., Lc.). Bailey (Lc.) employed the pan. of ZrO, zH,O to separate Zr from Fe, Nb, and Ti.

Mg by treatment with dilute HClAq, washed with nnauy with ethergand dried in vacuo. He thus obtained a deep-black powder, which was unacted on by HClAd, HNO, Ara or H, SO, A. even on warming, a: I which burnt to ZrO, when heated in air. W. supposed this black powders to be ZrO. Yor. IV. water containing HCl, then with alcohol, and

Zirconium, oxyacid of. Hydrated airconia, ZrO, xH.O, reacts as a weak soid towards strong bases (v. Zirconates, p. 896).

Eircenium, oxybromide of, ZrOBr_xH_O.

ZrBr, dissolved in water; on evaporation, transparent needle-shaped crystals are formed, to which Mellis (Z. [2] (2.296) gave the composition ZrOBr_7H_O. Bysissolving ZrO_xrH_O in HBrAg and evaporating, Weibull (B. 20, 1394 [1887]) obtained lustrous needles of ZrOBr_8H_O, isomes Block with ZrOCI 8H, COCI. 8H. isomorphous with ZrOCl, 8H O.

Zirconium, oxychlorides of. Zirconium, oxychlofides of. Various oxychlofides have been described. (1) ZrOCl_xxH₄O; prepared by dissolving ZrO_xxH₄O in HClAq and evaporating (10) details as to the best conditions v. Weibull, B. 20, 1394). Hermann (J. pr. 81, 77) gave the formula as ZrOCl₂9H₄O; Mellia (Z. [2] 6, 296) gave 2ZrOCl₂9H₄O; and Weibull (L.c.) ZrOCl₂8H₄O (c. also Paykull, B. 6, 1467; and Bailey, Pr. 46, 74, (2) Zr₂OCl₂; prepared by Troost a. Hautefeuille (C. R. 73, 563) by passing steam and vapour of ZiCl₄ through a red-hot tube. (2, 2Zr₂O₂Cl₂15H₄O; prepared by Ende-Various oxytube. (3) 227.0,Cl.,15H.0; prepared by Endemann (J. pr. [3] 31, 219) by adding ether to a warm alcoholic solution of ZrOCl., xH.0.

Zirconium, expiodides of By adding the calculated weight of Bal, in solution, to Zr(SO;) dissolved in a slight excess of H.SO, Aq, filtering, evaporating over H.SO,, any removing free I from the residue by CS, Hinstory (4. 239, 253 [1887]) obtained a white, amorphous powder, easily soluble in water, giving off I in moist air to which he gave the formula ZrIO, H, xH,O (x probably = 3).

Zirconium, oxysulphide of; v. Zirconium BULPHIDES (infra).

. Zirconium, salts of. The salts formed by the replacement of H of acids by Zr belong to the forms ZrX," and ZrX,; many basic salts are known. The following are the chief salts of are known. Zr derived from oxyacids: Arsenates, borates. carbonates, nitrates, oxalates, phosphates, selen tes, silicates, sulphates, and sulphites.

Zirconium, silicofluoride of, (?)Zršif, probably obtained by Berzelius by evaporating a solution (? of ZrO_xHI_O in H_Sif_sAq) (v. Lehrbuch, 3, 505 [5th ed.]).

Zirconium, sulphides of. According to Berzelius (v. Lehrbuch, 2, 189 [5th ed.]), a compound of Zr and S is formed by heating the clements together in vacuo, or with H. compound, to which no formula is assigned, is compound, to which in lothing is assessed of described by B. as a dark-brown coloured powder; unacted on by H.SO.Aq. ISNO.Aq. or HClAq; slowly attacked by boiling apua regia; dissolved easily by HFAq, giving off H.S.; insol. in KOHAq, and decomposed by usion with KOH to K.S and ZIRCONIUM MONOXIDE (7) Zrd. By heating ZrO. By strongly heating ZrO, in vapour of ZrO, and powdered Mg, in the ratio ZrO. Mg, in CS., Rremy (A. Ch. [3] 38, 326 [1863]) obtained a stream of H, Winkler (B-23, 2668 [1890]) by a graphite-like solid, which was rapidly acted tained a black powder, which he allowed to cool on, by HNO, Aq. with separation of S; Fremy in H, then kept for some time in CO, free from supposed that the substance might be an oxysulphide.

Zirconium, sulphocyanide of a By adding Ba(SCN), to Zr(SO₄)₂ solution, Hornberger (A. 181, 232 [1876]) obtained a solution which, he said, contained Zr(SCN),; this solution quickly

M. M. P. M.

ADDENDA

[DESCRIPTIVE ENORGANIO CHEMISTRY ONLY.]

ALUMINIUM (vol. i. p. 141). Preparation .-By electrolysing a molten mixture of All'₃.KnaF with NaGl (Minet, C. R. 111, 603 [1890]). The best results are obtained by using the salts in the ratio AlF₃.SnaF.6NaCl; details of the quantities are obtained by using the salts. tities to be used, the strength of current, &c., are

Properties.—Minet (C. R. 111, 603 [1890]) gives m.p. of Al as 675°; and S.G. at 820° as 1.76. The S.H. of Al is given by Richards (C. N. 65, 97 [1892]) as 224 at 20°, 232 at 100°, and 2845 at the m.p. = 625°; the S.H. of molten Λl at $650^\circ = 308$, according to Pionthon (C. R. 115, 162 [1892]). The molecule of Al in dilute'soluat 1892 = ove, according to the field [1892]). The molecule of Al in dilute solution in tin is perhaps diatomic (Heycock a. Neville, C. J. 57, 376 [1890]).

Reactions.—Volatilises in electric furnace,

with current of 250 ampères and 70 volts (Moissan, C. 12. 116, 1429 [1893]). Not appreciably acted on by NO₂ at 500° (Sabatier a. Senderens, C. R. 115, 236 [1892]). An amalgam senterens, C. L. 113, 230 [1892]). An amalgam is formed by bringing Al into a solution of a mercuric salt (Klaudy, C. C. 1893 [1] 201; abstract in C. J. 64 [11] 376 [1893]). Heated with NaPO₃ in a current of H, from 28 to 31 p.c. of the P distils over ; P is also obtained by heating Al with any phosphate of Ca or Mg (Rossel a. Frank, B. 27, 52 [1894]). According to Lunge (C. N. 65, 110 [1892]), vessels made of Al may be used for holding articles of food, at least at the ordinary temperature, without danger of the metal being dissolved; this result is confirmed by Balland (C. R. 114, 1536 [1892]).

Aluminium, alloys of (vol. i. p. 143). alloy with gold, Al, Au, v. Heycock a. Neville (C. J.

65, 74 [1894]).

Aluminium, chloride of (vol. i. p. 144). Nilson a. Pettersson (Z. P. C. 4, 206 [1889]) made a number of determinations of the V.D. of "AlCl₃; they find that the compound gradually metal. The reactions of liquid NH₃ with CrC dissociates above its b.p. until c. 800°, when its and FeCl₃ are described by Christensen (Zeit. V.D. becomes constant and corresponds with the anong. Electric, 4, 227; abstract in C. J. (211, 480 (1992)) formula AlCl₂. AlCl₃ may be prepared by heating an alloy of Al and Cu-alcarly to redness in dry an aloy of Al and Ol-learly to redness in dry HCl; AlCl, distils over unmixed with any Cu compound (Mabery, B. 22, 2658 [1889]). Sabatier (Bl. [8] 1, 88 [1889]) says that crystals of the hydrated chloride after being in vacuo fog three months at 20° over H₂SO, have the composition AlCl, 6H,O. AlCl,.6H,O.

AlCl. 6H.O. Aluminity, oxides of (vol. i. p. 146). By heating Al.O. with Mg, in the ratio Al.O. Mg, Winkler (B. 93, 780 [1890]) obtained a brownish-black powder which, he says, contained a considerable quantity of an oxide lower than Al.O., probably AlO. By the incomplete combustion of Al, Pionchon obtained a dark grey powder, said by P. to have the composition Al, 0, = 2Al, 0, Al, 0 (C. R. 117, 328; abstract in C. J. 64 [11] 572 [1893]). By heating amorphous Al, 0, to in-

cipient redness in HCl gas at a pressure of three ethen reduces in He ages as a prosent contact at most, Hautefeuille a Perrey (C. R. 110, 1038 [1890]) obtained crystals of corundum. According to Read (C. J. 65, 313 [1894]), Al₂O₄ is unchanged at c. 1750°.

Aluminium, phosphide of (vol. i. p. 146). A grey crystalline powder, Al, P, was obtained by Rossel a. Frank (B. 27, 52 [1894]) by heating Al in vapour of P, and then heating the product

till P ceased to come off.

AMMONIA (vol. i. p. 196). Formation.— According to Loew (B. 23, 1443 [1890]), traces of Nfl, are formed by shaking Rt black with very dilute NaOHAq in the air. NH, is also formed dilute NaOFAq in the air. NH, is also formed by the combined action of Pt black and dextrose

on KNO₃Aq (L., l.c., p. 675).

Properties.—Ludeking a. Starr (Am. S. [3] 45, 200 [1892]) give S.H. of liquid NH3 as 8857. For measurements of the wave-lengths of the lines in the emission spectrum of NH, v. Mag-Incs in the emission spectrum of Mily v. mag-nanini (Z. P. C. 4, 435 [1889]). Perkin (C. J. 55, 689, 728 [1889]) gives M. M. of NH, in Aqueous and alcoholic solutions; also Mol. R. of various NH, salts in solution. Tables showing the solubility of NH, in alcohol of various conbentrations, at 10°, 20°, and 30°, are given by Delépine (J. Ph. [5] 25, 496; v. abstract in C. J. 62, 1049 [1892]). For the freezing-points of aqueous solutions of NH₃ v. Pickering (C. J. 63, **181** [1893]).

Reactions.—Dry NH, does not combine with dry hydrogen chloride when these gases are mixed (Baker, C. J. 65, 611 [1894]). Nor do dry NH, and dry carbon dioxide combine (Hughes a Soddy, C. N. 69, 138 [1894]). Michel a. Grandmongin (B. 26, 2565 [1893]) say that the products of passing NH, over heated peroxide of Ba, Pb, Mn, or No, are N with a little HNO, and HNO, and oxide or hydroxide of the metal. The reactions of liquid NH₂ with CrCl

anong. Chemie, 4, 227; abstract in C. J. 64 [11] 459 [1893]). AMMONIUM COMPOUNDS (vol. I. p. 200). Ammonium amalgam (50l. i. p. 201). From measurements of the polarisation given by this ubstance in a solution of NH Cl against zino amalgam, and a comparison of these measurements with the polarisations given by metallic analgams, Le Blanc concludes that ammonium amalgam really exists (Z. P. C. 5, 467; abstract in C. J. 58, 1204 [1890]).

Ammonium chloride (vol. i. p. 202). Baker dC. J. 65, 611 [1894]) asserts that the V.D. of the dry salt at 350° is 28.7, corresponding with that sequired by the formula NIECL. B. also says

that no reaction occurs when dry NH Cl and dry CaO are heated together.

ANTIMONY (vol. i. p. 282). Reactions.—
Montenattini (G. 22, 384, 426) finds that no

appreciable quantity of NH, is formed byothe! interaction of Sb and HNO, Aq varying from 2 to 70.3 p.c. HNO₃; NO₂ is practically the only gaseous product of the reaction; when 70 p.c. HNO, Aq is used, the residue probably has the composition (SbO)NO3.

Artimonates (vot. i. p. 285). Several salts have been prepared by double decomposition from the K salt, by Beilstein and O. v. Biase (C. C. 1889, 803; abstract in C. J. 56, 1123). All the compounds are salts of $HSbO_3$; R. a. 1. conclude that the only well-marked antimonates are derived from this acid. Ebel (B. 22, 3011

[1889]) describes several metantimonates.

Antimonites (vol. i. p. 285). For antimonites of K and Na v. Corminba uf (C. R. 115, 1305; abstract in C. J. 61 (11', 171 (1893').

Antimony, bromid of (vol i. p. 286). The b.p. of SbBr, is given as 275° by Freyer a. V. Meyer (Zeit. f. amorg. Chemic, 2, 1 [1892]).

Antimony, trichloride of (vol. i. p. 286).

Boils at 283° (Freyer a. V. Meyer, Lc.).

Antimony, pentachloride of (vol. i. p. 287). The V.D. at 218° and 58 mm, pressure was found to be 1447 (corresponding with the formula SbCl₃) by Auschütz a. Evans (.1, 253, 95 (1890.). Double compounds of SbCl, with 1664 and CsCl are described by Saunders (.1m. 14, 152 [1892]), and by Wheeler (.1m. S. [3] 46, 269 [1893]).

Antimony, fluoride of (vol. i. p. 287). The double compound ShF₃.2AmF is described by H. von Helmholt (Zeit, f. anorg. Chemie, 3, 115 [1893])

Andmony, hydride of (vol. i. p. 288). temperature whereat decomposition of SbH, begins is given by Brunn (B. 22, 3202 [1883]) as c. 150°. For the reactions of SbH, with AgNO Aq v. Vitali (abstract in G. J. 6 111], 206 (1893).

Antimonic exide (vol. i. p. 290). When heat d to dull redness Sb₂O₂ gives off O₂ forming Sb₂O₄, which at c. 1750 is further reduced to Sb.O. (Read, C. J. 65, 313 [1891]).

Antimonious sulphide (vol. i. p. 291). Black Sb.Sa is formed, according to Mitchell (C. N. 67, 291 [1893]), by passing CO, into hoiling water with ordinary Sb.S, in suspension. Picton (C. J. 61, 142 [1892]) obtained a colloidal Sb S_J in very fine suspension in water, by allowing solution of tartar emedic to flow into saturated

H₂SAq. Antimony thio-chlorides and thio-indides of (vol. i. pp. 292-3). Ouvrand (C. J. 116, 1516 (1893) describes SbSCl and Sb₄S Cl., obtained by the action of H.S on SbCl_s; and SbSl formed by heating SbI_s to 150° in dry H₂S, and Sb₂S_sI_s formed by heating Sl₂S_s with I and crystallising from CS.

• ARSENIC (vol. i. p. 301). A full account of the different forms of As obtained, along with As O_B by subliming As in a tube is given by Retgers (Z. P. C. 4, 403; abstract in U. J. 44 [11], 570 [1893]). Petersen gives the following heats of oxidation, and stomic volumes, of the allotropic forms of As (Z. P. C. 8, 601 [1891]):—

At whime •[As²,0`] \$56,830 Grey, rhom hedric Grey-black, amorphous 154,840 Brown, amorphous 163,500 163,500 . 15.99

Arsenic, bromide of (vol. 1, 309). AsBr. combines with NII, to form AsBr., 3NH, (Besson, CoR. 110, 1258 [1890])⊾

Arsenates (vol. i. p. 307). For arsenates of Cd v. A. de Schulten (Bl. [3] 1, 473 [1889]); for arsenates 36 Cu, and of Cu and Na, v. Hirsch (C. C. 1891 [1], 15; abstract in C. J. 60, 6441; many double agreement of K, and of Na, with Cd. Co, Mg. Mn. Ni, and Zn are described by

fevre (C. R. 110, 405 (1890)). For this arsenates of Cn. Hg. Zn; and Zn and

Na, v. Preis (A. 257, 178 (1800)). Arsenites (vol. i. p. 306). For the preparation, by double decomposition from the salt 2KASO As O and proporties, of the arsenites of the following metals v. Reichard (B. 27, 1019 [1894]):—Al, Ba, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Hg, Ni, Pd, Pt, Ag, Sr, Sn, Ti, U, and Zn (references and criticisms of former investigations are given). Stavenhagen (Zeit. f. angew. Chemie, 1891, 165) obtained the double salt of Kaysenite and sulphate, KASO, 10K SO, by evaporating solutions of the constituents after mixing.

Arsenic acid (vol. i. p. 307). For a detailed account of the reaction of H S with solutions of H.A.O. v. Brauner a. Tomeetchek (C. J. 53, 145. [ISSS].

Arsenious chloride (vol. i. p. 310). According to Besson (C. R. 109, 519 [1880]), AsCl. solidifies at -18°, forming white meedles; at - 30 'AsCl, absorbs much Cl, forming a liquid which does not solidify at 60°, and which with water gives off much Cl and forms As,0,Aq. Besson (C. R. 110, 1258 [1890]) says that the compound formulated by Rose as 2AsCl, 7NH, is really AsCl. 4NH

. Arsenious fluoride (vol. 7, p. 310). Moissan (4. Ch. [6] 19, 280 [1891]) prepared AsF, by heating As₂O₄ with HF; he gives b.p. as 63° at 750 mm., and says that it solidifies to white crystals at -8.5°. Besson (C. R. 110, 1258) [1890]) describes the compound 2AsF₃.5NH₂.

Arsenic, trihydride of (vol. i. p. 310). Brunn (B. 22, 3202 [1889]) finds that the first products of the action of air, or O, on AsH, are solid nAsH and H.O, and the next products are As mast and H.O. AsH, and the next products are As and H.O. AsH, and H.S. do not react in absence of air as the ordinary temperature either as gases or in solution (B., L.c.). AsH, begins to decompose at c. 230° (B., L.c.). For the reacons of AsH, with AgNO,Aqv. Vitali (abstract in C. J. 64 [11] 206 [1893]).

Arsenious iodifie (vol. i. p. 311). (C. R. 110, 1253 [1890]) describes the compounds AsI, 4NH, and AsI, 12NH.

Arsenious sulphide (vol. i. p. 315). Picton (C. J. 61, 140 114 [1892]) obtained an aqueous solution of colloidal As.S., containing also some very finely divided sulphide in suspension, by allowing As.O. eq to flow into saturated H.S.Aq, into which H.S. was columnally bassing, and re-

moving H.S by a stream of H.

Arsenic pentasulphide (sol. i. p. 315) As₂S, is obtained, according to McCay (Am. 12, 547 [1891], by passing H.S for a long time into a het solution of an alkali dihydrogen arsenate,

and then ppg. by a mineral acid.

Armanic, thiochlorides and thio-iodides of (vol. i. p. 316). Olivard (C. R. 116, 1516 [1893f] obtained As,S,Cl, by passing H.S into

AsCl., and washing the pp. with CS. By heating 1 pt. As.S., with 10 pts. AsCl. to 150° he obtained AsSCl. AZO-IMIDE (v. Hudrazoic acid. p. 219. Addenda).

BARIUM (vol. i. p. 440). Richards, in 1893, riade an elaborate experimental revision of the at w. of Ba (P. Am. A. 28, 1; 29, 55). As a mean result of the most trustworthy experi-

ments, R. adopts 137 1 as the at. w. 7 Ba (O=15.96). Limb (C. R. 1'2, 1434 [1891]) failed to obtain any Ba by electrolysing fused

Bacl₂, or Bacl, mixed with NaCl.

Barium, carbide of. By heating a mixing of Ba amalgam and powdered charcoal in H, Maquenne (C. R. 114, 361 [1892]) obtained grey

maquenne (C. R. 114, 301 [1892]) obtained grey BaC₂; decomposed by water, giving BaO₂H.Aq and C₂H₂; v. also Moissan, C. R. 118, 683 (abstract in G. J. 66 [1], 314 [1894]).

Barium, chloride of (vol. i. p. 441). By bringing BaCl₂ into contact with liquid NH₃, and allowing the gas to escape at 0° and 760 mm.

Joannis obtained BaCl₂:8NH₃ (C. R. 112, 337 [1801])

Barium, fluoride of (vol. i. p. 441). BaF, is obtained in microscopic crystals by adding wall, Aq (3.6 p.c.) to beiling KFAq (1 p.c.), boiling, washing, drying, and heating strongly (Moissan, BL. [3]5, 5, 152 [1891]). Poulence (C. R. 116, 987 [1893]) obtained BaF, in well-

formed octahedra by fusing amorphous BaF, with KHF, and KCl. Barium, nitrides of. Maquenne (C. R. 114. 220 [1892]) obtained a mixture, probably containing some Ba,N,, by heating Ba amalgam to reginess in a current of N. Berthelot a. Matignon

(A. Ch. (7) 2, 144 [1834]) say that BaN, is formed

by heating AmN_sAq with BaO₂H_sAq.

Barium monoxide (vol. i. p. 442). BaO is unchanged at c. 1750° (Read, C. J. 65, 313 [1894]); it liquenes at c. 2,000°, but is not decomposed at c. 2,500° (Moissan, C. R. 115, 1034 (1894)).

1034 [1892]).

Baium dioxide (vol. i. p. 443). BaO₂ is decomposed by salts of Al, Cr, Co, Fe, &c.; some " valts -e.g. those of Ca, Li, K, Na-do not react with BaO, (v. Kwasnik, B. 25, 65). For decomposition of BaO, by heat v. Le Chatelier (C. R. 115, 654; dostract in C. J. 64 [11], 71 [1893]).

BERYLLIUM (vol. i. p. 504). Krüss a. Moraht (B. 23, 727 [1890]) obtained hexagonal crystals of Be, mixed with BeO, by heating BeF_2KF to redness with Na., K. a. M. (l.c. p. 2552) obtained the value 9.03 for the at. w. of Be by

converting BeO into BeSG. 4H.O, and this again to BeO. Gibson (C. J. 63, 909 [1893]) describes

to Bec. Groson (C. J. 5., 909 [1993]] describes methods for preparing BeC from herpt.

Beryllium, fluoride of (vol. f. p. 506). Peterser (E. F. C. 5, 203 [1890]) gives the thermal 'ata H. J. [BeO*H*2HFAq] = 19, '83. The delible compound BeF, 'AmF is described by H. von Malwholt (Zeithern C. Chemic 2, 115 (1893)). compound BeF., AmF is described be to volume the limbol (Zeit. J. anorg. Chemie, 3, 115 [1893]).

Beryllium, oxide of (vol. i., p. 506). By dissolving BeO, xaq in KOHAq, Krüss a. Moraht (B. 23, 727 [1890]) chained potassium beryllate BeO, K. [?], mixed with K, CO, as a snow-white, allky solid.

BISMUTH (vol. i. p. 509). The at. w. of Bi was re-determined by Cla.sen in 1890 (B. 23, 928 [1890]), by converting Bi into nitrate and

988 [1890]), by converting Bi into nitrate, and

this into Bi O.; the Mean result was 20030 (O=15-96). Schneider (J. pr. [2] 42, 558; 44, 23 [1891]) criticises Classen's results and maintains that Marignac's value (almost exactly 208) is as trustworthy as that obtained by C. The

molecule of Bi in dilute solution in tin is perhaps diatomic (?) (Heyrock a. Nevill , C. J. 57, 376 [1890]).

Preparation.—Classen (l.c.) says that pure Bi is best prepared by electrolysing a solution of the enetal in HNO, Aq, using a cone of Pt as the negative electrode, then washing with alcohol, and fusing with KCy.

Properties.—Melts at 264°, according to Classen (l.c.): at 269 22°, according to Callendar a. Griffiths (C. N. 63, 1 [1891]). S.G. 9.7474 (C., l.c.; no temperature given'; 9.787 at 0. 9.673 solid at the m.p., 10.004 liquid at the m.p. (Vicentini, Rend. Acad. Lincci, 6 [11], 121, 147 [1891]). For S.G. of liquid Bi from 235° to 280°

v. Cattaneo (Rend. Acad. Lincei, 79 [11], 88 [1892]). For electrical resistance v. E. v. Aubel (C. R. 108, 1102 [1889]). Reactions .- According to Veley (Pr. 48, 458

Reactions.—According to valoy (Pr. 48, 438 [1891]), Bi does not dissolve in 30 p.c. HNO,Aq at 30° if HNO₂ is absent; but Bi dissolves readily in 1 p.c. HNO,Aq.

Bismuth, bromide of (vol. i. p. 511). BiBr. boils at 453° (V. Meyer, A. 264, 122 [1891]). Cavazzi a. Tivoli (G. 21 [11], 306 [1892]) describe a lustrous, black, hygroscopic solid, PBrH(BiBr2)3,

nistrous, black, hygroscopic soind, 1 Brit(BiBr₂), obtained by silowing BiBr, to fall gradually into PH, (abstract in C. J. 62, 279).

Bismuth, chloride of (vol. i. p. 512), Boils at 485°-441° (uncor.) (V. Meyer, I.c.). The only decuble chloride of Bi and K of those hitherto described that exists is BiCl, 2KCl. 2aq, according to Brigham (Am. 14, 164 [1892]). B. has also prepared BiCl₃.KCl. aq. Bismuth, fluoride of (vol. i. p. 512).

Helmholt describes the double flue ride BiF. AmF

(Zeit. f. anorg. Chemic, 3, 115 [1893]).

Bismuth, iodide of (vol. i. p. 513). Astre
(C. R. 110, 525 [1890]) obtained the double iodide 2Bil, KI by keeping I, KCl, Bi, and water in contact for some weeks, and then crystallising from Et acetate. Bismuthous oxide (vol. i. p. 513). Classen (B. 23, 938 [1890]) gives S G. as 9 044. Read (C. J. 65, J13 [1894]) found Bi₂O₂ to be unchanged

at c. 1750°. of Bismuth, oxysulphide of (vol. i. p. 516). By bassing dry H.S into boiling benzene containing Bi₂O₃ ire suspension, P. v. Scherpenberg (C. C. 1889. [11] 643) obtained Bi₂O₃S. Bismuth, selenide of (vol, i. p. 5-6). The double compound Bi,So, K,Se is described by P.

v. S. (l.c.).

Bismuth, sulphide of (vol. i. p. 516). S.,(l.c.) obtained the double compound Bi,S,.K,C by fusing Bi,O, with K polysulphide.

by fusing Bi_oO, with K polysulphide.

BORON (vol. i, p. 524). The at. w. of B has been determined by Abrahall by the analysis of BBr₂ (C. J. 61, 650 [1892]); the value obtained was 10 67 (O = 15/96). Also by Ramsay a. Aston (C. J. 63, 207 [1893]), by funding the perceltiage of water in crystalises borgx, and by distilling fused borax with HClAqa, d.CH., OH and weighing the residual NaCl; the values varied about 11, but showed considerable differences.

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Rimbach 4B. 26, 164 [193]), by titrating elutions of horax with standard HClAq, using methyl orange as indicator, obtained the salue of 10-91 (0=15-96). The following values for S.H. of amorphous B are given by Moñsan a. Gautigr (Co. R. 116, 924 [1893]): 0° to 100°=3066, 0° to 102°=3407, 0° to 234°=3573. For atomic refraction of B v. Ghira (G. 23 [1], 452; sostract in C. J. 64 [11], 517 (1893)).

Preparation.—According to Moissan (C. R. 114, 319 [1892]), the methods employed of gidentorphous boron yield substances containing from c. 45, to c. 72 p.c. of B. M. (l.c. p. 392) says that nearly pure amorphous B is obtained by heating to reduces a mixture of one pt. powdered Mg with 3 pts. fused B.O., washing with HClAq. KOIT in alcohol, HFAq, and water (the process is tedious, details are given); by fusing this product with 50 pts. B.O., and washing with HClAq &c., a brown powder is obtained containing c. 985 p.c. B, with traces of Mg and small quantities of other impurities.

Properties and Reactions.—The properties of anorphous boron are described by Moissan (C. R. 114, 617 [1892]). Brown powder; S.G. 2-45. Does not fuse in electric are, but volatilises (M., C. R. 117, 423 [1893]); increases in density when heated to c. 1500° in H. Specific electrical resistance = 801 megohms. Burns in air at c. 700°. Combines directly with Br, Cl, (not I), N at c. 12002, Se, S, (not Te); also with Al, Fc, Mg, Pt, and Ag. Reduces many oxyacids and oxides when heated therewith; HClO₃, HIO₃, and H.SO₄ are readily reduced; As,O₄ and AS,O₅, CO, N.O, P.O₅, SiO₂, steam, and SO₄ are also reduced; many metallic oxides are reduced to metals, often with explosive violence; molten KOH gives off H; metallic fluorides are generally decomposed, giving BF₄; many other metallic salts, both in solution and when heated as solids, are adduced by amorphous boron.

Boron, bromide of (vol. i. p. 525). Bly, boils at 90° (Freyer a. V. Meyer, Zeit. f. anorg. Chemie, 2, 1). Ghira (Z. P. C. 12, 768 [1893]) gives S.V. 94'72; and S.G. $\frac{\sigma}{e^2} = 2^{-64985}$. According to Besson (C. R. 112, 1001 [1891]), when a mixture of gascous HI and BBr, is passed through a glass tube at 300°-400° the products are BBr, I. BBr, and BBr, BBr, and BBr, are colourless liquids, distilling at c. 125° and 180°; they are rapidly decomposed by air and light. Tarible (C. R. 116, 1521, [1893]) says that BBr, combines with PBr, and PBr, as for form compounds easily decomposed by water, Cl., or NH, in the cold. Besson (C. R. 114, 542 [1892]) describes BBr, 4NH, obtained by massing dry NH, into BBr, in dry CCl. 50.

Boron, carbide of, B.C. Moissan (C. R. 18, 556 [1894]) says that B and C combines when amorphous B is mixed with c. i its weights.

Boron, carbide of, B.C. Moissan (C. R. 418, 556 [1894]) says that B and C combine when amorphous B is meted with c. i its with of sugar charcoal, and the mixture is heated in the electric furnace for some minutes using a current of 250-300 ampères and 70 volts. After treating the product with HNO,Aq, and then with KClO, and HNO,Aq, the carbide remains as a very hard, lugrous, black, crystalline powder; S. G. 2.512, burns very slowly in O at \$1.0000; sotted on by Gl below 10002 but not by Br, I, S. P. N. on miners acids; feacts with molten KOH. Tr. KNaCO, (abstract in C. J. 66 [11], 279 [1894]).

Boron, chloride of (vol. i. p. 525). BCl, boiling at 17° (Freyer a. V. Meyer, Zeit. f. anorg. Chemie, 2, 1). Ghira (Z. P. C. 12, 768 [1893]) gives S.G. 2° = 1.48386, and S.V. 81.94.

Boron shoride of (vol. i. p. 526). According to Besson (C. R. 110, 80 [1890]), BF, unites with PH, at c. -30° to four 2BF, PH, decomposed by water giving off H and PH.

Ammonium borofluoride is described by Stolbs. (C. Of 1896. [1] 211; abstract in C. J. 58, 560).

Boron, hydride of (vol. i. p. 526). Sabatier, (C. A. 112, 865 [1891]) says that the gas produced by adding HClAq to the brown powder forfied by heating B_iO₁ with Mg is H has a very disagreeable odour, barns with a green flame, gives a brown pp. with AgNO₂Aq, deposits B when passed through a glass tube, at a dull red hoat (H coming off), and is decomposed by electric sparks, giving pure H. The gas contains a little B hydride, according to S. (i.e.); of. Winkler (B. 23, 772 [1899]).

Boron, iedide of (vol. i. p. 527). BI, Prepared by Moissan (C. R. 112, 717 [1891]), (1) by heating I and B to 700°-800°; (2) by heating amorphous B (dried in I at 200°), in a stream of dry HI, in a tube of hard glass until the glass nearly softens; (3) by passing HI and BUL vapours through a porcelain tube heated to redness. The product is dissolved in OS, shaken with Hg, and allowed to crystallisee Colourless erystals, very hygroscopic, rapidly become coloured in light. Melts at 43° and bolls at 210°. Decomposed by water, giving HIAq and H,BO,Aq. (For other reactions v. abstract in C. J. 60, 979 [1891].) For compounds with NH, v. Besson (C. R. 114, 542 [1892]; abstract in C. J. 62, 771).

Boron, oxide of (vol. i. p. 527), B.O., For reduction by Mg powder, giving Mg borde, v. Winkler (B. 23, 772 [1890]). The compound B.O., P.O., (a BPO.) is obtained by evaporating H.BO., Aq mixed with H.PO., heating to redness, and washing with hot water (G. Meyer, Be 22, 2919 [1889]).

Borates (vol. i. p. 529). For some newborates of Li, Rb, and Cs v. Reischle (Zeit. f. anorg. Gleonic, 4, 166 [1893]). For remarks on the classification of alkali and aftaline earth borates v. Le Chatelier (C. R. 113, 1034 [1891]). Eyr a full account of Mn borate, v. Hartley et. 121 [1893]. The compounds GFeO.FeBr. 8B.O. and 6ZnO.ZnBr. 8B.O. are described by Rousseau a. Allaire (C. R. 116, 1445; abstract in C. J. 64 [141, 518 [1893]).

Boron, phosphide of. According to Besson (C. R. 113, 78 [18918), a phosphide of B is obtained by passing PH, into BBr, and heating the product, BBr, PH, to 300°, when it gives HBF and B phosphide. The phosphide is said to be a browspowder; insolubin in water, reacting with boiling cone. alkan solutions to give PH,; gives off B when heated to redness in N (för other reactions v. abstract in C. J. 60, 1418 [1891]).

• Boron, selenide of. (?B₂Se₂). • Obtained, as a yellowish grey powder, decomposed violently by water, giving H₂Se and some Se, by heating B to full redness in a current of H₂Se (Sabatier, C. H. 112, 1000 [1891]).

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Boron, sulphides of (vol. i. p. 531). For heat of formation of B2S, v. Sabatier (C. R. 112, 862; abstract in C. J. 60, 981 [1891]). Moissan (C. R. dostract in C. J. 00, 981 [1891]). Moissan (C. R. 115, 203 [1892]) gives details of various methods of preparing B₂S₃, and describes the reactions of this compound (v. abstract in C. J. 62, 1393 [1892]). According to M. (l.c. p. 271), boron pentassignitude, B₂S₃, is obtained by heating BI, with rather less than only equiv. of S in CS₂ solution at 60° for many hours. M. describes the compound, which was not obtained pure, as

a light white crystalline powder, S.G. 1.85.

BROMHYDRIC ACID (vol. i. p. 532). The
V.D. has been determined by Biltz at -15° and -28° (Z. P. C. 10, 354 [1892]); the results agree with the V.D. fequired by the formula HBr. The M. M.s of HBrAq from 15.47 to 65.59 p.c. HBr have been measured by Perkin

(C. J. 55, 706 [1889]).

Preparation .- 1. By the interaction of P. Br. and H.O, v. Fileti a. Crosa (G. 21, 64 [1891]; and 11.0, 7. 1664 a. 1053 (b. 21, 64 [137]),
 def. Gassman, abstract in C. J. 64 [11], 453 [1893]).
 By passing H.S into Br covered with water (Recoura, C. R. 110, 784 [1890]).
 By adding H.SO.Aq S.G. 141 to KBr (Feit a. Kubierschky, J. Ph. [5] 24, 159; abstract in C. J. 60, 1320 [1891]; v. also Addyman, C. J. 61, 97 [1892]; of. Léger, abstract in C. J. 64 [11], 114 [1893]).

Hydrates.—Pickgring (P. M. [5] 36, 11 [1894]) has isolated HB: 3H₂O and HBr.4H₂O; the former melting at -48° and the latter at -55.8°.

Reactions.—For the decomposition of HBrAq by H₂SO₂Aq of different concentrations v. Addyman (C. J. 61, 98 [1892]).

BROMINE (vol. i. p. 534). Mol. w. in solu-mion in water or acetic acid = 159.5 (Br.) (Paterno a. Nasini, B. 21, 215, [1888]). The V.D.s of Br from 15° to 280°, and at pressures from 15 to 760 mm., have been determined by Perman (Pr. 48, 45 [1891]); no indications of dissociation were obtained. For measurements of the absorption of light by Br v. Camichel (C. R. 117, 807; abstract in C. J. 64 [11], 561 [1893]).

Srocates (vol. i. p. 538). Lithium bromate LiBrO,; prepared by the interaction of Ea(BrO₃)₂Aq and Li₂SO₁Aq (Potilitzin, J. R. 22, 392; abstract in C. J. 62, 1275 [1892]). Potassium bromate KBrO₃. The decomposi-tion of this salt by heat has been studied by Cook (C. J. 65, 802 [1894]); decrepitation occurs ar c. 180°, with evolution of Br; the salt fusos at a higher temperature, and O is evolved, without any Br, until KBr remains; no oxy- compounds are formed.

Strontium bromati begins to decompose at c. Strottle orbital change is to SrBr. and O, but SrO is also formed (Potilitzin, J. R. 22, 454; ubstract, with summary of quantitative results, in O. J. 34 [11], 11 [1893]).

Leter inations of the at. w. have been made by Partridge (Am. S. [3] 40, 377 [1891]), and by Morse a. Jones (Am. 14, 261 [1892]). P. converted CdC₂O₂ into CdO by heating in H₂S, and CdC₂O₄ into CdS by heating in H₂S. M. a. J. converted Cd into Cd(NO₃), and this into CdO by heating. The results all lie about 112 (v. abstract in C. J. 60, 399; cf. Clarke, ibid. 390 [1891], and 62, 1397 [1892]). Lorimer a. Smith

(Zeit. f. anorg. Chemie 1, 364 [1892]) obtained values varying from 112 182 to 111 908 (O = 16). The molecule of Cd in dilute solution in tin may be diatomic (v. Heycock a. Neville, C. J. 57, 376 [1890]). Cd mets at 320 68°, according to Collendar a Griffiths (determined by Pt thermometer, C: N. 63, 1 [1891]). For the line spectrum of Cd v. Ames (P. M. [5] 30, 33 [1890]). According to Williams (Ame 14, 273, 1892), Cd wintelling in beautiful and the spectrum of Cd v. Ames (P. M. [5] 30, 33 [1890]). crystallises in hexagonal and polyhedral forms; arial catio a:c=1:1.6554. Cd is superficially oxidised at a dull-red heat by nitric oxide (Sabatier a. Senderens, C.R. 114, 1429 [1892]). Montemartini (G. 22 [1] 250; v. ubstract in C. J. 62, 1278 [1892]) has analysed the gases produced by the interaction of Cd and nitric acid; with excess of HNO, Aq (27.5 p.c.) at 80, N, NO, N2O and NH3 are produced.

Cadmium, alloys of (vol. i. p. 655). For an alloy with gold, C&Au, v. Heycock a. Neville (C. J. 61, 914 [1892]; cf. ibid. 65, 65 [1894]). For alloys with copper, gold, and silver, pre-pared by immersing Cd in solutions of salts of the other metals, v. Mylius a. Fromm (B. 27,

630 [1894]).

Gadmium, bromide of (vol. i. p. 655). the double compounds $CdBr_xxCsBr$, x = 1, 2, and3, v. Wells a. Walden (Zeit. f. anorg. Chemie, 5,

266 [1893]).

Cadmium, chloride of (vol. i.p. 655), Wasnik (Ar. Ph. 229, 569; abstrach in C. 3. 62, 566 [1892]) describes CdCl., 2NH, and CdCl., NH, For the double compounds CdCl, CsCl and CdCl₂·2CsCl, v. Wells a. Walden (lc.). Double compounds with HCl; NII,Cl, LiCl, and KCl, of the form CdCl. MCl. raq, are described by Classevant (A. Ch. [6] 30, 5; v. abstract in C. J. 66 [11], 18 [1894]).

Cadmium, fluoride of (vol. i. p. 655). CdF. is obtained by (1) the interaction of HF and Cd at a red heat; (2) the interaction of HF and fused CdCl, or CdO at a red heat; it is a colourless, transparent solid; S.G. 6.64; somewhat soluble water, insoluble alcohol of 95° (Poulenc, C. R. 116, 581 [1893]).

Cadmium, iodide of (vol. i. p. 656). For the double compounds CdL_xCsI, when x = 1, 2, and 3, v. Wells a. Walden (i.c.).

Cadmium, oxides of (vol. i. p. 656). CdO is unchanged at c. 1750° (Read, C. J. 65, 313 [1894]).

According to Kouriloff (J. R. 22, 171; Distract in C. J. 62, 1278 [1892]), the compound CdO, CdO, H, is obtained by heating CdO, H, with H.O.Aq. Morse a. Jones (Am. 12, 488: abstract in C.: J. 58, 1376 [1890]) obtained small orystals, which they say were cadmous oxide Cd.O. by gently hearing CdOH; the hydroxide war obtained by hearing CdCl. CdBr, or CdL. with excess of Cd, to the melting-point, in N, or coo, and treating with water, when Colling CdBt, or CdI, dissolved, a little CdO, H, separated, and CdOH remained as a white amorphous powder.

Cadmium, salts of (vol. i. p. 656). For the electrical conductivities of very clittle solutions of CdBr., CdCl., CdI., K,CdI., Cd(NO.), and CdSO. Wershoven (Z. P. C. 5, 481. [1890]). Cadmium, sulphide of (vol. i. \), 657). Two forms (and perhaps more) of CdS seem to exist,

one lemon yellow and the other red; they differ

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low is said to change to the red by friction (v. Buehner, Chem. Zeit. 11, 1087, 1107; 15, 778; von Klobukoff, J. pr. [2] 39, 412; abstracts in C. J. 54, 224 [1888]; 56, 946 [4889]; 62, 778 [1892]). A solution of colloidal CdS was obtained by Prost (C. C. 1888, 32; abstract in tanicary Frost (Co. C. 1886, 52; abstrace in J. 54, 653 [1888]) by completely ppg, an ammoniacal solution of CdSO, by H.S. washing well, suspending the pp. in water and passing in H.S. A solution with 4 grms. CdS part little remained clear for many days; one with 11 grms. coagulated in 24 hours.

CÆSIUM (vol. i. p. 657). According to Beketoff (v. abstract in C. J. 62, 274 [1892]), Cs is obtained by heating CsOH with c. 1 its weight

Casium, haloid compounds of (vol. i. p. 658). A series of compounds of the form CsX_3 , where $X_3 = Br_3$, I_3 , or Br and I, Cl, Br and I, &c., is described by Wells a. Penfield (Am. S. [3] 43, 17; abstract in C. J. 62, 773 [1892]). Double compounds of Cs haloids with haloid compounds of Cd, Cu, Mg, Hg, Pb, and Zn are described by Wells (and others) (Am. S. [3] 41, 221; Zeit. f. anorg. Chemic, 3, 195; 5, 266, 273, 300, 304, 306; abstracts in C. J. 64 [11], 67, 322 [1893]; 66 [11], 45, 47 [1894]).

Cosing, hydroxide of (vol. i. p. 658).

S.G. 6 4-0178; [CsOII,A4] = 15,876; [CsOIIAq,HCiAq] = 13,790 (Beketoff, C. C. 1891.

[11] 451).

Cæsium, oxide of (vol. i. p. 658). According to Beketoff (J. R. 25, 433, abstract in C. J. 66 [11], 234 [1894]). Cs.O reacts with slightly moist H to give Cs and CsOH.

CALCIUM (vol. i. p. 663). The molecule in dilute solution in tin may be diatomic (v. Heycock a. Neville, C. J. 57, 376 [1890].

Calcium, carbide of. By heating 120 g. CaCO.

with 70 g. sugar charcoal in the electric furnace with a current of 350 ampères and 70 volts, Moissan (C. R. 118, 501 [1894]) obtained lustrous, yellow crystals of CaC,; S.G. 2.22 at 187; insoluble in most solvents; reacts with Cl, Br, and I at 250°-350°; burnt to CaCO, by O at a red heat; interacts violently with water giving off pure acetylene, and with steam giving CaCO, C, H, and C₂H₂ (destruct in C. J. 66 [1], 313 [1852]).

Calcium, oxide of (vol. is p. 666). CaO is unchanged at c. 1750° (Read, &. J. 65, 312 [1894]). According to Veley (C. J. 65, 821 [1893]); 66, 1 [1894]), dry CaO does not appreciably combine with dry CO, SO, or Clabelow 300°. Baker (C. J. 65, 611 [1894]) says that dry **S00°. Baker (C. J. 65, 611 [100*]) 60, nor with dry SO,, nor with dry NH,Cl. Moissan (C. R. 115, 1031 [1892]) obtained electric furnace.

Calcium, oxychloride of (vol. i. p. 666). Prepared by boiling CaO with conc. CaCl. Act; crystallises in thin, lustrous needles; decomposed by water, alcohol, &c.; dissolves in glycerin. Composition is probably 3CaO.CaCl., 15aq (Zahorsky, Zeit. f. 1002. Chemie, 3, 34 [1893]).

**Calcium, oxylodide of. By heating out with Cal. Act in a feeled tube at 150° for 6 shours, Tassilly (Bl. [3] 9, 629 [1893]) obtained needles of Cal., \$2aO.16aq. pared by boiling CaO with conc. CaCl2Aa; crys-

CARBON (vd. i. p. 684).
Diamond. Moissan (C. R. 116, 218; 118, 320; abstracts in C. J. 64 [11], 275; 66 [11], 189, [1893] and 1894)) obtained grey-black carbonato. by dissolving U in iron, heating to 2000; 3000; and rapidly cooling the exterior by water or by plunging into a bath of melted lead; the fiquid integer expands as it cools and produces a very high pressure. Diamond blackens, swells, and changes to graphite in the electric furnace (M., C. R. 117, 423 [1893]). For various reactions of diamond, v. Moissan (C. R. 116, 460; abstract in C. J. 64 [11], 319 [1893]).

Graphite. For accounts of graphites prepared in different ways, the compositions of the graphitic oxides obtained, and the H.F.s of these oxides, v. Berthelot a. Petit (C. R. 110, 101, 106; abstract in C. J. 83, 448 [1890]). For the action of cone. HNC on various graphites, v. Luzi (B. 24, 4085; 26, 1412 [1892 and 1893]).

Amorphous carbon. Mixter (Am. S. [3] 45, 363; abstract in C. J. 64 [11], 571 [1893]) doscribes the interactions of charcoal and N. S. O. and the halogens. According to Ernst (J. pr. [2148, 31; antend tin C. J. 64 [11], 461 [1893]). the composition of the products of combustion of coke (CO and CO,) depends almost wholly on the temperature; the maximum formation 36 CO₂ is at c. 700°, at 1,000° CO is the only product.

Allotropy of carbon. The following heats of combustion, and atomic volumes, are given by Petersen (Z. P. C. 8, 601 [1891]):

Amorphous . 96,530 to 96,980 6.7 to 8 Graphite . . . 93,360 5.R Diamond . . . 93,240 to 94,550 8.4

For the reactions of various forms of C with and H₂SO₄ v. Wiesner (M. 13, 871; abstract in C. J. 62, 1273 [1892]); and with HNO₂ and KClO₃ v. Schutzenberger (C. R. 111, 774; abstract in C. J. 60, 265 [1891]).

Carbon, tetrabromide of (vol. i. p. 688). Collie (C. J. 65, 262 [1891]) finds that very many compounds of carbon give CBr, when heated with NaOHAq and Br.

Carbon, bromochorides of (vol. i. p. 688). The three compounds CBrCl, CBr,Cl, and CBrCl, are formed by heating CHCl, and Br to 225° in a sealed tube (Besson, C. R. 114, 222

[8892].)
Carbon, tetrafluoride of, CF., Mol. w. 88-87. V.D. 44.6. Prepared by the direct union of O (purified lampblack) and F at the ordinary temperature; by the reaction of F with CCl, slightly heated, or with CHCl, at 100°, or with CH (Moissan C. Re 110, 296, 951; abstracts in C. J. 58, 557, 944 [1890]); also by heating Age with CCl, to 220° in a scaled tube (Chabrid, C. R. 110, 279 [1890]). M. recommends to pass vapum of CCl, over AgE 1195°-200°, to let the vapours pass through a serpentine tube kept at -23°, and to collect the gas over Hg; the gas is kept inacontact with fragments of caoutchouc (to remove CCl,), then shaken with absolute alcohol, in which it dissolves, and then V.D. 44 6. Prepared by the direct union of C solute alcohol, in which it dissolves, and then expelled by heat, collected and shaken with H₂SO_p (to remove alcohol vapour); metal vessels must be used. CF, is a colourless gas, liquefying at - \$5° and 760 mm. pressure, or at 20° under

washing the crystals with NaHSO:Aq, drying, and slowly subliming in vacio. CI, reacts

with Cl to form CCl, and chlorides of I; reduced to CHI, by H at 140° (for other reactions v.

Carbon monoxide (vol. i. p. 689). For some experiments on the sparking of CO, with the formation of brown solids, v. Berthelot (C. R. 110, 609) and Schutzenberger (C. R. 110, 500; abstracts in C. J. 58, 691 [1890]). Winkler (B. 24, 878 [1891]) finds that CO is reduced to C, at a full red heat, by Mg; carbides of Mg are probably formed (cf. W. B. 23, 2612 [1890]).

bably formed (cf. W., B. 23, 2642 [1890]).

Carbon dioxide (vol. i. p. 691). For S.H. of

CO. v. Kurnakoff (f. r. 22, 493; abstract in

C. J. 64 [11], 5 [1893]). CO., is reduced by
heating to redness with Mg, amorphous C, and
some CO being formed (Winkler, B. 23, 2642;
24, 873 [1890-91]). Dry CO. is said not to combine with dry NH, (Hughes a. Soddy, C. N. 69,

W. Carbon awahleride of (vol. i. z. 600). CCC.

Carbon, oxychloride of (vol. i. p. 692). COCl. becomes viscid, by tremains clear, at -75° (Haase, B. 26, 1052 [1893]).

Carbon disulphide (vol. i. p. 693). tractions observed when mixtures of CS, and air are exploded show that the reaction is more complicated than is shown by the equation CS₂+8O₃-CO₂+2SO₂; the volume of CO₂ cornd is, practically, in accordance with the equation, but the volume of SO₂ is smaller; some of the N of the air is oxidised (v. Podler, C. J. 57, 625 [1890]). By heating CS₂ with excess of aqua regia, Schlagdenhauffen a. Bloch (J. Ph. [5] 28, 241 [1893]) obtained SO(OCCl₃)Cl. Decomposition of CS₂ heated in dry N, begins at 216°, and explosion with O at a higher traperature (Baker, C. J. 65, 611 [1894]).

Tricarbon disulphide C.S. B. von Lengyel
[33. 26, 2860 [1893]] obtained this compound by

keeping the vapours of CS, in an electric arc between C poles for some hours, filtering off the black substance formed, allowing the red filtrate to stand over Cu for 6 to 8 days, and evaporating in a current of dry air. C,S, is a deep-y#1 liquid, S,G. 1:27399; the vapour, even in minute quantities, causes violent catarrh; can. be distilled, with partial change to a black solid, at 60°-70° and reduced pressure; insqluble water, but dissolved by EtOH, Et.O. CS., CHCl., or C.H. A cono. solution in CS. deposits a black solid; the same solid is formed by gently heating the liquid, if heating to 100°-120° is rapid the change is explosive. The black solid is probably, polymeride. A so-tion of O.S., in CS, reacts with Br to form C.S.Br., (For other reactions, v. abstract in O. J. C6 [11], 91

[1894].
Carbon, thiobromide of, C.S.Br., ; formed by
the action of Br on a solution of C.S. in CS. (v.

Carbon, thiochloride of (vol. i. p. 695). The polymeride of thio-carbonyl chloride has the molecular formula (CSCl₂), according to the

-a pressure of 4 atmos. Other fidorides seem to be formed along with CF₄; Chabrie (l.c.) says that AgF and C₂Cl₄ yield C₂F₄.

Carbon, tetra-iodide of (vol. i. p. 689). Moistan (C. R. 113, 19; abstract in C. J. 60, 1420 in compounds of Di and La, v. Schottländer (B. [1891]) prepares Cl₄ by heating CCl₄e(free from CHCl₄) with excess of Bl₄ to 90° in a scaled tube, with the excess of Bl₄ to 90° in a scaled tube, are the compounds of Cl₄ and La, v. Schottländer (B. [1894]).

Carlon Hard Carlon (C. R. 113, 145 (1894)).

Cerium, hydride of. According to Winkler (B. 24, 873 [1891]), a compound of Ce and H. p. obably CeH., is formed by reducing CeO. by Mg in Cresence of H.

Cerium dioxide (vol. i. p. 725). CeO, is unchanged at c. 1750° (Read, C. J. 65, 813

CHLORHYDRIC acid (vol. ii. p. 5). Biltz (Z. P. C. 10, 354 [1892]) finds that the V.D. at -77° agrees with the formula HCl. Perkin (C. J. 55, 703, 705 [1889] has determined M. M. of HClAq and HCl in iso amyl oxide; the values obtained for HCl in Eq are c. double those for HCl in iso-amyl oxide. For measurements of the E.C. of HCl in different solvents, A Kablukoff (Z. P. C. 4, 429 [1889]). For revised tables giving S.G. of HClAq, v. Lunge a. Marchlewski (Zeit. f. anorg. Chemie, 1891. 133).

For the relations between the number of molecules of HCl required to ppt, one mok of different chlorides, and the reduction of the freezing-points of solutions of the chlorides and of HCl, v. Engel (C. R. 117, 845; abstract in

of HCl, v. Engel (C. 48. 111, 820; accessed in C. J. 65, 40 [1894]).

Bailey a. Fowler (C. J. 53, 755 [1888]) find that when HCl stands over P₂O₂ the gas is absorbed, with production of POCl₂ and HPO₃; and that when HCl and O stand over Hg an oxychloride, probably Hg₂OCl₂H₂O₂, is formed.

Direct (C. J. 65, 611 [1891]) states that dry HCl deem not combine with dry NH, when the gases does not combine with dry NH, when the gases

CHLORINE (vol. ii. p. 10). For the S.G. of liquid chlorine from -80° to 77°, and the vapour pressures from -88° to 146°, v. Knietsch (A. 259, 100 [1890]). For the preparation of Cl (C. J. 61, 445 [1892]) finds that Cl obtained by heating PtCl, always contains some HCl and O, with water, and perhaps a trace of N. Clexpands when brought into sunlight. Richardson (P. M [5] 32, 277 [1891]) has constructed an instrument wherein the expansion is used to measure the intensity of light. Baker (C. J. 65, 611 [1894]) found that no explosion occurred when a mixture of equal vols. of dry Cl and dry H was exposed to bright sunlight; and that after exposure to bright sunshine for two days, and to diffused light for two days, more than a

quarter of the mixture remained unchanged.

Pedler (C. J. 57, 613 [1890]) has examined the interaction of Cl and water in tropical sun highit; he finds that there is very little action, unless there is an extremely large excess of water. on With very much water and little Ci, exposed to the full light of the sun in the hot season in India, the main reaction is 2H, O * 2Cl., + Aq = 4HC; Aq + O, ; † with diffused suplight HClAq and HClOAq art formed at first, and fightly "HClAq, HClO, Aq, and O. Harker (E. P. O. 9, 673 [1892]), from an extended investigatien of the explosion of mixtures of Cl. H, and O, concluded that when there is insufficient H to

domoine with an the Orang an the O, a division of the H between the Cl and O occurs; and that the product of the numbers of molecules of Hol and 0, divided by the product of the numbers of molecules of H₂O and O₁ is a constant, on in other words, that the law of Guldberg a. Waago holds good. According to Gautier a. Charpy (C. R. 113, 597 [1891]), there is no reaction between Mg or Zn and liquid Cl at the ordinary temperature, very little reaction with Fe or Ag, and rather more with Cu. **Chlorates (vol. i., p. 18). Spring a. Prost (Bl. [8] 1, 340 [1893]) have determined the quantities of Cl obtained by decomposing by heat chlorates of Al, Ba, Cu, Ph. Hg, K, Ag, Na, and Zn; the amount of Cl varied from 20 p.c. from MClO₂ to 14.45 p.c. from Zn(ClO₃). Calcium chlorate. Dry Ca(ClO₃). melts between 300°-350°, having previously given off

from 3 to 5 p.c. of its weight of O; the rate of evolution of O increases, at 330°, until c. 60 p.c. of the total O is given off, after which the rate decreases. For the quantities of O evolved, of Ca(ClO₃)₂ decomposed, and of CaCl. and Ca(ClO₄)₂ formed, v. abstract in C. J. 62, 1275 [1892].

*Potassium chlorate. McLeod (C. J. 55, 184)

*Recognition of the appearments that

when KClO, is heated with MnO, some KMnO,
is formed and again decomposed (c. Manganser Peroxide, vol. iii, p. 183), and that Cl is always given off in this reaction. In 1893 (B. 26, 1790) Brunck stated that Cl is not given off when KClo, and MnO, are heated together, but that ozone is produced. McLeod (C. J. 65, 202 1894)) has proved that Cl is produced in the reaction. Fowler a. Grant (C. J. 57, 272 [1896]) have studied the influence of various oxides on the decomposition of KClO, (references are given to older memoirs); they support McLcod's tiew of the reaction with MnO₂, and think that the exides of Fe, Co, Cu, and Ni react similarly to MnO₂; acidic exides, such as V₂O₃, U₃O₃, and WO3 cause evolution of O accompanied by much Cl, a vanadate, uranate, or tungstate being also formed; powdered glass or san l'also assists the reaction, but only when very finely divided (v. summary of conclusions, C. J. 57, 281-2). According to Thome a. Perry (C. J. 61, 925 [1892]), the main reaction which occurs when 1802), the main reaction which occurs when an intimate mixture of KClO, and iodine is heated is 2KClO, + 1.= 2KlO, + Cl., and some of the Cl reacts with unchanged I to form ICl and ICl. Basset (C. J. 71, 760a [1890]) examined the reactions between KClO, water, and iodine; he concluded that the main reaction, at 80°, in the presence of a very small quantity of HNO, M. Is as shown by the equation 612 + 10KClO, + 6H,O + Aq - KKH,O, Aq + 4KClAq + 6HClAq; in evaporating the solution to dryness. Cl was given off, and the results of several experiments led to the representation of the chance produced We vano-

the results of several experiments lead to the vaporesentation of the change produced by evaporation to dryness as 12KHLO, +8KOI+12HCI-11KHLO, +9KCI+6H-O, + ICI+ICI-HCI+4CI, For determinations of the quantities of oxidising gases (Cl and oxides of Cl) removed by apassing air through PCIO-Aq mixed with HCkAq, v. Pendlebury a. McKilloy (P. S. Proc. 1893-4. [No. 189 211]. Strontium chlorate. For experiments on the decomposition of this salt by heat, giving SrCl Sr(ClO4), and O, v. Potilitzin (J. R. 21, 451; ab-

by Rawson in 1889 (C.-J. 55, 213) by strongly heating (NH.) Cr.O., measuring the N given off, and weighing the Cr.O., that remained; also by reducing (NII.), Cr.O.Aq to CrCl.Aq by HClAq and Ricohol, ppg. by NH.Aq, and weighing Cr.O. produced; the mean value thus obtained was 5226, or 51.98 reduced to 0° and a vacuum

52200, or 51:38 reduced to 0° and a vacuum (O = 16:96). Menicke in 1851 (A. 261, 39); abstract in C. J. 60, 882 [1891]) re-determined the at. w. of Cf by estimating (1) Ag and Cr, and also O, in Ag,CrO, and in Ag,CrO,NH, (2) O in K,Cr,O,; (3) wand Cr in (NH,),Cr,O; the extremo values, from Chirty-six experiments, were 52:12 and 51.83; twenty-eight of the experiments gave values between 51 9 and 52. According to Prinz (C. R. 115, 392 [1893]), or crystallises in minute cubes with pyramidal faces. For the absorption spectra of salts of Cr, v. Lapraik (J. pr. [2] 47, 305 [1893]). Prenaration .- Glat 2el (B. 23, 3127 [1890])

says that almost perfectly pure Cr can be have tained by reducing CrCl, KCl by Mg powder (for details v. abstract in C. J. 60, 152 [1891]). Placet (C. R. 115, 945 [1892]) prepares Cr by electrolysing a solution of Cr alum, containing an alkali sulphate and H.SO. Moissan (C. R. 116, 349 (1893)) says that Cr can be obtained by reducing a mixture of Cr.O, and C in the electric furnace, using a current of 50 volts and 100 ampers, and then breaking up the product, which contains from 8.6 to 12.9 p.e. C, and heating it, furnace in a carbon crucible.

Chromic acid (vol. ii. p. 154). Miss. Field (C. J. 61, 405 [1892]) has found that only CrO. is obtained by working according to Moissan's directions for preparing H.CrO.. Determinations of the increase in the b.p. of water caused by solution of CrO_3 led to the conclusion that an aqueous solution of CrO, contains some H,CrO and probably also H2Cr2O7.

Chromic bromide CrBr, (vol. ii. p. 161). Recoura (C. R. 110, 1029, 1193) obtained green CrBr, 6H,O by boiling saturated CrO,Aq with a large excess of HBrAq and concentrating; deliof escent crystals, soluble alcohol, insoluble ether. Unchanged when kept solid but solution soon becomes blue and then violet, with rise of temperature. By boiling a green solution, then saturating with HBr while cold, filtering, and saturating with HBr while cold, filtering, and drying the pp. thus, formed on porous plates, crystals of the blac variety, CrBr, 6H,O, were obtained; very soluble water, insol. arcohol. Heat of splution of blue crystals = 28,700; and of green = 1,860. The blue solid a changed to the green at 100°. (For more decade v. abstract in C. J. 58, 1063-(1890)).

"Chromic chloride CrCl, (vol. ii. p. 161). Max chetti (G. 22° [11], 375 [1892]) finds that the molecular lowering of the freezing-point of water than that caused by the green form.

Chromic fluoride CrF, (vol. ii. p. 162) Tabris (G. 20, 582 [1890]) obtained CrF, 9H, Casa green crystalline pp., by adding excess c

as a green crystalline pp., by adding excess o

"NH FAq gradually to a cold solution of violet Cr2(SO4)3. Slightly sol. water; insoluble NH, FAq or alcohol; heating in air leaves Cr. Q., Poulenc (C. R. 116, 253 [1893]) obtained Cr.F. in green crystals by heating CfCl₃, Cr₂O₃, or CrF₃, xH₂O in HF.

Chromous fluoride. According to Poulenc (L.c.), CrF₂ is formed by kenting Cr to redness in HF, or by the interaction of CrCl₂ and HF at the ordinary temperature. CrF₂, after fusion, is described as a transparent, green, crystalline mass; S.G. 411; slightly sol. water, insol. alcohol. Heated in air it gives Cr.O₃. (For thore details v. abstract in C. J. 64 [11], 281 [1893].)

Chromic oxide Cr.Q. (vol. ii. p. 664). Moissan (C. R. 115, 1034 [1892]) found that Cr.Q. melted to a black mass, dotted with black crystals, in an electric furnace, using a current of 55 volts and

30 ampères.

Chromium trioxide CrO, (vol. ii. p. 164). For action of water v. Chromic acid, p. 905. Re-For action of water v. CHROMIC ACID, p. 905. Reduced to Cr₂O₃ by NO & the ordinary temperature (Senderons a. Sabatier, C. In 114, 1476 [1892]). For the reaction of Cr₀Aq with Q and BaO₄H₂Aq—said to give a pp. approximately BaCrO₃—v. Péchard, C. R. 113, 39 (abstract in G. J. 60, 1431 [1891]).

Chromium salts (vol. ii. p. 167). According to Recours (C. R. 112, 1439; abstract in C. J. (20, 1430 [1801]).

60, 1430, [1301]), the green solutions obtained by heating solutions of the normal violet chromic salts contain free acid and a soluble basic salt; in the case of the sulphate this soluble basic salt is said to be 2Cr2O, 5SO,. For preparation of green soluble normal sulphates v. Recoura, C. R. 115, 857 (abstract in C. J. 62, 411 [1882]).

**CHROM.AMMONIUM COMPOUNDS (vol. ii. p. 158). Petersen (P. P. C. 10, 580 [1892]) finds. by cryoscopic determinations, that the formulæ usually assigned to the chief salts of this class are probably molecular. For a discussion of the [2] 42, 206; 45, 274).

CHROMATES; and derivatives (vol. iit p.

Ammonium chromates. According to Jäger s. Krüss (B. 22, 2028 [1889]), normal ammonium chromate has not hitherto been obtained pure; they prepare the pure salt by adding excess of NH,Aq S.G. 9 to Cro,Aq free from H.So,Aq, warming until the solid that separates dissolves, and placing in a freezing mixture. (NH₁)_cCeO₄ crystallists in long, monosymmetric, golden needles, a:b:c=1.9603:1:2.4452; S.G. 1.886 at

Ammonium trichromate (NH₁)₂Cr₃O₁₀ is prepared by J. a. K. (l.c.) by dissolving (NH₄)₂Cr₂O₇ in hot conc. CrO, Aq, concentrating, and drying at 100° the fed crystals that separate on cooling; S.G. 2:342 at 18°; explodes at 190°, giving off NO₂, and leaving Cr₂O₂.

Ammonium Letrachromate (RH₂) r₁O₁, is

Ammonium iterrachromate (NH₄)²Ur₄O₁₃ is formed by discolving the trichromate in warm HNO₂Aq S.G. 1.09, at detting cool slowly; S.G. 2.343 at 10°; 'melts at 170°, and suddenly decomposes at 175°, giving off NO and leaving Or₄O₂. J. c.k' K. (l.c.) failed to obtain heatschromate; they say that no nitro-chromates are obtained by treating ammonium characters. obtained by treating ammonium chromates with HNO.Aq. (For more details v. abstract in C. J. H.O (C. J. 41, 113), and also compounds of Or.O., 56, 1117 [1889].) Various double compounds of SO,, K.O and H.O. Recoura (C. R. 114, 477

(NII), Cr.O, with HgC are described by J. a. K.

Ceric dichromate CeO, 2CrO, 2H, O. pared by passing a current of 2.5 to 3 volts through a slightly acid solution formed by dis-solving Ce₂(CO₂), in CrO₂Aq; insoluble water; boiling water forms yellow Ce(CrO₂), and then CeO..xH.O (Bricout, C. R. 118, 145 [1894]). Lead chromates. For double compounds of

Bachard a. Lepierre, C. R. 110, 1035 (abstract in C. J. 58, 1065 [1890]).

Mercury chromates. For basic mercuric.

chromates and a double compound of HgCro, with NH HgCl v. Jüger a. Krüss, B. 22, 2028

(abstract in C. J. 56, 1120 [1889]).

Potassium chromates. Jägen a. Krüss (l.c.) prepare potassium trichromate K2Cr3O10 by treating K,Cr,O, with HNO,Aq S.G. 1.19, pouring off from KNO, that separates, and crystallising; S.G. 2648 at 11°. K.Cr.O., is quickly decomposed by water to Cro, Aq and K.Cr.O., Aq; melts at 250°. Potassium tetrachromate K.Cr.O., is prepared by J. a. K. (*l.c.*) by dissolving K.Cr.o, in hot cone. HNO, Aq S.G. 1:41; s.G. 2:649 at 11°; not deliquescent; decomposed by water; crystallises unchanged from HNO, Aq S.G. 1º41. Schmidt (B. 25, 2917 [1893]) says that no nitro-chromate is obtained by the action of HNO Aq on K.Cr.O.; the substances obtained by Darm. städter (v. vol. ii. p. 158) were mixtures of KNO, and K₂Cr₃O₁₃.
Silver chromates.

Pure silver chromate Ag₂CrO₁ is prepared by J. a. K. (l.c.) by repeatedly boiling Ag₂Cr₂O₇ with water as long as anything dissolves; it is a neep-green solid,

incol. water.

Sodium perchromate. Häussermann (J. pr. [2] 48,70; abstract in C. J. 64 [11], 471) describes a salt Na₆Cr₂O₁₅. 2Saq, prepared by adding Na₈O₂ to a thin paste of CrO₃H₃ and water, kept at 10^{2}

Thallium chromates. For preparation of Tl. CrO, and the double compound Tl. CrO, K. CrO, v. Lachaud a. Lepierre, Bl. [3] 6, 232 (abstract in C. J. 62, 567 [1892]).

For double uranul Uranium chromates. chromates, v. Formanek, A. 257, 102 (abstract in

C. J. 58, 852 [1890]

1010/PHROMATES (rol. ii. p. 157). A series of salts of the forms, IO_O.CrO_COM' and (IB_O.CrO_CO), Mu has been obtained by Berg C. R. 101, '1514 [1887]; 111, 42 [1890]); Mi -NH, Li, & Ag, and Na; Mi'=Co, Cu, Mg, and Ni. Most of the alkali salts were formed by dissolving the alkali iodate in excess of CrO_AQ and crystallising; the other salts were usually retrieved by disselving the discovered or corphometer. prepared by disselving the oxide or carbonate of the metal in excess of CrO₃Aq and adding H[O₂Aq. (For details v. abstracts in C. J. 59, 770 [1887]; 58, 1378 [4890].)

PHOSPHOCHROMATES. By adding conc. H, PO, A4 + CrQ, Aq to K, CO, Aq, Blondel (C. R. 118, 194; abstract in C. J. 66 [11], 193 [1894])

obtained compounds of the form mK_0.P_20,nCrO, raq, m being 0 and 3, n 4 and 8, and x being 0 or 1.

SECTHOCHEOMATES. In 1885 Cross a. Higgirf described a compound of or 0, SO, and

[1892]; 116, 1367; 117, 37, 101 [1893]) has explodes (S. a. ..., cl. [3], w, one (1993]). Monte-made a more complete examination of these and martini (G. 22 [1], 250) finds that the gases proallied compounds. By evaporating, at 100°, solutions containing violet Cr₂(SO₄), and H.SO₄, and H.SO₄ in the molecular ratio 1:1, 1:2, and 1:3, 1, obtained chromosulphuric acid H_cCr_c(SO_c), chromodisulphuric acid H_cCr_c(SO_c), and chromodisulphuric acid H_cCr_c(SO_c), and chromodisulphuric acid H_cCr_c(SO_c), and 1:30 chromodisulphuric acid H_cCr_c(SO_c). chrometisulphuric acid H_cCr_z(SO_z)_z, and chromo-trisulphuric acid H_cCr_z(SO_z)_z; by using various sulphates in place of H_cSO_z he obtained chromo-sulphates, chromodisulphates, and chromotr-sulphates. The acids are green powders casil sol, water; they gradually decompose in solu-tion; dilute BaCl_zAq ppts. Ba chromosulphates, but cone RaCl_zAq ppts. Ba Chromosulphates, but cone. BaCl,Aq gives BaSO. R. obtained chromopyrosulphurio acid Cr. (OH. (S.O.H.), by evaporating a solution of Cr (SO₄)3 and H₂SO₄, in the molecular ratio 1:5, at 100°, and heating the dark-green syrupy liquid so obtained to 140'-115° for some days. The acid forms brittle, transparent, pale-green lambur. Salts of the form Cr2(S2O,)2(OM), are obtained by adding alkalis to the acid in solution; these salts B. calls pyrosulphochromites. By adding cone. Calls pyrosuppocuromites. By adding cone. HCIAq or H.SO, to a solution of chromoprosupportion abid, R. obtained a compound Cr₂(OH)₂(S₂O₂)₂, pyrosulphochromic hydroride, isomeric with chromosulphuric acid Cr₂SO₂(H₂). (For more details v. abstracts in C. J. 62, 783

[1892]; 64 [11], 470,528 [1893])

COBALTA (vol. ii. p. 217). Winkler has redetermined at w. of Co, (1) by dissolving electrolytically deposited Co in RCLA, evaporating to dryness, and determining Cl in the CoCl, obtained (Zcit. f. anorg. Chemie, 4, 10 [1893]);
(2) by finding the quantity of Ag deposited from solution of Ag₂SO₁ by electrolytically deposited Co (*l.c.* p. 462). The values obtained were all about 59.6 (Ag = 107.66).

Alleged decomposition of cobalt. Krüss a. Schmidt (B. 22, 11, 2026 [1889]) supposed they had separated Ni into two constituent, (r. vol. iii, p. 500); and they thought that Co also was probably not a homogeneous substance. Reminler, in 1893, obtained a number of specimens of • Co₂O₃, by ppg. CoCl.Aq Ly KOHAq and Br water, treating the pp. with NH Aq, which gradually dissolves it, decanting off the agmoniacal solutions of the agmoniacal solutions. tion at intervals during 9 months, evaporating each and heating i. CO₂; the different specimens of Co₂O₃ were heated in II, and the quantity of Co obtained in each case was determined. The values thus obtained for the at. u of Go varied from 59:53 to 58:3. R. concluded that Co purified by the ordinary methods is not a flouro-geneous substance. Winkler's determinations of the at. w. (v. supra), however, gave very constant values.

Reactions.—Heated in 20 to 150°, CoO is formed (Sabaticr a. Senderens, C. R. 114, 1429 formed (Sabatier a. Senderens, U. R. 114, 142) [1892]); finely divided Co burns in No, at the grdinary temperature, giwing Co.O.; but if the NO, is largely diluted with N, a black compound is formed, Co.NO, called by S. a. S. (Co.R. 115, 236 [1892]) nitro-cobalt. This compound reacts rapidly with H,O, giving off NO, and forming a solution contairing Co(NO), with a very little Co(NO), Co rem lining insoluble, and sometimes also a basis nigrite; when heated is No great solution covers and then sand decompassition. duced by the interaction of Co and excess of HNO, Ao (27.5 p.c.) are NH, N,O, and N (excession C. J. 62, 1278 [1892]).

AND AGE (212 D.c.) are KIII, M.O., and A washer act in C. J. 62, 1278 [1892]).

Cobalt chloride of (vol. ii. p. 219). For the solubility of CoCl, in water, and the changes of colour produced by disting the solution, with a discussion of the hydrations and dehydrations that accompany these changes, v. Etard, C. R. 113, C. G. (costract in C. J. 62, 278 [1892]);

Engel, Bl. [3] & 239 (abstract in C. J. 62, 569 [1892]); and Polilitzin, Bl. [3] 6, 264 (abstract in C. J. Le. p. 571). The double compounds CoCl., HCl. 3aq. CoCl., LiCl. Saq. and CoCl., NH, Cl. 66aq are described by Chassevant (A. Ch. [6] 30, 5 [1893]).

Cobalt, flugrice of (vol. ii. p. 220). Poulenc (C. R. 114, 1426; v. abstract in C. J. 62, 1159 [1892) prepares CoF, by heating CoCl, with excess of NH, F for 15 minutes, and repeatedly washing the double thouside CoF, 2NH, F thus

washing the double fluctide CoF, 2NH, F thus obtained with boiling alcohol. By heating CoF, to 1200 1300 in IIF, the salt is obtained in singl, rose red prisms; S.G. 4.13. The double compound CoF_2KF is 5 med by heating CoCl, with KHF₂ (P., Le. p. 74); abstract, Le. p. 781). Cobalt, iodide of (vol. ii. p. 220). For some bility in water of CoI, and the formation of various hydrates attending polution, v. Etard, C. R. 113, 699 (abstract in C. J. 62, 278 [1892]).

Cobaltous oxide CoO (vol. ii. p. 220). oxide melts in the electric furnace, and forms rose-coloured crystals (Moissan, C. R. 115, 1034

[1892]).

Cobaltous hydroxide CoO.H. (vol. ii., p. 220).

A. de Schulten (C. R. 109, 266 [1889]) obtained as this compound in microstopic, brownish-red, four-stiled prisms, S.G. 3-597 at 15°, by heating 10 g. CoCl, 6aq in 60 c.c. water with 250 g. KOH, in a flask filled with coal-gas, letting stand for 24 hours, and washing away the lighter amorphous products of the reaction.

ous products of the reaction. • Cobalto-cobaltic oxides (vol. ii. p. 221). Regarding Co,O, and oxides intermediate between this and Co2O2, v. Schröder, C. C. 1890. [1] 931 (abstract in C. J. 58, 1213 [1890]). Co.O. heatel to c. 1750° loses all its O, and leaves Co (Read,

C. J. 65, \$13 [1891]).
Cobalt, dioxide of. By the reaction of IAq and NaOHAq on CoSO, Aq, filtering, and acidifying with acetic acid, Vortmann (B. 24, 2744) abstract in C. J. 60, 1429 [1891]) obtained a greenish-black pp. nearly agreeing with the formula CoO... For compounds of CoO, with Bab v. Rousseau, C. R. 10t, 61 (abstract in C. J. 56, 1115 [1889]).

1115 [1889]).

Cobalt, salss of (vol. ii. p. 221). Marshall
(C. J. 59, 760 [1891]) has prepared the salts
Co.(20], 18aq and Co.(Co), 3(NH₁), Co, 6aq
by electrolysimps solution of CoSO, in H.SO, Aq,
and of CoSO, (a) containing (NH₂), 20, 4.

COBALTAMMINES (vol. ii. p. 222). By
cryoscopic determinations, Petersen (Z. P. C.
10, 580 [1892]) concludes that the formula generally given to the chief cobaltarumines are mole-

rally given to the chief cobartammines are molesolution containing $Co(NO_2)_p$ with a very new countries of the constitution of $Co(NO_2)_p$. Co remaining insoluble, and sometimes also a basis mitrite; when heated in Ni estimates of N are given off and then aspid decomposition of N are given off and then aspid decomposition occurs with formation of 60 and oxides of Coq shen mixed with combustible substance Co_2NO_2 berg (B. 22, 2649), and V. a. Magdeburg (B. 22, 2649), and V. a. Magdeburg (B. 22, 2649), and V. a. 2680; absträcts in C. J. 58, 14 [1890]). V. a. Morgulis (B. 22, 2644; abstract in C. J. 58, 13 [1890]), describe several mercuricobaltammines. Anumber of croceo-, luteo-, and xantho- salts and salts, are described by Jörgensen in Zeit. f. anorg, Ghemie, 5, 147 (abstract in C. J. 65 [11], 50 [1894]). also several flavo- salts isomeric with the croceo-

COPPER (vol. ii. p. 251). An elaborate investigation of the at. w. of Cu has been made by Richards, P. Am. A. 26, 240 [1891] (v. C. N. by McMarkey, $A.M. A. 20, 240 [1631] (8.00.14), 65, 236, &c.; abstract in G. J. 64 [11], 12 [1893]). CuSO, <math>5H_2O$ was analysed and synthesised, and CuO was analysed; the final value obtained by B. is 63.604 (Q=15.96). The molecule of Cu i. dilute solu-(U = 10 '90). The inolectic of the fitted solution in tin is probably monatomic (Heycock a. Neville, C. J. 57, 376 [1890]). For the absorption spectra of solutions of OuCl₂, CuSO, and Cu(NO₁), v. Evan, P. M. [5] 33, 317 (abstract in C* J. 64 [11], 149 [1893]).

Preparation. - For the preparation by electrolysis of pure copper v. Richards (P. Am. A. 25,

199, 206 [1890]).

Reactions .- Heated in the electric furnace, using a current of 70 velts and 350 ampères, Cu rapidly volatilises, and the vapour forms CuO in the air (Moissan, C. R. 116, 1429 [1833]). According to Neumann (M. 13, 40 [1893]), the H occluded in Cu, prepared by reducing CuO by . H, cannot be wholly expelled by heating in a stream of CO,; some of the CO, is also absorbed by the Cu. N. also says that Cu reduced by vapour of MeOH or EtOH, or by coal gas, retains very small traces of C and II after being heated to 220°. Montemartini (G. 22, 484, heated to 220%. Montemartin (c. 22, 2004, 2007, with a little N₂O₂, and with 70 p.c. acid only NO₃ is given' off; no appreciable quantity of NH₃ is produced with acid from 3 to 27.5° p.c. HNO₃. According to Freer a. Higley (Am. 15, 71 [1893]), the only gaseous products of the reaction of Cu with excess of HNO₄Aq S.C. 1.4 (c. 65 p.c. HNO₃) are NO₂ and N₂O₃, c. 90 p.c. NO₃ and 19 p.c. N₂O₄. Cu is superficially oxidised in NO at a dull red heat (Sabatier a. Senderens, C. R. 114, 1429 [1892]). Reduced Cu absorbs NO, at the ordinary temperature, forming a brownish powder Cu, NO, (S. a. S., C. R. 115, 236 [1892]). For the reactions of this nitrocopper v. S. a. S., C. R. 116, 756 (abstract in C. J. 64 [11], 874 [1893]).

Copper, alloys of (vol. i. p. 253). For a description of alloys of Cu with Oc, Sn, and Zn, prepared by immersing plates of Cd, Sn, or Zp, in solutions of salts of Cu, v. Mylips a. Fromm, B. 27, 630 (abstract in O J. 66 [11], 235 18941). li a

Cupric browlde (vol. ii. p. 254). According to Sabatier (C. R. 118, 980 [1894]), the green erystals that separate from CuBrAq are CuBr, 4sq. A solution of CuBr, in conc. HBrAq hee an intense purple colour which becomes less marked on dilution, but even with ·0015 mgm. Cu in solution the colour can be detected (S., l.c.) The double salts CuBr. CsBr and CuBr. 2CsBr are described by Wells a. Walden

(Zgit. f. anorg. Chem**p**, 5, 304; abstract in U. J. 66 [11], 47 [1894]).

Qupric chloride (vol. ii. p. 255). Tzuchanoff (J. R. 25, 151; abstract in C. J. 66 [11], 47 [1894]) ands that the E.O. of dilute blue-coloured CuOl, and increases with increase of concentration to a maximum, after which if decreases while the colour changes to yellowish-brown. For heats of polution and dilution of CuCl., 2aq, v. Reicher ..

Jointon and dilution of Cubl., 2aq, v. Reicher Leventer (Z. P. C. 5, 559 [1890]).

**Diable salts.—CuCl., HCl. 3aq,
CuCl., LiCl. 2aq, CuCl., HCl. 2aq, CuCl., ECl, and CuCl., 2Cl. 2aq, (Chassevant, 4. Ch. [6] 30, 5 [1893]); CuCl., CsCl,
CuCl., ECl. 2aq (x = 0 and 2), and 2CuCl., 3CsCl
CuCl., 2CsCl (xaq (x = 0 and 2), and 2CuCl., 3CsCl
CuCl., 2CsCl (xaq (x = 0 and 2), and 2CuCl., 3CsCl
CuCl., 2CsCl (xaq (x = 0 and 2), and 2CuCl., 3CsCl (Wells a. Dupree, Zeit. f. anorg. Chemie, 5, 300

(18931). Cuprous chloride (vol. ii. p. 255).

(L.c., p. 306) describes the double saits
2CuCl.CsCl, 2CuCl.3CsCl, and CuCl.3CsCl. aq.
Cupric fluoride (vol. ii. p. 256). Poulenc
(C. R. 116, 1446; abstract in C. 7. 64 [11],
525 [1893]) prepares CuF₂, as a white amorphous
powder, by heating NH₄F with CuF₂. 2aq; by
heating in HF at 500° (not above) the CuF₂ becomes exvisalling. Cyptalling CuF₃ is also ob. comes crystalline. Crystalline CuF, is also obtained by heating CuO, or CuF₂. 2aq, in "HF at 400° (P., l.c.). Heated to 300° in air CuO is formed; heating in steam gives CuO and HF; H₂S forms CuS and HF; HCl forms CuCl₂. CuF₂. absorbs water from the air, and becomes blue. H. von Helmholt (Zeit. f. anorg. Chemie, 3, 115 [1892]) describes the double salts CuF. KF,

CuF, RbF, CuF, AmF. x: aq, and CuF, 2AmF. 2aq.
Cuprous fluoride (vol. ii. p. 256). According to Mauro (Real. Acad. Lincei, 1892 [1], 194; asstract in C. J. 64 [11], 124 [1893]), Cu,F, does not exist, and the substance obtained by Berzelius was almost certainly merely impure copper. Poulenc, however (C. R. 116, 1446; abstract, in C, J. 64 [11], 525 [1893]), says that Cu_xF₂ is formed by heating Cu_xCl_x to dull reduces in HF (the action is not complete until 1100°-1200°); also by heating CuF₂ in HF at c. 600°, raising the temperature to 1100°-1200° towards the end of the reaction. P. describes Cu.F. that has been fused as a ruby-red, transparent solid, with a crystavline fracture; exposed to moist air it changes to CuF₂. xaq; it is easily reduced by H at a red heat.

Cuprous iodide (vol ii. p. 256). Brun

Cuprous iodide (vol. ii. p. 256). Brun (A. R. 114, 667; abstract in C. J. 62, 1157 (1893)) describes double compounds with (NH,)520, and NH,I, and also with (NH,)820, and Cu,820; Cuprous exide (vol. ii. p. 258). Russell (C. N. 68; 308 (1893)) prepares Cu,0 by completely reducing Ch2O,Aq mixed with excess of NaCl by SO, heating till excess of SO, is removed, and then ppg. by Na,CO, added solid 42 file (not solution. With HFAq, CuFA4 and Cu are formed (Poulenc, C. R. 116, 1446 (1893)). Cuproc. exide (vol. ii. p. 258). Moissan (C. R. 115, 1034 [1892]) says that CuO is entirely decomposed in the electric furnace at c. 2500°, yielding Cu and a cryst/lline compound of CuO and CaO (the reaction was effected in a block of CaO). By heating CuO to whiteness, in a 14etcher injector-furnace, iff an oxidising amosphere, Bailey & Hopkins (C. J. 57, 269) almosphere, Bailey at Hopkins (C. J_v.57, 269 [1890]) obtained a very hard, yellowish-red

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solid agreeing with the formula Cu.O. Richards (P. Am. A. 26, 281 [1891]) found that CuO decludes gas, chiefly N ; when prepared by heating Cu(NO_s), the oxide retained c. 08 p.c. of its weight of N, which could not be removed by heating. For experiments on the deliveration of

heating For experiments on the defidration of CuO.xin 0 v. Spring a. Lucion (Zeit. f. amorg. Chemic. 2, 195; abstract in C. J. 64 [11], 210 [193]). For colloidal, jelly-like CuO.xH 0 v. J. van Bemmelen (Zeit. f. amorg. Chemia, 5, 466; abstract in C. J. 66 [11], 191 [1894]). Copper, oxybromides of (vol. ii. p. 260). Dupont a. Jansen (Bl. [3] 9, 193; abstract in C. J. 64 [11], 463 [1893]) obtained the salt 3CuO.CuBr. 3aq by heating Cu.Br. As with CuO in a sealed tube at 200°, or, better, by heating neutral dilute Cu.Br. Aq at 225°; the compound crystallised in green rhembohodral plates, S.G. crystallised in green rhembohedral plates, S.G. 4.39.

Copper, oxychlorides of (vol. ii. p. 260), v. Rousseau, C. R. 110, 1261 (abstract in C. J. 58, 1058 [1896]).

Copper, exysulphides of (vol. ii. p. 260), v. Cliche, Ar. Ph. 228, 374 (abstract in C. J. 58, 1211 [1890]).

Copper, phosphides of (vol. ii. p. 260). For descriptions of Cu₂P₂ and Cu₂P, prepared by heating Cu in vapour of P, v. Granger, C. R. 113, 1401; and for Cu₂P₂, prepared by heating red P with excess of Cu-phosphite and water, v. G., C. R. 117, 292 (abstracts in C. J. 62, 410 [1892]; and 64 [11], 526 [1893]).

Cupric sulphide. From experiments on the

interaction of H₂S and CuSO₄Aq, and CuSO₄Aq in presence of acetic acid, Linder a. Pictod (C. J. 61, 120 [1892]) conclude that a compound TOUS.II.S is formed, and that then such configurates as 9CUS.H.S and 22CUS.H.S are produced, and finally (CUS), is formed.

COPPER.AMMONIUM COMPOUNDS (vol. ii. p. 262). Several derivatives of curriammonium

bromide are described by Richards a. Shaw (P. Am. A. 28, 247 [1893]).

FERRICYANIDES. Barium ferricyanide (vol. ii. p. 337); v. Ranmelsberg, J. pr. [2] 39, 455 [abstract in C. J. 56, 950 [1889]).

Lead ferricyanide (vol. ii. p. 339); v. Ram-

melsberg (l.c.).

Potassium ferridyanide (vol. ii. p. 339); v. Kassner, Chem. Zeit. 13, 1701 (abstract in C. J. 58, 352 [1890]).

DIDYMIUA (vol. ii. p. 382). For an investigation into the separation of Di and Er. v. Krüss, A. 265, 1 (abstract in C. J. 68, 1424 [1891]). For the emission spectra of oxides of neodymium and praseodyn up, v, Haitinger, M. 12, 362 (abstract in C. J. 62, 2 [1892]). Read (C. J. 65, 313 [1894]) says that Di.O. is unchanged at c. 1750°.

ERBIUM (vol. ii. p. 456). For the separation of compounds of Er and Di. v. Krüss, A. 2657 I (abstract in C. J. 60, 1424 [1891]).

FERRITES ool, ii. p. 547). J. van Bernmelen a. Hobb's (J. pr. [2] 46, 497 (18.78) say that Fe₂O₂K₂C and Fe₂O₂No₂O are obtained, in crystals by continued heating Fe.O. with conc. KOHAq and NaOHAq respectively; these ferrites are decomposed by sater, giving Fe,O,H,O.

FLAME (vol. ii. p. 549). Reference should

be made to Smithells a. Ingle on 'The Structure and Chemistry of Flames' in C. J. 61, 204

and Chemistry of Flames in C. J. 61, 204 [1892], and to Lewes on 'The Luminosity of Coal-gas Flames' in ibid, p. 322. FLUORHYDRIC AUD (vol. ii. p. 558). Berthelot a Moissan (C. R. 109, 209 [1889]) give the thermal data [H.F] = 37,600; [H.F.Aq] = 49,400. For the description of an apparatus for purifying HFAq. v. Hemilton (C. N. 60, 252 [1889]).

FLUORINE (vol. ii. p. 560). Moissan (C. R. 111, 770 [1890]) determined the at. w. (L) by converting Na₂CQ, into NaU, and shis into NaSO. verting Na₂Ck, into Nat', and shis into Na₂Ck, (2) by converting CaF, into CaSO, and (3) by converting Bak, into BaSO,; the mean of the results regarded by M. as the most trustworthy was 19.05. V.D. at the ordinary temperature, 18.3 (Moissan, C. R. 109, 861; v. abstract in C. J. 58, 208 [1890]). A column of F one metre long shows no definite absorption bands (M. Lc. 19. 937) • for the emission spectrum v. M. (i.e., abstract in C. J. 58, 329 [1890]). F does not liquely at -95° at the ordinary pressure (M. A. Ch. [6] 25, 125 [1893]). Gladstone (P. M. [5] 31, 1 [1891]) has determined the atomic 1870 fraction of F in C.H.F to be as follows for the different lines of the solar sportrum, at 22.8°;—
A C D A A H
at refraction 63 63 53 48 44 35

The values are much smaller than those for Cl, Br, or I, which are 10.0, 15.23, and 25.2 for the line A.

Kormation. - According to Brauner. (C. J. 65, 393 [1894]), F is given off when 3KF.PbF., HF ... LEAD TETRAFLUORIDE, p. (45) is heated to dull redness.

Reactions.—F combines with the more porous forms of carbon at the ordinary temperature, with incandescence, forming CF4; the denser forms of C combine with incandescence at from 50° to 100° (Moissan, C. R. 110, 276; abstract in C. J. 58, 557 [1890]). For a discussion of the chemical relations of F, v. Moissan, Bl. [3] 5, 880 [1891].

GALLJUM (vol. ii. p. 597). Lecoon de Boisbaudran (C. R. 114, 815; abstract in C. J. 62, 930 [1892]) gives measurements of the chief links in the spark emission spectrum of Ga; the spectrum varies much according to the condi-

GERMANIUM (vol. ii. p. 610). A new mineral from Bolivia, antipolate, Ag. GeS., identical in composition with argyrodite from Freiberg, but crystallying in isometric forms (the form of argyrodic is monoclinic), is described by Kenfield in Am. S. [3] 46, 107 (abstract in C. J. 66 [11], 12 [1894]).

9. GOLL (vol. i. 9. 647). Majlet (Pr. 46, 71; abstract in C. J. 68, 708 [1890]), has re-deter-

mined the al. w. of gold by various methods; the mean value obtained is 1969, but the value 196.88 M. thinks is more trustworthy. The molecule of gold in dilute solution in tinis probably monatomic (Heycock a. Neville, C. J. 57, 878. [1890]). Gold volatilises considerably in the electric furnace with a current of 70 volts and 360 ampères (Moissan, C. R. 116, 1429 [1893]).

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Concerning the volatilisation of gold v. Rose (C. J. 63, 714 [1893]). Neumann (M. 18, 40 [1892]) says that gold absorbs from 33 to 46.5 [1892] says that gold absorbs from 35 to 350 whene its volume of O at c. 450°. According to Petersen (Z. P. C. 8, 601 [1892]), the heats of formation of Au.O., 3H, O from gold A(1) reduced from AuGl., (2) from AuBlr., and (3) from AuBr, differ very markely. From the results AuBr, differ very markelly. From the results of many experiments on the reaction between gold and KCNAq, Maclaurin (6. J. 63, 721 [1893]) concludes that O must be present to accomplish solution, and that the equation $4Au + 8KONAq + O_q + 2HLO = 4(AuCN.KCN)Aq + 4KOHAq (Elsner, J. pr. 37, 323 [1846]) expresses the proponion between K and Au in the solution$ and Au in the solution.

Gold, alloys of (vol. ii. p. 648). For an alloy with Cd, AuCd, v. Heycock a. Neville (G. J. 61, 914 [1892]). For alloys with Cd and Sn, v. H. a. N. (G. J. 59, 936 [1891]). For alloys with Al and Sn, Cd and Bi, Cd and Pb, and Cd and Tl, v. H. a. N. (C. J. 65, 65 [1894]). For alloys with Cd and with Zn, prepared by immersing plates of Cd and Zn in solution of a salt of geld, v. Mylius a. Fromm (B. 27, 630; abstract in G. J.

66 [11], 235 [1894]).

66 [11], 256 [1894]).

Gold, bromides of (vol. ii. p. 648). Petersen

(J. pr. [2] 46, 328) upholds the existence of

Au, Br, against the statements of Krüss a.

Schmidt (B. 20, 2041); in a later paper (J. pr. [2] 47, 301) K. a. S. still maintain that AuBr, is the ultimate product of the reaction of Br with gold (v. abstracts in C. J. 64 [11], 126, 284). For the double salts AuBr. CsBr and AuBr. RbBr. v. Wells a. Wheeler (Am. S. [3] 44, 157 [1892]).

Wells a. Wheeler (Am. S. [3] 44, 187 [1832]).

Gold, ohlorides of (vol. ii. p. 649). Petersen

(T. pr. [2] 46, 328; 48, 88) maintains that

Au.Gl, is a definite compound; Krüss a. Schmilt.

G. pr. [2] 47, 301; Zeit. f. anorg. Chemic, 3

421) say this substance is a mixture (v. abstracts in C. J. 64 [11], 126, 284, 474 [1893]).

Double sails of AnCl, with CsCl and RbCl are described by Wells a. Wheeler (L.c.); for a double sail AnCl, AgCl, v. Hermann (B: 27, 596; bbstract in C. J. 66 [11], 234 [1894]).

Gold, sulphides of (vol. ii. p. 651). Concerning the conditions of formation of Au.S., v. Antony a. Lucchesi (G. 19, 545; abstract in C. J. 58, 1216 [1890]).

58, 1216 [1890]).

Auric sulphide Au₂S₂. This compound is formed, according to A. a. L. (G. 20, 601; 21 [11], 209; abstracts in C. J. 60, 526; 62, 480 [1892]), by passing H.S into a solution of AuCl₂-LiCl kept at -10°, extracting LiCl by absolute alcohol, and drying in N at 70°. Au₂S₂ is a brack, anorphous solid; decomposed by heat at 200°-205° to Au and S (for other reactions abstracts, Lc.).

v. abstracts, i.e.).
Schneider (U. S. Geol. Survey Bull. No. 90, 56 [1892]) obtained aqueous solutions of collisidal Au S and Au S

HYDRAZOIC ACID (v. p. 919, Addenda).
HYDROGEN (volvii, p. 719). The ratio between the densities of H'and O is 1.15-882; the weight in grams of 1 litre of H is '08991 (Rayleigh, Pr. 45, 134 (1893)). For solubinary in water, and in alcohol, v. Timotéeff (Z. P. C. 6, 141); Winkler (B. 24, 89). Henrich (Z. P. C. 9, 435); (abstracts in C. J. 60, 15, 384 [1891]. For the line spectrum of H, v. 82, 1043 [1892]). For the line spectrum of H, v.

Ames (P. M. [5] 80, 48 [1890]); and cf. Grun wald (M. 13, 111; abstract in C. J. 62, 1381

[1892]). Wilm (B. 25, 217; abstract in C. J. 62, 568 [1892]) describes a lecture experiment to show the occlusion of H by Pd. Regarding the occlusion of H by other metals v. Streintz (M. 12, 642; abstract in C. J. 62, 567 [1892]).

Baker (C. J. 65, 611 (1894)) found that a linkupe of equal volumes of dry H and dry Cl tid not explode in bright sunlight, and that more than a quarter of the mixed gases re-

more than a quarter of the mixed gases remained uncombined after exposure for two days se diffused light and two days to bright sun-

Reactions.—Neumann (Z. P. C. 14, 193 [1894]) has examined the reducing action of H occouded by Pt on solutions of salts of Al, Sb, As, Bi, Cd, Cu, Co, Au, Fe, Pb, Mg, Mn, Hg, Ni, Pd, Ag, Sn, Tl, and Zn. Regarding the rate of combination of H and O, v. Water (p. 860). Regarding the explosion of mixtures of H with

O and Cl, v. Chlorine (Addenda, pp. 904, 905).

'Hydrogen dioxide (vol. ii.,p. 722). Schöne (B 26, 3011; 27, 1233 [1893-4]) affirms the occurrence of H.O. in the atmosphere against the

contention of Ilosva (B. 27, 920).

Formation .- Regarding the formation from ether v. Dunstan a. Dymond (C. J. 57, 574, 988 [1890]). H.O.Aq is formed by the action of light on II.C.O.Aq, excess of O being present (Richardson, C. J. 65, 450 [1894]). Richardson (C. J. 63, 1110 [1893]) has examined the formation of

11.0, in urine exposed to sunlight.

Preparation.—By making commercial 3 p.c.
17.0 Aq distinctly alkaline by Na₂CO₃, filtering, seaking with 10-12 vols. of ether, separating the ethereal solution, evaporating this to 01-0025 of its original volume on a water-bath, and removing the rest of the ether by standing in a bell-jar over solid paraffin, Shiloff (J. R. 25, 293; abstrect in C. J. 66 [11], 186 [1894]) obtained a thick, transparent, slightly acid liquid, S.G. 1-2475, containing 79.6 g. H.O. in 100 c.c. For preparation of conc. H.O.Aq v. Talbot a. Moody

(abstract in C. J. 64 [11], 369 [1893]).

Molecular & eight. Tanmann in 1889 Molecular steight. Tammann in 1889 (Z. P. C. 4, 411) by cryoscopic measurements determined mol. formula to be H₂O₄; but T.'s results stere called in question by Carrest in 2000 (Z. 0.5) who found red w 29.00 1893 (G. 22 [1], 341), who found mol. w. 33-92 (A.O.) com cryoscopic measurements, and this resulf was confirmed by Orndorff a. White (Am. 15, 347-[1893]), and also by Tammann himself (Z. P. C. 12, 431 [1893]).

Reactions.—Regarding the reaction between H₂O₂Aq and KMnO₄Aq, v. Engel (Bf. [3] 6, 17; c. asstract in C. N (2), 277 [1892]).

Hydrogen sulphide (vol. ii. p. 725). Henrich (Z. P. C. 9, 435 [1892]) gives the absorption coefficient of H.S. by water as 4 4015-089117. says that ILS dried by CaCl. and P.O. does not readen dry litnus paper, and does not read with redden dry lithnus paper, and dees net react with BaO, or Fe.O., nor with salts of Sb, As, Bi, C3, Co, Cu, Pb, Hg, Ag, or Sk. According to Peller (*C. J. 57, 625 [1090]), the equation 2H.St. 30, 22SO, 22H.O correctly represents the explosion of H.S and air or O.

HYDROXYLAMINE (vol. ii. p. 734), c.NH.OH has been isolated, as a solid by Lobert 1.

(R. T. C. D. 100; 11, 184 aostracis in C. J. 62, | Hertz (Z. P. C. 1, 358 [1890]) found the value 402, 1891 [1892]). NHOH.HCl dissolved in 254 for the mol. w. of iodine.

MeOH is treated with CH,ONa solution, and most According to Meineke (Chem. Zeitung, 10, of the MeOH is distilled off at 100 mm. pressure; the residue is distilled in small portions at 40 mm, pressure (for details v. C. J., L.c.). For the preparation from 2NHOH.ZnCl, v. Crismer, Bl. [3] 6, 793 (abstract in C. J. 62, 771 [1812]). For details of suitable apparatus for the fractionation of NHOH. of NH₂OH in vacuo, v. Brühl (B. 26, 2508 [1893]) cf. L. de B., B. 27, 907, and reply by Be bid 67. L. de B., B. 27, 907; and reply by 18, 50d 1847 [1894]. For thermal data of NH.OH. v. Berthelot a. André (C. R. 110, 830; abstract in C. J. 58, 934 [1890]). Hydroxylamine is a whito inodorous solid, melting at 8, 33°, and remaining superfused at 0°; boils at 58° under 22 mm. pressure; decomposes at 90°–100°, and detonates at a higher temperature. S.G. 1:35; S.G. when liquid, I:23. A drop heated in a test tube explodes very violently (v. Brühl, L.c.). B., L.c., discusses the molecular refraction of NH₂OH. NH₂OH is fairly sable up to 15°, then gradual decomposition occurs, giving NH₂, IRVO, and H.N.O., which react with unchanged NH.OH producing 20 and N M. de B. B. 27, 967s abstract in f. J. 66 (11), 278 (1891). For a full acount of the reactions of NILOH v. Lobry de Fruyn (L., ; abstract in C. J. 62, 1391 [1892]). IH,OHLICI in water and NaNO,Aq react to orm Na,NO,Aq (v. Tamatar, J. R. 25, 312; bstract if C. F. 66 [11], 136 [1894]; cf. Visilicenus, B. 26, 771; abstract in C. J. 64, 18, 1892. Earther continued to the control of the control 18 1892). For the reactions of 2NH OH H SO vith NaOHAq v. Kolotoff (J. R. 25, 295; abtract in C. J. 66 [11], 187 [1894]). For combounds of NH₂OH with metallic salts, v. Crismer Bl. [3] 8, 114); Goldschmidt a. Syngros (Z. Q. . anorg. Chemie, 5, 129); and Feldt (B. 27, 401) (abstracts in C. J. 58, 558 [1890]; 66 [11], 45, 187 (1894)). Kolotoff discusses the constitution of NH.OH in J. R. 23, 3 (abstract in C. J. 64 [11], 114 [1893]). Kjellin (B. 26, 2377) describes NHEt.OH and NHMe.OH (abstract in C. J. 66 [11], 9 [1894]).

INDIUM (vol. iii. p. 1). The molecule of indium in dilute solution in tin is perhaps diatomic (v. Heycock a. Neville, C. J. 57, 376 [1890]). Linder a. Picton (C. J. 61, 131 [1892]) [1890]]. Linder a Picton (C. J. 61, 131 [1892]) failed to isolate indiam lydrosulphides but they think that it is formed by passing ILS into water with In.O., xH.O in suspension; the continued passage of ILS produces, In.S., Read (C. J. 65, 3130 [1894]) found that indiam sequi-octide, In.O., is unchanged at continue sequi-octide, In.O., is unchanged at continue to the Mol. R. of, HIAq strong 20.77 to 67392 p.c., v. Perkin (C. J. 55, 708 [1889]), y For a research on the dissociation of III, v. Indienstein (Z. P. C. 3, 56 [1894]), photon 20.77 to 3.61 [1894], pho

on the dissociation of HI, v. Bodenstein (Z. P.C.).
13, 56 [1894]; abstracts in C. J. 64 [11], 369;
56 [14], 12 [1893-4]). Micking (B. 26, 2007) has isolated three hydrates of HI: HI.2H.O., melting at o. -43°; HI.3H.O., melting at q. -48°; and HI.4H.O., melting at c. -30°.5°.

10DINE (vol. iii. p. 14). The mol. w. of iodine dissolved in Et. or CS, was found by Beckmann (Z. J. C. 5, 76 (1890)) to be 274, from determinations of the boiling-points; tackeresults were coffrmed by Sakurai (C. J. 21, 997, 1892)). By determining the lowesing of the [1892]). By determining the lowering of the t.p. of naphthalene by solution therein of I,

According to Meineke (Chem. Zeitung, 10, 1213, 1230), very pure I is prepared by covering ordinary. I with a solution of CaCl., S.G. 1.85, ordinary. I wind a solution of Chicle. S.G. 1-20, mixed with a little cone. KIAq and a few drops of HClAq, heating until the I fuses, letting cool, washing the I, drying and subliming K twice, the first time with addition of a little BaO.

1-3r the reactions of I with KClO₂, and with

KClO and water, v. Potassium chiorate (Ad-

denda, p. 905).

Iedine monochloride (vol. iii, p. 17). therfinal data bearing on the two forms of ICl, v. Sortenbekey (Z. P. C. 10, 483; abstract in C. J. 62, 1987 [1892]). Tannar (J. R. 25, 97; abstract in C. J. 64 [11], 514) gives details of the

methods for preparing the two forms of ICl.

Iods'es (vol. iii. p. 21). For iodates of casium and rubidium, v. Wheeler, Am. S. [3] 44, 123 (abstract in C. J. 64 [11], 68 [1894]). Pure potassium iodate is prepared, according to Gröger (Zeit. angew, Chemic, 1894, 13), by heating to 100 for 20-30 minutes 20 g. KI in as little water as possible mixed with 40 g. pure KMnO. in 1,000 c.c. water, reducing excess of KMnO, by cautious addition of alcohol, filtering, adding acetic acid till acid, evaporating to c. 50 cm. washing the crystals of KIO, with cone alcohol, and drying. By heating KIO, till it fuses, O and some I are given off, and KI finally remains: no other oxy- compounds are formed (Cook, C. J. 65, 802 [1894]).

oo, 802 (1894)).
IRIDIUM (vol. iii. p. 46). From analyses of the salts ICl₂3KCl. aq and ICl₂3NH Cl. aq, Joly deduced the value 192-75 for the at. w. of Ir (C. B. 110, 1131 [1890]). According to Prinz (C. R 116, 392 (1893)), ir crystaleses in regular octa-hedra and in forms derived therefrom. Mylius a. Foerster (B. 25, 665 [1892]) stated that Ir is slightly volatilised when heated in a current o CO and Cl to c. 238'; Antony, however (G. 25 [11], 547 [1893]), asserts that no trace of an volutile compound of Ir is formed under thes conditions.

Irid-ammonium salts (vol. iii. p.47). Palmae (B. 22, 15; 23, 3810 [1889-90]) describes a nurber of irido-ammonium compounds. He call then irrido-amminium compounds. He call them irridium pentammine satis, and formulate them as Ir(NI₁)₂X₁; compounds are describe where X₁ · Cl₂, GlBr₂, ClL₂, ClSO₃, Cl(NO₂), Cl(NO₂), ClC₂O₅, ClPtO₄; also where X₄ · B; BrSO₄, and Br(NO₂)₂. One-third of the Cl is the salt when X₂ · Cl, is not removed by the action of cold II.SO₄O₄ or cold AgNO₄O₄; the rection of cold II.SO₄O₄ or cold AgNO₄O₄; the rections of the salts are similar to those of the purpureo-cohaltanumines (v. vol. ii. p. 227) (abstracts in C. J. 56, 352 [1889]; 60, 402 [1891] In B. 21, 2090 (b. abstract in C. J. 60, 11 [1861]) P. describes compounds analogous with the reso₂cobasic salts Co₂(NH₂)₁₀(H₂O₂)₂N₁, xfq; at the I. Walts are almost coldurless, P. thinks the prefix rosco- is unsuitable, he calls them irridium artuopen ammines and formulates them as Ir(NH₂)₂(H₂O)X₁, Salts are described in which X₁=Br₁, Cl₁, and (NO₂)₂. The chlorids In(NP₂)₂(H₂O)Z₁; is formed by boding, for five boufs, S. g. Ir(NH₂)₂(I₂), with 1½ times the calculated weight of KOH in 50 c.c. water, filtering, partially freezing the filtrate, adding 30 c.c. tuming HClAq, washing the pp. thus formed them ir diumpentammine salts, and formulate faming HClAq, washing the pp. thus formed

with 22 p.c. cold HClAq and then with alcohol. dissolving in water, and again ppg. by conc. HCIAq (for details v. abstract in O. J. 60, 1166

Iridium tribromide (vol. iii., p. 48). · Compounds of this bromide with PBr, age described by Goisenheimer (C. R. 111, 40; abstract in C. J. St., 1383 [1890]). By heating IrO...xH.O with IrBr, and PBr, red heedles of IrBr, 3PBr, and PBr, the street in the property of the street in the stre are formed; by heating this with PBr, plack crystals of IrBr, 2PBr, are producedo

Iridium tetrabromide (vol. ifi. p. 48). Geisenheimer (l.c.) describes the compound IrBr, 2PCl,

obtained by heating IrBr₃.3PBr₃ with PCl₃.

Iridium trichloride (vol. iii₁₁ p. 48). The fohowing compounds with PCl₃ are described by Geisenheimer (C. R. 110, 1004; abstract in C. J. 58, 1068 [1890]). IrCl₂,32Cl₃; IrCl₂,2PCl₃; IrCl₂,PCl₃,2PCl₃; IrCl₂,PCl₃,2PCl₃; IrCl₃,PCl₃,2PCl₃, Yarious compounds of IrCl₃ with H₃PO₃ and H₂PO₄. and salts of these, are also described. (C. R. 110, 1336; abstract in C. J. 58, 1069 [1890]) also describes the complex compounds 2IrP_Cl₁.5AsCl₂ and IrCl₂.2PCl₂.2AsCl₃. For the salts IrCl₂.3KCl. aq and IrCl₃.32mCl. aq, v. Joly (C. R. 110, 1131; abs/ract in C. J. 58, 1067 [1890]). For a description of IrCl, 37, iCl. xaq, v. Listony (G. 23 [1], 190; abstract in C. J. 64 [11], 880 [1893]). According to A. (G. 23 [1], 184; abstract in, C. J. 64,[11], 379 [1890]), the passage of H2S hrough a 2 p.c. solution of IrCl, 3KCl produces pps. which are mixtures of Ir₂S₂ and IrS₂.

Iridium dioxide (vol. iii. p. 50). For methods

of preparing IrO, v. Geisenheimer (C. R. 110, 855; abstract in C. J. 58, 948 [1890]).

• Iridium disulphide (vol. iii. p. 50). IrS₂ is obtained by passing FLS over IrCl₃3LiCl at 42, 170 [1890]. to 7°, washing with absolute alcohol, and drying at 90° to 100° in a current of CO. (Antony, G. 23 [1], 190; abstract in C. J. 64 [11], 380 [1893]).

IRON (vol. iii. p. 51). Lockyer (Pr. 54, 359 [1893]) gives the emission spectrum obtained by using vary fine electrolytically deposited iron as

using wiry fine electrolytically deposited iron as the poles of an electric lamp.

Properties and Reactions.—Iron volatilises in the electric furnace, using a current of 850 ampères and 50 volts (Moissan, C. R. 116, 1429 [1892]). Iron is superficially oxidised by heating to dull redness in NO (Sabatier a. Senderons, C. R., 114, 1429 [1892]); heated in NO tea 850° reduced iron is oxidized with fix. NO, to c. 850°, reduced iron is oxidised with in-NO₂ to 0. 550°, reduced from is exidated with incondescerice to Fe₀O₂ (S. a. S., C. R. 115, 236 [1992]; cf. abstract in C. J. 66 [11], 95 [1894]). Montemartini (G. 22₁[1]₆:7.50) says that NH₃, N₂O, and N are formed by the solution of iron in excess of 27:5 p.c. HNO₃ q (for, quantities, v. abstract in G. J. 62, 1278 [18.32]). For quantities of the district of the district of the conduction tities of iron dissolved by HNO, Aq of different concentrations, v. Gautier a. (Parpy (C' R. 112, 1451; abstract in C. J. 60, 126 ft 91]).

Passivity of iron. Concerning the passivities of steel and wppught iron to HNO, Aq. v. Andrews (Pr. 48, 146, 40, 41), abstraction

Tron, by acchloride of. The comegund

Iron, by acchloride of. The compound Febril, was obtained by Lenormand (J. R. 116, 820; abstract in C. J. 64 [11], 371 by heating FeCl, with excess oi. Br in a sealed tube at c. 100°. The compound is opaque in thin

sections, and green by reflected light; very de-liquescent; crystallists probably in hexagonal plateg; easily sol. alcohol and ether, CS., &c., can be sublimed by heating in a tube containing a little Br.

Iron catelide. Arnold a. Read (C. J. C.5, 788 [1894]) confirm the existence of Fe₂C in steel (v. Abel, Proc. Inst. Mechan. Engineers, 1885, CO; also Müller, Stahl und Eisen, No. S); ... a. R. say that two forms of Fe₂C are found ih stee

Iron carbonyls. In 1891 Mond a. Quinote (C. J. 59, 604) obtained a compound of Fe with CQ; further investigation of the reaction by Mond a. Lenger (C. J. 59; 1090 [1891]) led to the isolation of two compounds.

Ferropentacarbonyl F. (CQ). 195.55. V.D. at $142^{\circ} = 93.2$, S.G. $\frac{16^{\circ}}{100} = 1.4664$: distils completely, without decomposition, at 102.8° under 749 mm. pressure; solidifies at -21°.

Preparation.—FeC.O., ppd. by adding a slight excess of K.C.O.Aq to hot FeSO.Aq, is well washed, and dried at 120°, it is then heated in a slow stream of H, temperature being raired until the substance in the tube is black, and then kept constant until gas ceases to come off, when the current of H is stopped; the product is allowed to cool in H, placel in water without coming into the air and treated with successive quantities of boiling water until sulphate is removed; it is then quickly dried on plates of gypsum, placed in the combustion tube, heated to c. 300° in H till quite ky, and allowed to cool in H. The tube is then con ngeted with a gas-holder containing CO, and the II is completely displaced by CO; one end of the tube is then sealed, and the open end is kept in connection with the supply of CO. After 24 hours the tube is heated to c. 120°, while a slow current of CO is passed through it, and the issuing gases are passed through a tube kept at -20°. When iron carbonyl ceases to come over, the tube is let cool, and is then again put in connection with the CO supply. These processes are repeated many times; the daily yield of the carbonyl is not more than c. 1 g. from 100 g.

Properties.—A pale yellow, somewhat viscous liquid; unchanged in the dark, but in-sunlight gipts solid Fe₁(CO), (v. in/ra); slowly decomposed on exposure to air, giving chiefly Fe₂O₂±H₂O; ann letely decomposed at 180° to Fe and CO; soluble in EtOH, Et₂O, Ch., mineral tile, &c. (For S.G., V.D., &c., v. supra.) Fe(CO), in not acted on by dilute H₂SO₂A₂, HClA₂ or HNO Aget the ordinary to respect to the contraction. HClAq, or HNO, aq at the ordinary temperature; bu is rapidly decomposed—to Fe(NO,),Aq, FeCl,Aq, or FeBr,Aq -by conc. HNO,Aq, ClAq, ar ZrAq.

Eiferroheptacarbonyl Fe (CO), Obtained by expang Fe (CO), in a sealed tube to sunlight for some hours, collecting the solid that forms, washing with ether, and drying over H.SO, for a short time. Yellow, listrous finkes; gradually decomposed by exposure to air turning brown.
Not of 5d on by H,SO,Aq or HC! Aq at the
ordinar, temperature; decomposed by HNO,Aq,
Of or Br.

Iron carbonyls seem to be present in water-

also semetimes in compressed coal-gas a. Ferrous chloride (vol. iii. p. 53). Chasse-ant (A. Ch. [6] 30, 5 [1898]) describes the leuble solds FeCl, 2AmCl, FeCl, LiCl, 3aq, and toe a. Scudder, C. J. Proc. 1891. No. 10 FeCl. 2KCl.

Ferril chloride (vol. iii. p. 54). By determining the vise of b.p. of alcohol and ether when FeCl. is dissolved in these solvents, Müller (C. R. 118, 644; abstract in C. J. 66 [11], 282 [1894]) finds that the molecular formula of the chloride in these solutions is FeCl, FeCl,Aq reacts with many metallic sulphides, when heated therewith in scaled tubes; FeCl.Aq. S. and a chloride of the metal & the sulphide are and a chloride of the increase of the sampling generally formed (Cammerer, C. C. 1891 [11]. 370; abstract in C. J. 62, 18 [1892]). Seehert a. Dorrer (Zeit. f. along Chemic, 5, 339, 411; v. abstracts in C. J. 66 [11], 140, 190 [1891]) have made a full investigation of the interaction of FeCl, Aq and KIAq; their results are in keeping with the hypothesis that the direct reaction $FeCl_{q}Aq + KIAq = FeCl_{q}Aq + KClAq + IAq$ is counterbalanced by the reverse reaction Fecl.Aq + KeAq + IAq = FeCl.Aq + KIAq. S. a. D. think that the first stage of the resaction is to produce an iodochloride; thus $FeCl_{2}Aq + KIAq = FeICl_{2}Aq + KClAq$; that this then decomposes, more or less completely then decomposes, more or less compared, according to conditions of concentration, time, temperature, and mass), into FeCl, Aq and IAq; and that FeICl, Aq, and probably FeCl, Aq, are re-formed until equilibrium is established. S. a. D. do not agree with the explanation of the mechanism of the reaction given by Carnegie (v. vol. iii. p. 55). Roozeboom (Z. P. C. 10, 477 [1892]) Has investigated the conditions of equilibrium in aqueous solution of the hydrates of FeCl.; he has isolated hydrates 2FcCl.xH₂O where x = 4, 5, 7, and 12. (For details, v. abstract in C. J. 64 [11], 119 [1893]). For a study of the interaction of FeCl.₃Aq and archivestic Lawring C. P. 112 [14]. oxalic acid, v. Lemoine, C. R. 116, 981 (abstract in C. J. 64 [11], 405 [1893]). A compound of of Cl, with nitroxyl chloride, FeCl, NOCl, was obtained by Sudborough (C. J. 59, 660 [1891]), by immersing iron in liquid NOCl, and letting the liquid stand over HSO,; the compound forms small golden-brown, deliquescent crystals

torms small golden-brown, deliquescenterystals (cf. vol. iii. p. 56; Combinations, No. 7).

Forsus fluoride (vol. iii. p. 56). FeF₂ was obtained by Poulenc (C. R. 115, 941; abstract in C. J. 64 [11], 122 [1893]) by passing alr-free HF over red-hot, from or dry FeCl₃; small, white, rhombic prisms; S.G. 4-09; decentioned by beauting with HSO. No CO. steam air, HCl. heating with H2SO4, Na2CO4, steam, air, HCl,

or H.

Ferric findride (vol. iii. p. 56). Poulche (l.c.)
obtained FeF, in small, very refractive, greenisty
crystals, S.G. 3-87, by passing HF over red-hot
ifon, FeO, FeF, xaq, or FeCl, ; also by dropping
FeF, xaq into fused AmCl and heating in a curcrystal or input green. FeF does not five at or H. rent of an inert gas. FeF, does not fuse at 1000°; but is decomposed by heating in ar, also, by fusion with Na CO₂, by heating in Ax, also by fusion with Na CO₂, by heating in steam, or with HCl or H. O₂. According to Speraksky (J. R. 24, 294; Abstract in C. J. 64 [11], 314 [1 33], FeF₂Adjshows a very small plectical conductivity; there is, therefore, no appreciable all strolyte dissociation; as the solution scarcely in the strong of some suggest R. Amplides. effects any inversion of cane sugar, S. concludes | l.c. p. 524).

that there is practically no hydrolytic dissocia-tion. Cryoscopic determinations showed that the molecules in a dilute aqueous solution are chiefly FeF, but indicated the existence of Fe,F.

chiefly FeF, but indicated the existence of FeF, in more gene solutions.

Iron, nitrides of (vol. iii. p. 59). Fewler (C. N. 68, 15 [1893]) obtained Fe,N by heating reduced iron in a rapid stream of NH,., (For details v. abstract.in C. J. 66 [11], 50 [1894]).

Fewic oxide (vol. iii. p. 61; also p. 57 for hydrate.). Atc. 1750° Fe,O. is completely changed to Fe,O. (Read, C. J. 65, 313 [1894]); in the electric furnace Fe,O. is formed, partly metted and partly crystallised (Moissan, C. R. 115, 1034 [1892]). According to J. van Bemmelou a. Klobbio (J. pr. 22 46, 497 (1893)), crystallised Fe,O. [140 is okained by treating with water the Fe O. H.O is obtained by treating with water the hexagonal crystals of Fe O. Na O formed by heating Food, for some time with cone. NAOHAq; the crystalline Fe,O, HO is not hygroscopic; H₂O is given off below 100°.

Iron, oxychlorides of (vol. iii. p. 62). Rousseau (C. R. 110, 4032; 113, 643; 116, 392; abstracts in C. J. 58, 1083 [1890]; 62, 119 [1892]; 64 [11] 280 [1893]) describes compounds xFeCl_xyFe₂O_y some crystalline and some amorphous, formed by heating FeCl, Aq at different temperatures, and also by the interaction of FeCl, and steam.

LANTHANUM (vol. iii. p. 116). Bettendorff (4, 256, 159 [1890]) obtained the value d38-28 for the at. w.; and Brauner (B. 24, 1328 [1891]) the value 138-21 (O = 16).

Winkler (B. 24, 873 [1891]) obtained results, by heating La O, with Mg in H, which pointed to the existence of a hydride of La (cf. Brauner,

LEAD (vol. iii. p. 122). The molecule in diffice solution in tin is probably monatomic (Heycock a. Neville, C. J. 57, 376 [1890]). The m.p. of lead was found by Griffiths a. Calendar using a Pt thermometer) to be 327-69° (C. N. 63, 1 [1891]). Lohmann (Z. K. 17, 274 [1890]) says that lead separated electrolytically, by a weak current, crystallises in leadets that are probably monosymmetric, but that the crystals are regular octahedra when separated by a strong current. Veley (S. C. I. 10, 206; summary of conclusions in C. J. 62, 410 [1892]) has examined the interaction of lead and nitric acid: an acid of intermediate concentration acts most rapidly; when HNO, is present the action in-preates. Montemartini (d. 22, 384, 397, 426 [1892]) found that a little NH₂ was preduced, esfecially with dilute IINO,Aq. Lead rapidly oxidises to PbO when heated in NO; oxidation occurs at c. 200° in NO₂, with for nation of a basic nitrate (Sabatier a Senderens, C. R. 114, 1429 – 115, 236 (1892). Lead rapidly

[11], 324 [1893]); and for K,Pb,Br, 4aq and K,Pb, (BYI), 4aq, v. Wolls, i.e. p. 190 (abstract,

8 N

Lead, chlorides of (vol. iii. p. 125). The statement, on p. 125 (vol. iii.), that only one chloride has been isolated is no longer true;

chloride has been isolated is no longer wue; PbCl, was prepared by Friedrich in 1893.

Lead tetrachloride (vol. iii. p. 126). PbCl, has been obtained by Friedrich (B. 26, 1484; abstract in C. J. 64 (11], 415 [1803]; cf. M. 14, 505; abstract in C. J. 66 [11], 16 [1804]), by passing cl into HCl. Andontaining PbCl, in suspension, adding NH,Cl to the solution thus obtained, separating and drying the compound PbCl, 2NH Cl thus formed, adding it to conc. cooled H.S. allowing the oily drops that formed to collect at the bottom of the vessel, and shaking these drops repeatedly (and duickly) with conc. H.SO. PbCl, is a transparent, yellow, very refractive liquid, furning in moist air with formation of PbCl2 and Cl; it is unchanged in contact with cold conc. H.SD, but when heated with the acid it decomposes explosively to PbCl, and Cl; when heated with conc. H.SO, in a ourrent of Cl, some PiCl, passes over, but at c. 105° explosion occurs. PbCl, has S.G. 3·18 at 0°; at c. -15° it solidifies to a yellowish, crystatic. talline mass. A hydrate is formed with a little water; but addition of mend water produces HClAq and PbO. By adding PbCl, to a little cooled cone. HClAq, a crystalline compound, probably PbCl .2HCl, is formed.

Several double salts of PbCl, with alkali chlorides haven been isolated. Classen a. Zahorski, (Zeit. f. anorg. Chemie, 4, 100) give the formula 2PbCl, 5AmCl to the salt formed by the formula 2PbCl_{*},5AmCl to the salt formed by digosting PbCl₂ with liquid Cl and furning HClAq, and adding AmCl; but Friedrich (l.c.) says the compound is PbCl_{*},2NH_{*},Cl. For compounds PbCl_{*},2MCl, when M=NH_{*}, Cs, K, and NBb, v. Wells (Am. S. [3] 46, 180; abstract in C. J. 64 [11], 523 [1893]); C. a. Z. (l.c.) describe compounds of PbCl_{*} with the hydrochlorides of compounds of the compound of the hydrochlorides of compounds of the compound of the hydrochlorides of compounds of the compound of the hydrochlorides of compound of the hydrochlorides of compound of the hydrochlorides of the hydrochlorides of compound of the hydrochlorides of compound of the hydrochlorides of the hydrochlo pyridine and quinoline (abstract in C. J. 64 [11],

461 [1893]).

Lead dichloride (vol. iii, p. 125). Several double convounds with alkali chlorides are described by Randall (Am. 15, 494 [1893]) Wells L. Johnston (Am. S. [3] 46, 25 [1893]); and Wells

L. J. Ahnston (Am. S. [3] 46, 25 [1893]); and Wells (I.c. p. 34). The compounds are of the forms, PbOl, 2MCl., PbOl, 3MCl. raq, and 2PbCl_MCl (v. abstracts in C. J. 64 [11], 523, 524 [1893]).

Lead, fluorides of (vol. iii, p. 127). Brauner (C. J. 65, 393 [1894]) has prepared the compound PbF, 3KF.HF in various ways; the simplest process being to dissolve Pb(C, H, O.), (R. Brackley b. 124, 24), (and p. first) in various ways. (v. RED OXIDE OF LEAD, Addenda, infra) in conc. HFAq and adl KF. By acting on this salt with cone. H₂SO₄-B. obtained evidence of the formation of lead setre, Loride, PbF₄, but he did

formation of lead *etr. f. toride, PbF., but he did not succeed in isolating the con sound.

Lead, iodide of (vo. iii. p. 127). Several double compounds of PbL, with alkali ibdides have been isolated by Well-, W. a. Johnstyn, and Herty (v. References under Lea. Browner, p. 91.5). For the compound PbL, 2MgL, 16a0, b. Otto a. Drowes (Ar. 'Fin. 229, 179; abstract in C. J. 64 [11], 984 [1893]).

Lead iodobromidee and ir-dochlorides (vol. iii. p. 128). Miss. Field (C. J. 63, 540, 11803).

iii. p. 128). Miss Field (C. J. 63, 540 [1893]) has dev. ibed the compounds 2Pf 7r. FbI., 2PbCl., PbI., and 5PbCl., PbI.

[1894]). The hydrage 2PbO.H.O (v.l. iii, p. 12: is obtained in large crystals by allowing a solution of PbO in KOHAq to cool in the air; CO is absorbed, and the hydrate is deposited in colourless, tetragonal crystals, a:b:c = 1: 82

Cloudekings Am. 13, 120 [1891]).

Red exide of lead (vol. iii. p. 180). Hutchin son a. Pollard (C. J. 65, 1136 [1893]) have son a with glacial acetic acid, and have isolated lead tetractate. acid, and have isolated lead tetrachtate. Pb(C;H,O,), melting at c. 175°, and decomposing a little above that temperature.

posing a little above that temperature.

Note.—The formula PbO(OC₂H₂O)₃ said to be assigned by Jacquelain to the salt obtained by him (vol. iii. p.,130, cbl. 2, line 28 from top; and p. 1,21, col. 2, line 24 from bottom) should have been given as PbO₂(C, H₂O₃), old notation.

Plumbates (vol. iii. p., 132). Kassner (Ar. Th. [3] 28, 109; abstact in C. J. 58, 561 [1890])

describes plumbates of Ba, Ca, and Sr. Regarding the dissociation of Ca plumbate, v. Le Chatelier (C. R. 117, 109; abstract in C. J. 64 [11], 524 [1893])

Lead oxylodides (vol. iii. p. 132). Gröger (M. 13, 510; abstract in G. J. 62, 1892) describes

the compound PbO.PbI... iii. p. 132). The salt Pb(O.H.O.), (v. supra, Red oxide of lead) belongs to the type PbX', to which form PbOl.

also belongs.

Lead, sulphide of (vol. iii. p. 18'i). According to Hannay (C. J. Proc., Noz. 139 and 141 [1894]), when air is passed into molten PbS, one half of the lead remains as lead, and one half is volatilised, and deposited as PbS; H. accounts for this change by supposing the reastion to be 2PbS + O₂ = Pb + PbS.SO₂, the volatile PbS.SO₂ being decomposed in the colder part of the apparatus to PbS and SO.

Lead sulphobromide and sulphochloride (vol. iii. p. 133). Parmentier (C. R. 114, 298; abstract in C. J. 62, 685 [1872]) obtained the compounds PbS.PbBr, and PbS.PbCl, by dissolving the halides in their acids and shaking the liquids while H2S was passed over the sur-

faces of the solutions.

LITH UM (vol. iii. p. 147). Guntz (C. R. 117, 732 [1893]) recommends to use a mixture of equal weights of LiCl and KCl, for the electrolytic preparation of the metal; the mixture melts t 450° and the m. decreases as electrolysis proceeds. (For ditails as to size of elec-"woden streagth of current, &c., v. abstract in C. J. 66 [11], 91 [1894].) Holt a. Sims, C. J. 65, 445 [1894], find that traces of a peroxide are formed, along with Li,O, by burning Li in O. Lithium, amide of LiNH₂. Formed by

gently yeating clean Li in a stream of NH, until violent action ceases, and then heating to c. 400° until the reaction is finished. A white, crystalline, transparent solid; melts between 5,00° and 400°; lecomposes in cold water slowly, is 30° and 400°; tecomposes in cold water slowly, giving LioHAq and NH; decomposed by heating it, air, but without taking fire (Titherley, U. J. 55; 504 [1894]; g. v. for further reactions). Lithium, bromide of (vol. 40ii. p. 150). The hydrates LiBr. xaq, where x 11 and 2, are described by Bogorodsky (J. R. 25, 3.3 [1895]).

Lithium, chlowide of (vol. 41i. p. 150). For LiC. aq and LiCl. 25q v. Bogorodsky (L.). For the dayle company LiCl MCl. area, where

Lead protoxide (vol. iii. p. 128). PbO is, LiC. aq and LiCl. 22q v. Bogorodsky (Lc. unchanged at c. 1750° (Read, C. J. 65, 818) the double compounds LiCl.MCl. 22q,

The Car Fe, Mh, or Nias: Chasecvant (C. R. 115, 640; 115, 118; abstracts in C. J. 62, 118, 1177 [1993]).

Lithium, Sucride of (vol. iii. p. 150). Poulenc (B. [3] 11, 15 (1994)) obtained LiF in regular of tabedra by Reating the amorphana fluoride with KHF, and KCl, and washing with water; al. soft water, insol. 95 p.o. alcohol; melts at c. 1000° in H, and partially volatilises at 1100°—12476°. 12/00

Lithium, hydroxide of (vol. iii. p. 150) For the freezing-points of adveous solutions of LiOH v. Pickering (C. J. 63, 899 [1893]).

Lithium, nitride of. Ouvrard (C. R. 114, 120 [1692]) obtained a black solid, probably Li, N. by heating commercial Li to dull redness in N.

Lithium, oxides of (vol. iii. p. 151). Almost the only product of heating Li in O is Li₂O; only traces of a peroxide are formed (Holtes. Sims, C. J. 65, 448 [1894]).

WAGNESIUM (vol. iii. p. 157). Burton a. Vorce (Am. 12, 219 [1890]) obtained the value 24.22 (O = 15.96) for at. w., by converting pure Mg into Mg(NO₃), and this to MgO. The molecule of Mg in fillute solution in tin is probably monatomic (Heycock a. Neville, C. J. 57, 376 [1896]). Mg crystallises in holohedral hexagonal ferms, a:c=1:1:6202, isomorphous with Zn and Be (B a. V., l.c.).

According to Montemarini (G. 22, 381, 397,

426 [1892]), a considerable quantity of H is given off when Mg interacts with HNO, Aq (c. 13 p.c.); the quantity of NH, formed increases with conthe quantity of MI, formed increases with concentration of the acid up to 40 p.c. HNO,, after which it decreases. Mg burns in NO at a dull red heat (Sabarter a. Senderens, C. B. 115, 236 [1892]). Giorgis (G. 21, 510 [1891]) sayse that Mg dissolves in water saturated with CO₂: that H is given off, and crystals of MgCO3. 3aq are deposited. For the interactions of Mg and chlorides v. Sewert a. Schmidt (A. 267, 218; abstract in C. J. 62, 776 [1892]). Winkler has made an extended examination of the interactions of Mg and oxides (B. 23, 44, 120, 772, 2642; 24, 873, 1966; abstracts in C. J. 58, 331,

2022; 24, 617, 1900; 60, 801, 155 [4891]).

Magnesium, bromide of (vol. iii. p. 159).

Beketoff (v. abstract in C. J. 62, 762 [1992])
gives H.F. [Mg.Br²] = 121,700. The double sail
2Mg2. PbBr., 16aq is described by Ottoa. Drewes
(Ar. Ph. 229, 585; abstract in C. J. 62, 566

[1892]).

Magnesium, chloride of (vol. iii. p. 159). Skinner (C. J. 61, 341 [1892]) gives the beiling-points of solutions of MgCl, in water and alco-

bol, from c. 4.5 to c. 14.5 p.c. MgCl.,

Magnesium, ioditie of (vol. iii. p. 161).

Beketoff (l.c.) gives H.F. [Mg, I^{*}] = 94,800.

Magnesium, nitride of (vol. iii. p. 161). For

description of an experiment to demonstrate the formation of Mg.N. v. Mero (II 24, 8,940; assarat in C. J. 62, 409 [1892]). **

Regnessium, oxide of (vol. iii. p. 161). MgQ is unchanged at c. 1750° (Read, U. J. 65, 315

Is unchanged at c. 1750° (Read, U. J. 65, 313° action of MnU., xaq'and II,O.4q. Heated in the [1894]); heated in the electric furnace, it needs clearly formation of the electric furnace, in the el

ing very strengty, retained c. 10 times its volume of gas, chichy O and N.

Magnesium, silicides of (vol. iii. p. 162).

Regarding the formation of compounds by heat-

regarding the formation of compounds by heating together Mg and Si, v. Winkler (B. 23, 2642a abstract in G. Je-68, 1878 [1890]).

MANGATESE (vol. iii. p. 177). Moissane (C. R. 116, 549 [1893]) tained Mn containing to 5 p.o. G. by fusing MnO with charcoal (keeping MnO in excess) by means of a current of 60 volts and 800 ampères. Prelinger (M. 14, 353; abstract in C. J. 66 (111, 40 [1894]) pre-353; abstract in C. J. 66 [11], 49 [1894]) propared pure Mn by heating Mn amalgam (formed by electrolysing MnCl. Au using a cathode of

Hg) in pure H.

Mn is described by P (l.c.) as a grey porous metal; unchanged in dry air; reacts slowly with cold, rapidly with warm, water; dissolves in NH, Clar giving off NH, and H; S.C. 7-4212 referred to water at 4°. Moissan (C. R. 116, 1429 [1893]) found that Mn volatilises readily in the electric furnace, using a current of 80 volta and 380 ampères. Montenarthi (O. 22, 384, 397, 426 [1892]) says that the gaseous products of the interaction of Mn and 1800, Aq are H, NH, N, and N.26. Finely divided Mn roacts with CO at c. 400°, producing MnO and C (Guntz, C.R. 114, 115 [1892.).

Manganese, alloys of. The presence of & 5 p.c. Mn in iron or steel scarcely affects the properties, except by slightly increasing the tenacity and malleability; a very hard tool-steel is formed with c. 1½ p.c. Mn. Alloys with iron containing from 7 to 30 p.c. Mn are extremely

hard and tough.

Manganese, amalgams of (vol. iii. p. 179).
Prelinger (M. 14, 353; abstract in C. J. 36 [11],
49 [1894]) prepared Mn.Hg, by passing a curvet from a kathode of Hg through saturated MnCl.Aq to an anode of C, or Pt-Ir, in a porous vessel, washing in running water, squeezing out excess of Hg, and drying in H over CaCl. By heating gently in a stream of pure, dry H, pure Mn was obtained.

Menganous chloride (vol. iii. p. 179). Chasse vant (A. Ch. [6] 30, 5 [1893]) describes several vani (A. Ch. [6] 30, 5 [1835]) userines several double salts of MnCl.; viz. MnCl.,2AmCl. 2aq, MnCl.,2AmCl. aq, and MnCl.,LiCl. 3aq. For the double salts M.KCl. 2aq, M.CsCl. 2aq; M.2xCl. 2aq; X = NH., Cs., Rb; 2M.MgCl., 12aq (M = MnCl.), v. Saunders (Am. 14, 127; abstract in C. J. 62, 780 [1892]).

Manganic chlorides (vol. iii. pa 180). Regarding the composition of the chlorida in the solution obtained by dissolving MnO, in HClAq. v. Vernon (P. M. [5] 31, 469), and Pickering (P. Mo [5] 33, 284) (astracts in G. J. 62, 19,

687 [1892]).

Manganese peroxide (vol. iii. p. 183). Regarding the compositions of the hydrated oxides, garding the compositions of the nythest approximately MnO.3. and, prepared by different methods, at Googen (Bl. [8] 4, 16 [1891]). G. (C. R. 120, 867; whatfact in U. J. 58, 946 [1890]) gives some details regarding the interaction of MnO. xac and I.O.44. Heated in the additional content of the content of t cleater of annoy sag and reposed. Heated in the cleater furnace, MnO, melts gives off O, and leaves MnO (Moissan, C. R. 115, 1034 [1892]). Mn,O, what to be formed by heating MnO, to c. 400° in NO (Sabatire a. Senderens, C. R. 114; 1476 [1891]). Molocal (C. T. Se. and Cleater). Permanganates (vol. iii. p. 186). Regarding the interaction of permanganates with H₂O₂Aq, Regarding v. Gorgeu (C. R. 110, 958; abstract in C. J. 58, 1062 [1390]). Klobb (Bis [3] 3, 508; abstract in C. J. 58, 947 [1890]) describes compounds of NH, with permanganates of Cd, Cu, Ni, and Zn.

Barium permanganate BaMn.O. (the formula is wrongly printed BaMnO, in vol. iii. p. 186). For the preparation of this salt from KMnO, Aq and Ba(NO₃), Aq v. Muthmann (B. 26, 1016, abstract in 7. J. 62 [11], 324 [1893].

Calcium permanganate. The formula given on p. 186 of vol. iii. is wrong; it should be

CaMn₂O₈.5H₂O.

Polassium permanganate (vol. iii. p. 186). Tivoli (G. 19, 630 [1890]) gives the following as the reactions that occur when pure AsII, is passed into dilute KMnO,Aq.: (1) 2KMnO,Aq.+AsH₁ = K,HAsO,Aq.+Mn₂O₂+ H₂O₃ (2) 2KMnO,Aq.+AsH₂= K₃HAsO₂Aq.+2MnO₂ th.D. Silver permanganate (wi. iii. p. 187).

stiver permanganate (vs. 111. p. 487).

AgMnO, decomposes plowly at the ordinary temperature, rapidly at 100°, and very rapidly at 125° (Gorgeu, U. R. 114, 912; abstract in C. J. 62, 942 [1892]).

Margenous su'phide (vol. iii. p. 188). The pp. produced by adding (NH₄)HSAq to an ammoniacal solution of a Mn salt, after washing in an atmosphere of H.S and drying in CO. at 70°, is MuS; S.G. 17° = 3.55. By heating to 300°-320°, or by leaving in contact with (NII,)HSAq for some days, the reddish MnS becomes green wit out changing its composition; the green form of MnS is crystallific, S.G. 170 = 3.63 (Antony a. Donnini, G. 23 [1], 560 [1892]).

MASRIUM. In 1892 (C. J. 61, 491) Richmond a. Husseinoff obtained indications of the existe ce of an element before unknown in specimens of Egyptian fibrous alums. The suprosed new element gave reactions indicating analogies with Be, Ca, and Zn; the results obtained by decomposing the oxalate by heat led to the at. w. of c. 228. The authors suggested the name masrium, from the Arabic name for Zgypt.

MERCURAMMONIUM COMPOUNDS (vol.

iii. p. 206).

Mercuro-ammonium salts NH_{1-x}Hg_xX (vol. iii. p. 207). Barfoedis cealclusion that these supiii. p. 207). Barfoed's ocalclusion that the sapposed compounds are really mixtypes of mercuricompounds and Hg is sonfirmed by Pesci (G. 21 [11], *69 [1891]). The product of the interaction of HgCl and NH, Aq. described as dimercuro-ammonium chlorider NH, Hg., *l. invol. iii. (p. 208), leaves metallic Hg when treated with ammoniacal (NH,), *SO, Aq. according to P. When the reaction of HgCl with NH, Aq. proceeds out of the light, P. says that the change is 2Hg, Cl., *4NH, Aq. (NHg,), *W,NH, Cl. *2NH, ClAq + 2Hg. S villarly the reaction of NH₂Aq with Hg₂SO, produces a double compound of dimercuro-ammonium sulphate ((NHg₂)₂SO₄, (NK₁)₂SO₅) and Hg; and

(NHg,)NO, NH, NO, and Hg are formed, according to P., when HgNO, Aq is treated with NH, Aq. Mercuri-ammonium salts NH, Hg. X. Regarding the conditions of formation of compounds

of mercuri-ammonium obloride MH-Hg.Cl (vol. Ri. p. 208) with HgCl and NH₄(Hg₂O)Cl c. Balestra (J. 21 [11], 294; abstract in G. J. 62, 276 [1892]).

Dimercuri-ammonium salts NHg.X (vol. iii. 2.209). Pesci (G. 20, 485 [1890]) has examined the onditions of formation of various salts of this class, especially the nitrate NHg, NO, and compounds of this with NH, NO,. The sulphate (NHg.), SO, 2aq was formed by saturating conc. RH,Aq with HgSO,, allowing the solution to evaporate in an atmosphere of NH, over CaO,

and collecting the first orop of crystals; various compounds of (NHg₂)₂SO₂JAith (NH₃)₂SO₄ are also described (v. abstrart in C. J. 60, 208 [1891]).

MERCURY (vol. iii, p. 212). Heycock a. Neville's results (J. J. 57, 376 [1890]) show that some condensation from monatomic molecules perhaps occurs in dilute solutions of Hg in tin. For corrected tables of the vapour pressures of Hg for each 10° from 180° to 480°, and each 1° from 830° to 860°, v. Young &C. J. 59, 629 [1691]).

Jäger (W. 48, 209 [1893]) recommends to prepare pure Hg by converting Hg that has been distilled in vacuo into IIgNO, and electrolysing a solution of the salt, using Pt as isachode and distilled IIg as anode. Shenstone (F. J. 61, 452 [1892]) noticed that IIg adheres to glass when brought into contact with Cl, Br, or I. Montemartini (G. 22, 384, 397, 426 [1891]) finds that the amount of NO produced by the interaction of Hg and HNO, Aq decreases as concentration of the acid increases; that NO2 is produced with acid more cone. than 27.5 p.c. HNO3, HgNO3 is formed with 25 p.c. acid, but Hg(NOs)2 with 50 to 70 p.c. acid; no NII, is formed with 27 and 50 p.c. acid.

Marcurio bromide (vol. iii. p. 215). HgBr, boils at 325°, according to Freyer a. V. Meyer (Zeit. f. anorg. Chemic, 2, 1 [1892]).

Mercurous obloride (vol. iii. p. 215). Harris

a. V. Mey'r have re-determined the V.D. of calomel at 4489 and 518°; the value obtained was 117.5. M. a. M. obtained considerable quantities of Hg and HgCl, by allowing the vapours obtained by heating calomel to c. 465° to diffuse along a glass tube; also by ceating chome at 420° for half an hour in a distillation flask at 33 mm. pressure. By heating calomel to \$40,22002, and bringing a piece of KQH, which had been heated to c. 250%, into the vapou, they noticed that the surface of the KOH at once became cover d with yellow HgO; they also found that a piece of gold leaf held or a moment in the vapour was amalgamated (if kept for some time in the hot vapour the yellow Colour was restored. H. a. M. think their re-sults leave no doubt that the vapour obtained by heating calomel is Hg + HgCl₃, and that the molecular formula of calomel is Hg.Cl₃.

The reaction of Hg₂Cl₂ with NH₄Aq gives (NHg₂)Cl.NH₄Cl and Hg, according to Pesci (v. 1977. MERCURO-AMONIUM SALTS).

Therefrie chloride (vol. iii. p. 217). HgCl, boile at 307° (Freyer a. V. Meyer, Zeit. f. anorg. Themie, 2, 1 [1892]). The white Substance

progress by one reaction of HgCl.Aq with a bilver photographic intege, or with pulverulent Ag, is HhAgCl., according to Jones (S. C. S. 12, 985; abstract in C. J. 66 [11], 188 [1894]).

Marcuffe organide; for an account of the conditions of formation and properties of the clouble merculy-sine cyanide, v. Dunstan (C. J. 63, 668 [1892]).

**double mercury-sine cyanide, v. Dunstan (C. V. 61, 666 [1892]).

**Miceury, haloide compounds of (vol. iii. p. 219). Wells 44m. S. [3] 44, 221; abstract in C. J. 64 [11], 68 [1893]) describes a number of double compounds of mercury and session halides; the compounds belong to the fores (1) Ca.HgX., (2) Ca.HgX., (3) Ca.Hg.I., (4) Ca.HgX., (5) Ca.Hg.X., (6) Ca.Hg.X., (7) Ca.Hg.X., (8) Ca.Hg.X., (9) Ca.Hg.X., (1) Ca.Hg.X., (2) Ca.Hg.X., (3) Ca.Hg.X., (4) Ca.Hg.X., (5) Ca.Hg.X., (6) Ca.Hg.X., (7) Ca.Hg.X., (8) Ca.Hg.X., (8) Ca.Hg.X., (8) Ca.Hg.X., (9) Ca.Hg.X., (9) Ca.Hg.X., (1) Ca.Hg.X., (1) Ca.Hg.X., (2) Ca.Hg.X., (3) Ca.Hg.X., (4) Ca.Hg.X., (5) Ca.Hg.X., (6) Ca.Hg.X., (7) Ca.Hg.X., (8) Ca.Hg.X., (8) Ca.Hg.X., (8) Ca.Hg.X., (9) Ca.Hg.X., (1) Ca.Hg.X., (1) Ca.Hg.X., (1) Ca.Hg.X., (2) Ca.Hg.X., (3) Ca.Hg.X., (4) Ca.Hg.X., (5) Ca.Hg.X., (6) Ca.Hg.X., (6) Ca.Hg.X., (7) Ca.Hg.X., (8) Ca.Hg.X., (9) Ca.Hg.X., (1) Ca.Hg.X., (2) Ca.Hg.X., (3) Ca.Hg.X., (4) Ca.Hg.X., (5) Ca.Hg.X., (6) Ca.Hg.X., (6) Ca.Hg.X., (8) Ca.Hg. ferent halogens.

Mercury hydrosulphide; for experimental attempts to prepare a definite compound, v. Linder a. Picton (C. J. 51, 123 [1892]).

Mercury phosphide (vol. iii. p. 223). By heating Hg and PI, in a scaled tube for many

hours at 275°-300°, and removing HgI, by treatment with KIAq, Granger (C. R. 115, 229 [1892]) obtained Hg.P. in lustrous, metal-like, hexagonal crystals, appearing red by trans-mitted light; and giving a brown powder. The compound gives Hg and P when heated; heated in air it burns; detonates when mixed with KClO, and struck; burns in Cl; dissolved by aqua regia.

Mercutous sulphide (vol. iii. p. 224). Antony a. Sestini G. 24 [1], 193 [1894]) obtained a black powder by passing dry H.S., diluted with CO, over dry Hg,Cl₂ or Hg(C,H₂O₂), kept at -10°; when freshly prepared the black powder was scarcely changed in dry IsCl at -18°, but at a somewhat higher temperature (below 0°) Hg,Cl₂ was quickly formed. The substance dissolved in cold K,SAq or Na,SAq, but when temperature rose above 0° the solution became turbid and ppd. Hg. A. a. S. think their results show that Hg,S exists at low temperatures (abstract in C. J. 66 [11], 318 [1894]). in C. J. 66 [11], 318 [1894]).

Mercury sulphochloride (vol. iii. p. 225).

in C. J. 66 [11], 318 [1894]).

Mercury sulphochloride (vol. iii. p. 225).

The compound 2HgS.HgCl, is formed, according to Colson (C. R. 115, 657 [1892]), by passing H.S into a solution of HgCl, in dry benzone.

MOLYBDENUM (vol. iii. h. 421). Smith a. Maas (A. C. J. 15, 897 [1894]) obtained the nean value 95*85 (O = 15*96) hr the at. w. of Mo. by heating Ng.MgO, in a surrest of dry HCr and weighing the NaCl that remained (MoO, 2Hcl and H.O were formed, and semocal). Smith a. Oberholtzer (Zeit. f. anorg. Chemie, 63 [1893]) say that a mixture of MoOC', and Mo(CO)@, is formed by heating Mo to 150°—200° in CoCl.; and that Mo.S.Cl., is yu.duced by heating Mo to endness in S.Cl., Mo is said to ppt. Ag from AgNO,Aq, Av from AuCl,Aq, HgCl and then Hg from HgCl,Aq, and Cu farm solutions of its salts (Smith, Zeit. f. anorg. Chemie, 1, 860 [1891]). Montemartini (G. 22, 284, 897, 426 [1891]). Montemartini (G. 22, 284, 897, 426 [1891]) finds that no NH, is formed in the interaction of Mo and HNO,Aq with from 3 to 70 pc. HNO; the most vigorous action occurs with acid c. 50 p.c., but the whole of the metal is not wideed of MoO, a nitrate being probably formed; the gaseous products are MO and NO, the quantity of NO decreasing as the concentration of the soid increases.

Molystenum, carbides et. By heating a mixture if MoD, and charcoal in the electric furnace, doisean (C. R. 116, 1225 [1898]) obtained a very hard carbide, containing from 977 to 979 p.c. C; S.G. 86.

Molybdenum sesquioxide (vol. iii. p. 431). Heating Mo.O. in NO produces MoO. (Sabatier a. Senderans, C. R. 114, 1429 [1892]). Molybdenum trioxide (vol. iii. p. 432). MoO. partially volatilises, and is partially reduced to one of the blue oxides, at c. 1750° (Read, C. J. 65, 818 [1894]). According to Smith a. Oberholtzer (Zmit. f. anorg. Chemie, 4, 236 [1898]), the products of heeling MoO, in HBr are (1) MoO, 3HBr, and (2) Mo,O,Br.; when HI is blue oxide Mo₂O₃: raq is formed; HF at 300°-400° forms Mo₂O₃: R₄(v. abstract in C. J. 64 [11], 471 [1893]). Cammerer (Chem. Zeit. 15, 957; abstract in: C. V. 62, 944 [1892]). says that 2MOO, H.O. H.O. is formed by boiling MoO, with H2OzAq.

Molybdenum, oxybromides of (vol. iii. p. 438). Smith a. Oberholtzer Weit. f. anorg. Chemie, 4, 236 [1892]) describe Mo.O.Br.; square plates, color of KMnO. Formed, along with McO.3HBr, by heating MoO. in HBr.

Molybdenum, oxyclfforides of (vol. iii. p. 438) For the products of the interaction of MoO.C., and NH., v. Smith a. Lehner (Zcit. f. anorg. Chemic, 4, 374; abstract in C. J. 64 [11], 529 [1893]).

Molybdenum, oxyeganide of. By dissolving MoO₂ in KCyAq, and adding a strong-acid, Pechard (C. ll. 118, 804 [1894]) obtained MoO₂Cy₂. Easily decomposed by contact with MoO₂Cy₂. acids; double compounds with KCy and AgCy are also described.

Molybdenum, oxyfluorides of (vol. iii. p. 483) for Mo,O,F, a white, crystalline, deliquescent solid, obtained by heating MoO, in HF at 300°-400°, v. Smith a. Oberholtzer (l.c.).

Molybdenum, thiochloride of. For Mo.S.Cl.,

v. S. a. O. (l.c. 5, 63).
Molybdates, and derivatives thereof (vol. ili. p. 123). For compounds of molybdates of MI, and K with SO₂ and SeO₂, v. Péchard (C. R. 116, 1441; 117, 104; abstracts in C. J. 64 [1] 530 [1893]).

Permolybilates. By the reaction of H₁O₂Aq with K₂Mo₂O₁₀Aq, Péchard (C. R. 112, 720; abstract in C. J. 60, 988 [1891]) obtained potential permolybilate K₂Mo₂O₃, 4qq; the correspondent of the correspondent sponding NH, salt was also formed.

sponding NH, salt was also tormed.

Arseno-molybelates (vol. iii. p. 425). For salts of this class, v. Frighteim (Zeit. f. anony. Chemie, 2, 314; 6, 11, 27; abstracts in C. J. 64 [11], 283, 66 [11], 238 [1893-4]).

Iodonoifibelates. A great many salts of the form aMoO, yI, Q. 2MO are described by Blomstrah (Zeit. f. anory. Chemie, 1, 10; abstract in C. J. 64 [13], 122 [1893.]).

Phosphomolybelates (vol. iiis p. 426). Friedheim (Zeit. f. anory. Chemie, 3, 275; 6, 11, 27; abstracts in C. J. 64 (11], 472 9 66 [11], 288 [1893.4]) describes several salts of this class.

Fluomolybelates (vol. iii. p. 425), v. Piccini (Real Acad. Lincei, 7 [1], 267; abstract in C. J. 62, 44 [1892]), and Mauro (l.c., 1692 [1], 194; abstract in C. J. 64 [11], 124 [1893]).

MICKEL (vol. iii. p. 498). The at. w. has been re-determined (1) by Schützerloerger, by reducing oxides of Ni in H (C. R. 114, 1149 [1892]); (2) by Winkler, by estimating Cl in NiCl, prepared from electrolytically deposited Ni. (Lett. f. anorg. Chemie, 4., 10 [1893]). Schützenberger's values varied from 58-52 to Nick. (Wildland men value from 58-52 to 19.8: Winkler's mean value from the gravimetric determinations was 58.903, and from the volumetric determinations 58.910 (Cl = 35.37, Ag = 107.66). Kriiss a. Schmidt (Zeit. f. aporg. Chemie, 2, 235 [1892]) insist that the substance called nickel is not an element, but Winkler (l.c.) controverts this sty tement (v. abstracts in C. J. 64 [11], 212, 469 [1893]). The molecule of Ni in dilute solution in tinis probably monatemic (Heycock a. Neville, C. J. 57, 376 [1890]). Scautzenberger (Cc R. 113, 177 [1891]) says that a volatile compound is formed by passing dry HCl over finely divided Ni heated to dull redness. Montemartini (G. 22 [1], 250; ab Aract in C. J. 62, 1278 [1892]) gives the quantities of NH_s, N_sO, N, and HNO₂ (no NO) produced by the reaction of excess of HNO₃Aq (27.5 p.c.) with Ni. Heated to 200° in NO, the oxule NiO is NI. Heated to 200° in NO, the oxide NIO is formed without any Ni₂O₃ (Sabatier & Sandarens, C. R. 114, 1429 [1892]). Be epassing NO₃, diluted with N, over reduced Ni, nitro-nicket (? Ni₂NO₂) is obtained; it resembles nitro-cobalt

(gr.w., p. 908) (S. a. S., Bl. [3] 9, 669 [1893]).

Nickel carbonyl Ni(CO), (Nickel carbonoxide, vol. iii. p. 501.3 Mol. w. was confirmed by Mond a. Nasıni (Z. P. C. 8, 150 [1891]), by finding the depression of the freezing-point of benzene. S.G. 1.35613 at 0°, 1.27132 at 36° (water at 4° = 1); S.G. at b.p. = 1.25406; molecular volume = 186.04; critical temp. = 151°. For some reactions v. Berthelot (C. R. 112, 1343; abstract

in C. J. 60, 1427 [1890]).

Nickel, chloride of (vol. iii. p. 501). volatile substance, decomposed by heating, is said to be formed by passing dry HCl over dry NiCl, at dull redness (Schützenberger, C. R. 118, 177; v. abstract in C. J. 60, 1429 [1890]). Chassevant (A. Oh. [6] 30, 5 [1893]) describes the double compounds NiCl, AmCl. 6aq and

NiCl, L'Cl. 3aq.

Nickel, fluoride of (vol. iii. p. 502). Poulenc 'Q. R. 114, 1426 [1892]) obtained amorphous NiF, by heating NiCl, with excess of NH,F, and washing away NH,Cl with boiling alcohol; by heating in HF to 1200°-1300°, the amorphous MIF, became crystalline, forming green crisms, S.G. 4'63, not acted on by warm INO₂A₁, HOlAq, or H.SO.Aq. Heated in air, NiF, gives NiO; heated with S it gives NiS; and with H iPis reduced to Ni (for other reactions, v. abstract in C. J. 62, 1159 [1890]. The double salt NiF, KF is formed by heating NiCl. with KHF, and washing away KCl by water (F., C. R. 114, 746 [1892])

Nickal monoxide (vol. iii.). 502). NiO malts and forms green crystals in the dectric furnace (Moissan, C. R. 115, 1034 [1892]). NiO occludes small quantities of N and O (Richards a. Rogers, P. Am. 4, 28 200 [1992]).

P. Am. A. 28, 200 [1893]).
Nickel sesquioxide (vol. iii. p. 502). Ni.O. fuses, gives up all its O, and leaves Ni at c. 1750 (Read, O. 1.55, 313 [1894]).

Nickel peroxide (vol. iii. p. 503). Campbell

3. Trowbridge (J. Anal. and App. Chem. 7. 301;

abbtract in C. J. 86 [11], 288 [1894]) conclude that an oxide with more O than M.O. can be obtained by ppg. NiSC, Aq by Ma, CO, Aq in presence of Br at different temperatures.

Mickel monosulphide (vol. iii. p. 508). Regarding the oxidation of this galt in air, to NiSO, 6NiO, 40., v. P. de Clermont (C. R. 117; 229; abstract in C. J. 64 [11], 528 [1894]).

NYOBIUM (vol. iii. p. 505). Nb O, sise not changed at c. 1750° (Reads C. J. 55, 313 [1894]). Piccini (Zeit. f. anorg. Chemie, 2, 21 [1894])
las Prepared potassium fluoxyperniobate

bO.F. 2KF. aq.

NITRAMIDE NG₂(NH₂). Thiele a. Lachman B. 27, 1909 [1894]) obtained this compound by throwing NO₂.NK.CO₂K (potassium nitro-car-bamate) into a mixture of ice and excess of II.SO., exfracting with ether, and evaporating in a stream of air. Crystall #8s in clear prisms, which melt at 72° with decomposition; decomposed instantly to N.O and H.O by alkalis, alkali carbonates, borax, or Na acctate.

NITRATES (vol. iii. p. 509). Rodsseau a. Tite (C. R. 1!5, 174 [1892]) find that many basic nitrates are completely decomposed by heating with water at 150°-200°. Regarding Regarding negaring with water at 100-200. Regarding the formation of basic nitrates of Cd, Ca, Ni, and Zn, v. R. a. T. (C. R. 114, 1184); Riban (C. R. 114, 1357); and Werner (C. R. 115, 169); (abstracts in C. J. 62, 1156, 1157, 1276 [1892]).

NITRIC ACID [vol. iii. p. 517]. Pagazding

NITRIC ACID (vol. iii. p. 517). Regarding the colours produced by diluting ced fuming HNO₂Aq v. Marchlewski (B. 24, 3271 [1891]). For revised tables showing the composition of HNO, Aq of different concentrations v. Lunge a. Rey (S. C. I. 1891. 543). Regarding the magretic rotations of HNOsAq v. Perkin (S. J. 63, 57 [1893]). Hall (Am. 13, 554) has examined the rate of production of H and O, and the effect on the concentration of the acid, by the slow and steady electrolysis of HNO₃Aq (abstract in C. J. 62, 680 [1892]). The interactions of HNO, Aq with many metals have Joen examined by Montemartini (G. 22 [1], 250, 277, 384, 397, 426 [1891]; abstracts in C. J. 62, 1278, 1402 [1892]), Veley (S. C. I. 10, 206; and elsewhere), and

Veley (S. C. I. 10, 206; and elsewhere), and others; the results are noted under various metals. Pickering (C. J. 63, 436 (1893)) has isolated the hydrates HNO, H,O and HNO, 3H₂O; the fraczing points of HNO, eq. from 1-82 to 86:19 p.c. HNO, are given by P.

NITHOGEN (vol. iii. p. 556). S.G. of N. Lark = 1) = 97209; 1 litre weighs 1-25749 g. ξ_1 Ray-light, P. ξ_2 3, 434 (1893)). μ_D = 1-2053 at = 190° (liquid N. containing 5 p.c. O) (Liveing a. Dewar, P. M. [5] 36, 929 (1893)). Absorption coefficient in alcohol, w Henrich (Z. P. C. 9, 435 (1892)). Diffusion in water, v. Dunc. n. a. Hoppe-Seyler (Zeit. physiol. Chemia, 17, 147 (1893)). Preparations of pure nitrogen. Threlfall

Preparations of pure nitrogen. Threlfall (5: M. [5] 35, 1 [1893]) gives minute directions for preparing pure N by passing air and NH, www. hot Cu, and absorbing traces of 9 by CrCLAq; exact directions for preparing the CrCl.Aq are given, and the paper contains numerous details regarding the purifications of the

reagents used in the process. Supposed allotropic form of Atrogen. Threlfall (i.c.) has repeated experiments on sparking extre. sly ours N (u vol. iii. p. 557); no condensat on occurred down to -10° and c. 8 mm. pressure, but when Hg is present a compound of N and H is formed (probably Hg,N, v. vol. iii. p. 221). Regarding the fixation of nitrogen growing plants, H Beyerinck, also Sohloesing a. Laurent (abstracts in C. J. 62, 1019, 1021

Nitrogen, hydrides of (volt dii. p. 559).

Hydragoic acid N.H. For new methods of preparing N.H v. Curtius. (B. 24, 334; 26, 1263; abstracts in C. 7. 62, Fi.2; 64 (11], 463 (1892-3)).

Wislicenus (B. 25, 2084 [1892]) has obtained N.H by the interaction of N.H, and N.O.F. From § 5. to § 8. Na is heated in a stream of N.H, until all is converted into Kanh.; a current of Nr. N. of them presed over the Nanh.; at 150. dry N₂O is then passed over the NaNH₂, at 1502–250° as long as NH₃ is given off (2NaNH₂ + N₂O = NaN₃ + NaOH + NH₃). By dissolving the product in water, filtering, decomposing by dilute H₂SO₂Aq, and distring, N₂HAq is obtained.

The following salts are described by Curtius

(B. 24, 3341; abstract in C. J. 62, 112 [1892]): (NH₄)N₃ Pb(N₃)_v, HgN₃, NaN₃.

Nitrogen, iodides of (vol. iii. p. 560). Di-iodamine, NHI, is the product of adding excess of NH₂Aq to a conc. solution of I in conc. KIAq; by suspending NHI₂ in water, and adding an ammoniatal solution of AgNO₂ or Ag₂O₃ a black compound NAgI₂ is obtained which explodes when dry (Szuhay, B. 26, 1933; abstract in C. J. 64 [11], 568 [1893]; cf. Selivanoff, B.

in C. J. 64 [11], 568 [1893]; cf. Selivanoff, B. 27, 1012; obstract in C. J. 66 [11], 312 [1894]).

Nitrout oxide (vol. fit. p. 561]. Ramsay a. Shields (C. L. 63, 833 [1893]) give the m.p. of N₂O as -102·3°, and the b.p. as -80·8°. Villard (C. R. 118, 1096 [1894]) gives the following data for the S.G. of liquid N₂O: 9105 at 6°, 885 at 5°, 856 at 10°, 804 at 17·5°, 720 at 26·5°, 640 at 32°, 605 at 34·9°, 721 at 36·3°. Liveing a. Deway (P. M. (5) 34, 205 [1892.) give Liveing a. Dewar (P. M. [5] 34, 205 [1892]) give

$$\frac{\mu_0 - 1}{d} = 2634$$
, and $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 163$ at -90° .

Smith (S. C. I. 11, 867; 12, 10 [1893]) says that a regular stream of N₂O is obtained by heating to 240°-250° a mixture of 1 pt. dry NaNO, with c. 13 pt. dry (NH.),SO. By passing N₂O, mixed with a little H, over Pd black, the H is entirely converted to H,O, with formedion of N (Montemartini, Real. Agad. Lincoi, 7 111, 219 [1892]).

Nitric oxide (vol. iii. p. 562) Very pure NO obtained, according to Emily (V. 13, 73 (1897), by the interaction of copper and a mixture of H.SO, and HNO, Aq. Emich (i.e., p. 78) finds that NO is completely decomposed to and O by passing over netsoof Pt 8: Pel wire Rept ver? hot by an electric courent. Emich (L.c. p. 86) says that NO and O unite after being dried by long contact with P.O.; but Baker (C. J. 65, 611 [1894]) finds that dry NO and dry O do not combine at the ordinary temperature. Segarding the reactions between NO and metals and metallic oxides, v. Sabatier a. Sendering (C. R. 114, 1429; 1476; abstracts in C. J. 62, 1151, 1271 [1892]; results are noted under the different metals and oxides in Addenda).

Nitrogen rioxide (vol. iii. p. 565). For the reactions of N), with various metals and oxides v. S. s. C. (30.R. 115, 286; abstract in CaJ. 62, 1890 [1892]; results are noted unlar the different motals and oxides in Addended. different metals and oxides in Addenda).

Nitrogen tetroxide (vol. Mi. p. 565). For preparation of N.O., v. Cundall (C. J. 59, 1076... [1891]). U. (l.c.) has measured the dissociation of liquid N.O. in CHCl, up to c. 25°; Ostwald (C. J. 61, 242 [1893]) shows that the dissociation follows with the dissociation of the control of the

(C. J. 61, 242 [1892]) snows that the dissociation follows van't Hoff's law for dilute solutions. Mitrau, and (vol. iii. p. 567). Regarding the formation of HNO, in solution in HNO, p. Veley (Pr 52, 27; abstract in C. J. 04 [11], 413 [1893]). [1893]).

Hyponitron acid (vol. iii. p. 568). Tanata, (J. R. 25, 342; abstract in C. J. 66 [11], 186 [1894] propared Ag, N, O, by adding CaO to fairly conc. KNO, Aq is the latic CaO: KNO, then an equivalent of solid NH₂OH.HCl, heating to 50°, letting stand for a few days at the ordinary temperature, diltering, acidifying with acetic acid, ppg. by AgNO₂Aq, dissolving Ag₂N₂O₂ in HNO Aq (which leaves AgCl), and ppg. again by

OSMIUM '(vol. iii. p. 641). Os fuses readily in the electric are in a carbon capsule; when fused it has a constalline fracture, and

(John a Vezes, C. R. 116, 577 [1893]).

Osmic action (vol. iii. p. 646). Moraht a.

Wischin (Zeit, f. anory Chemic, 3, 163; abstract
in C. J. 64 [11], 880 [1893]) say that the black powder obtained by the interaction of acider and K₂OsO₂Aq (vol. iii. p. 645), when dried over P₂O₃ in vacuo till inceases to lose weight, is osmic acid H₂OsO₃. M. a. W. describe the is osmic acid H₂OsO₁. M. a. W. describe the compound as a sooty black powder, smelling of OsO, in moist air, but unchanged under water containing alcohol. By passing H2S over Os O.S. H.O is formed. Heated with conc. HClAq for many hours with a little alcoholy and evaporated, Os C. 7. was obtained; an alcoholy is gethern of this authorises. alcolodic solution of this substance with KClAq gave K, OsCl, and the filtrate yielded OsCl, 3aq: the substance Os,Cl, is therefore supposed by M. a. W. to be a mixture of OsCl, and OsCl. By heating H, OsO, with HIAq, violet black crystals, probably OsI, were obtained. No action occurs when Os is heated with I, or with Br.

Potassium osmiamate (vol. iii. p. 645). (C. R. 112, 1442 [1891]) prepares this salt dissolving 100 pts. OsO, in a solution of 100 pts. KOH in 50 pts. H₂O, keeping the solution at c. 40°, and adding 40 c.c. NH₂R₂; after a time the brown liquid becomes colourless, and time the brown liquid becomes colourless, and yellow crystalline pp. is formed. J. gives the formula KNOsO₃ to this salt. Heated in vacuo it is rapidly decomposed above 200°, and at 440° almost all the N is given off, the salt products being K₂Co₂, OsO₂, and KOsO₃ (v. abstract in C. J. 60, 1433 [1891]).

OXIDES (vol. iii. p. 658). Regarding the connections between the stability of oxides when heated and the periodic classification of the

connections between the stability of oxides when hested and the periodic classification of the eliments, v. Bailey (C. J. 65, 106, 321 [1894]).

OX TOEN 4701, iii. p. 703). Atomic weight of oxygen (vol. iii. p. 705). Distinar a. Henderson (C. N. 37, 127, 138, 151, 164; abstract in C. J. 64 [11], 410 [1893]), from careful determinations made by passing H over hot DuO, and religing the water and Cu prodlead, adopt the value 15-87 for the at. w. of O. By measurement of the combining volumes of O and H. combined the combined the combined that the combined the combined the combined that the combined the combined that the combined the combined that of the combining volumes of O and H. combi

ning the results with Rayleigh's determination of the S.G. of O. Scott (T. F34, 548 [1898]) got the value 15·862. The following values summarise the most recent determinations (v. D.c., H., L.c.), Cooke a. Richards, 15·868; Noyes, 15·885; Rayleigh (Pr. 45, 425 [1890]), 15·89; Keiser, 15·949; Ledue (C. R. 146, 1948 [1893]), 15·88; D. a. H., 15·87; Scott, 15·862, The value adopted in this Dictionary, 15·96, is almost certainly too high; the Lican of the values obtained by C. a. R., N., R., D. a. H., and S., is 15·875.

The ratio of the combining volumes of O and H was determined by Scott (l.E.) to be 2 00245:1 (v. Water, this vol. p. 861). S.G. of O referred to H = 15 882 (Rayleigh, Pr. 50, 448 [18/2]). For an examination of the whole of the spectrum of O, v. Eisig (W. 51, 747: abstract in C. J. 66 [11], 265 [1894]). Liveing a. Dewar (P. M. [5]

84, 205 [1892]) determined $\frac{\mu_0-1}{d}$ to be 1389, and $\frac{\mu^2-1}{(\mu^2+2)d}$ to be 1265, at -182° (cf. Olszewski a.

Witkowski; abstract in C. J. 64 [11], 853 [1893]). For diffusion of O in water, a Duncan a. Hoppe Seyler (Zeit. physiola Chemie, 17, 147 (1892]).

Regarding the division of O between H and Or when mixtures of these gases are exploded, v. Harker (Z. P. C. 9, 673 [1892]). Dry O does not combine with dr. NO at the ordinary temporature (Baker, C. J. 65, 611 [1894]); nor with dry K or Na, even when these metals are distilled

ir the gas (Holt a. Sims, C. J. 65, 440 [1894]).

OZONE (vol. iii. p. 788). Regarding the conditions of exemination of exygen, v. Shenstone a. Pries. (C. J. 63, 938 [1893]). Baker (C. J. 65, 611 [1894]) confirms the observation of Shenstone a. Cundall (C. J. 81, 610 [1887]) that day O is ozonised as rapidly as moderately diy O.

PALLADIUM (vol. iii. p. 792). The at. w. of Pd has been re-determined (1) by Bailey a. Lamb Pd has been re-determined (1) by Bailey a. Lamb (C. J. 61, 746;1892), by analyses of Pd(NH,Cl); (2) by Keller a. Smith (Am. 14, 423 (1892)), by,ppg. Pd elettrolytically from a solution of Pd(NH,Cl); in NH,Aq; (3) by Joly a. Leidić (C. R. 116, 146, 14893)), by electrolysing K,PdCl, in HOlAq; (4) by Keiser a. Breed (Am. 16, 20 (1894)), by determining the ratio of Pd to Cl in Pd(NH,Cl). B. a. L. obtained the value 105 459; K. a. S. the value 106 35; J. a. L. the value #95 665; and K. a. B. the value 106 37. and K. a. By the value $106^{\circ}27$ (Cl = $35^{\circ}27$; Ag = $107^{\circ}66$; N = $14^{\circ}01$; O = $15^{\circ}96$). The molecule of Pd in dil te solution in tin is probably monatomic (Heycock a. Neville, C. J. 57, 376 [1890]). Regarding he preparation of pur Pd, v. the memoirs referred to supra. Pd absorbs O at 450°, forming Pd.O (Neumann, M. 18, 40 [1892]), but when Pd sponge f: heated in city O till the weight is constant Pd.O is formed (Wilm, B. 25, 220 [1892]). Heated to 20° in NO. Pd. sponge that has been saturated with H becomes incandescent and the NO is completely changed to H₂O and NH₂, but oridation of the Pd does not occur (Sabatier a. Jenderens (C. R. 114, 1429 [1892]), Regarding palladium sulphides, v. Petrenks Aritschenko (Zeit. f. anorg. O'emte, 4, 247; abstract in C. J. 64 [11], 475 [1898]). Phosphopalladous compounds, PdCl.POl. and

Pddi, P(OH),, are described by Fink (C. H. 139, 170; abstract in C. J. 69, 1985 [1992]. Verse (C. R. 115, 111) describes polyseium palladosochiorcuitrite K.Pd(NO₂), Cl. (abstract in C. J. 39, 1804 (1994).

PHOSPHATES (vol. iv. p. 106). Rossel a. Frank (B. 27, 52) say that P is obtained by heating NgPO₂₅ or any phosphate of Ca or Mg, with Al in a current of H.

Al in a current of H.

Dipotassium-hydrogen orthophosphate (vol. 1. p. 111). According to Standenmaier (Zeit?f. anorg. Chemie, 5, 883 [A898]), K.Hl'O, cannot be isolated. S. (f.c.) describes acid safts, K.H.(PQ.), aq, K.H.(PQ.), 2aq, and K.H.(PQ.), Thorium orthophosphates (vol. iv. p. 112). Velok (Zeit. f. anorg. Chemie, 6, 101 [1894]) obtained Th(HPQ.), aq by adding dilute H.PO.Aq to ThCl.Ad.

to ThCl,Aq. Sodium pyrophosphate (.St. sv. p. 114). For a study of the reaction of HClAq with Na,P.O, v. Watson (S. C. I. 11, 224; abstract in C. J. 64

Watson (S. C. I. 11, 222; austrace in C. 11], 272 [1893]).

ORTHOPHOSPHORIC ACID (vol. 67, p. 125).

According to Watson (C. N. 68, 199 [1893]), H,PO, is changed completely to H,P,O, at 255°–260°, and HPO, begins to form at 290°–300°.

PHOSPHORUS (vol. iv. p. 120°). Regarding the complete state of continuous phoses.

the action of light and heat on ordinary phosphorus, v. Retgers (Z. P. C. 5, 211; abstract in

C. J. 66 [11], [1894]).

Phosphorus hydride (vol. iv. p. 136). PII, and O react at a low pressure to form H₁PO. (2PH₂+3O₂=2H₂PO₃); when the gases are allowed to diffuse with one another at less than 50 mm. pressure, the reaction is PH₃+O₂=H₂+HPO₂; slow oxidation at greater pressures proceeds approximately according to the equation $4PH_1 + 5O_2 = 2HPO_2 + 2M_3PO_2 + 2H_{2e}$ (H. J. van de Stadt, Z. P. C. 12, 322 [1893]). According to van de S., explosion occurs at a certain low pressure, and this pressure depends much on the amount of moisture present, the moisture preventing and retarding the explosion. Rovij preventing and retarding the explosion. Rövij (Z. P.-C. 12, 155 [1893]) has examined the rate of decomposition of PH₂ by heat. For the reaction of PH₃ with AgNO₂Aq v. Vitali (abstract in C. J. 64 [11], 206 [1893]). Phosphoric opide (vol. iv. p. 141). For de tails regarding the preparation of pure P₂O₃, and for methods of detecting traces of P in P₂O₃, v. Threlfall (P. J. 65] 35, 14 (1893)). Phosphorus suboxide (vol. iv. p. 189). Phosphorus suboxide (vol. iv. p. 189). Rival (B. 27, 1257 [1894]) thinks that P₄O is formed by the retardition of P₂O₃ and NH...

(B. 27, 1257 (1894)) thinks that P.O is formed by the interaction of P.O. and NH..

Phosphorus, sulphides of (vol. iv. p. 145). Helfi (Z. F. Q. 12, 809 [1893]) confirms the statemant that there are no definite compound P.S and P.S.; by heating together red P and S, he obtained P.S., P.S., P.S., and P.S.,

Phosphorus sulphicodide of. Ouvrard (C. R. 145, 1801; abstract in C. J. 64 [11], 164 [1893]) obtained P.S. by seventy are a solution of the there.

1202; also by evaporating a solution of the three elements in the proper proportion in CS, and heating the residue to 120° in an inert gas; also by dissolving I as a solution of P,S, in CS. The giving P.O., SO, and P; at c. 300° in prouvit

leparates into I and P.S.; decomposed by hot water, and explasively by fuming HNO.

Potassium hypophosphates (vol. iv. p. 153).
Bansa (Zeit. f. anorg. Chemic, 6, 128 [1894]) lescribes many double salts of K.H.P.O. with MH.P.O. where M = Cd. Co. Cu.Mn. Ni, or Zh.; ilso double salts MK.P.O., where M = Co or Ni. The double salts K.Na.P.O. 2aq is also described abstract in C. J. 66 [11], 279 [1894]).

Thallium hypophosphates. Joly (C. R. 118, 549 [1894]) obtained the normal sults Ti.P.O., and the acid salt Ti.H.P.O. (abstract in C. J. 56 [11], 282 [1894]).

PLATINATES (vol. iv. p. 281).

Sodium thioptatinates. Schneider has obtained the salts Na.PtS. and Na.S.PtS.2PtS. [J. pr. [2] 48, 411 [1894]).

Platino-oxalias (vol. iv. p. 285). Regarding

Platino-oxalines (vol. iv. p. 285). Regarding the constitutional fermulae of the K salts, v. Werner (Zeit. f. anorg. Chemie, 3, 267), and Söderbaum (ibid. 6, 45 [1894]).

PLATINUM-AMMONIUM COMPOUNDS (vol. iv. p. 292). Petersen (Z. P. C. 10, 580 [1892]) finds, from cryoscopic determinations, that most of the formulæ generally used for these compounds are molecular. For a discussion of the constitutions of several classes of these compounds, and for measurements of the electrical conductivities of aqueous solutions of some of them, v. Werner a. Miolati (Z. P. C. 12, 35

POTASSIUM (vol. iv. p. 297). Holt a. Sims (C. J. 65, 452 [1894]) found that K became soft at 54.5°, and remained soft to 60.5°, whereat it became brittle; complete melting occurred at 62.5 H. a. S. say that dry K may be distilled in dry Q without the formation of any compound of the two elements. They found the products of the oxidation of K to be K₂O₂, K₂O₃, and finally K.O₄ (v. Oxides, infra). Mixtures of KNO₂ and KNO, were formed by oxidising Kin NO and in the red oxides of N.

Potassium amide (vol. iv. p. 299). Titherley (C. J. 65, 504 [1894]) says that KNH, is white and wax-like, melting at 270°-272°. It may be distilled without change in H at 400°-500°. T. says that KNH, is not decomposed by heat-It says that KNH₂ is not excomposed by heating at c. 400° in a sliver boat; if a glass vessel is used, NH₂ is given off with some N and H, and K silicate is formed; a mall amount of tecomposition occurre in a silver boat at c. 500°, and at a full red beat the amide distils with

and at a full red heat the amide distils with partial splitting up into its elements. For other reactions of KNH,, v. T. (Lc.).

Potassammonium (vol. iv. p. 299). Joannis (C. R. NS, 713 [1894]) finds that there is no reaction between N and N.H.K., he says that N.O. produces KeH., NH,, KCH, and N. For the action of O. v. J. (C. R. 116, 1870; abstract in C. J. 64 [11], 462 [1893]).

Potassium bromide (vol. iv. p. 299). The nelling-point is given as 315° by V. Meyers. Riddle (B. 26, 2443 [1893]).

Potassium chloride (vol. iv. p. 300). Melts at 766°, according to M. a. R. L.C.).

Potassium hydroxide (vol. iv. p. 802). Melts at 1045° (M. a. R., Lc.).

Potassium chloride (vol. iv. p. 303). Melts at 128° (M. a. R., Lc.): Regarding the interaction of KlAq and FeCl. Aq. v. Ferrance ognorus, iddlenda, p. 913.

Iddenda, p. 913.

Potagium tri-fodide (vol. iv. p. 804).
'Jakovkin (Z. P. C. 13, 539 [1894]) has made an examination of the dissociation of KI, in aqueous solution to KI, and IAq (abstract in C. I. 66 [11] 271 [1898])

C. J. 66 (11), 271 [1891]).

Polassium nitride (vol. iv. p. 304). The experiments of Titherley (C. J. 65, 512 [1894]) show that K,N does not exist.

Potassium oxide (vol. iv. p. 304). Holt.a. Sims (C. J. 66, 432 [1894]) failed to obtain the monocide K.O by any of the methods said to give this compound, but they say that when K.O. is kept at a redehent & loses O and gives a substance the composition of which approaches that of K.O. By heating K in a fairly dry mixture of oracle. By heating K in a fairly ary mixture of O and N, oxidation proceeded until K,O, was formed (dry O is without action on K); when kept in water-vapour K,O, gave off O, and formed K,O,; and by heating K in N,O, H. a. S. obtained K,O, which on exposure to air became K O. K,O.

RUBIDIUM.

Rubidium haloid compounds (vol. 1v. p. 418). Wheeler (Am. S. [3] 46, 88 [1893]) has prepared wheeler [Am. S. [3] 46, 88 [1893]) has prepared double company of the forms 3RbX.AsX, and RbX.As.Q₄; and (l.c. n. 269) various compounds of RbX with SbX_v. For physical properties of various salts of Rb, v. Erdmann, Ar. Ph. 232, 8 (abstract in C. J. 66 [11], 351 [1894]).

SELENATES (vol. iv. p\$436). Basic salts of Co and Cu are described by Bogdan (Bl. [8] 9, 584; abstract in C. J. 66 [11], 16 [1894]); the compositions given are 4CoO.3SeO, aq ad 3CuO.2SeO, 4aq.

SILICON CHLORIDES (vol. iv. p, 458). In B. 27, 1943 [1894] Gattermann a. Weinlig detail the best conditions for peoparing SiCl, SiHCl, and Si₂Cl_a, from crude & obtained by the interaction of SiO_2 and Mg powder (v. vol. iv. p. 455). Si_2Cl_a melts at -1° ; with NH_2Aq it gives off **H** and forms SiO_2xH_2O (O. a. W., l.c.).

Silicon octochloride Si Cl. Mol. w. 366.9. Vab. 187.7. Obtained by G. a. W. (l.c.) by fractionating crude Si chlorides; boils from 210° to 215° ; does not solidify at -12° .

SILVER (vol. iv. p. 464). The molecules Ag in dilute solution in tin is probably monatomic (Heycock a Neville, O. J. 57, 376 [1890]). According to Lüdtke (W. 50, 678; abstract in C. J. 36 [11], 92 [1894]), thin deposits of Ag on the control of the control glass, mica, &c., are allotropic forms of the metal. Regarding alloys of Ag with cadmium, v. Heycock a. Neville (C. & 65, 65 [1894]); s. also Mylius a. Fromm (B. 27, 630 [1894]).

Silver chloride (volv iv. r. 468). By the action of EgCl.Aq on pulverulent silver, Jones.

action of TgCl.Aq on pulverulent silver, Jones. (S. C. J. 12, 983; dbstract in C. J. 66 [11], 188 [1904]) obtained the compound AgrigCl₂.

SODIUM (vol. iv. p. 473). The molecule of sodium in fillute solution in the probably monatomic Haycock a. Newille, C. J. 57, 376 [1890]). Holt a. Sims (C. J. 65, 440 [1894]) found that dry sodium may be distilled unchanged in dry 0; modium y 0 the products a limited volume of N.O forms Na,O; heating in N.O or the red exides of N. produces a mixture. NO or the red oxides of N produces a mixture of NaNO, and NaNO, (H. a. S., I.o.).

ledium amide (vol. 1v. p. 475). Eitherley (C. J. 65, 504 [1894]) describes Natvil, as a white, transparent solid, with a crystalline struce white, transparent solid, with a crystalline struce ture; softens at 149°, and is completely melted at 255° to a colourless liquid. NaNH, is obtained in transparent, crystalline speeder by heating Ra in NH, at 8. 400°, allowing the product to sublime through a narrow tabe, and again subliming by warning gently. NaNH, decomposes at a red heat into Ra, N, and H. It does not give NaN, as generally stated (T., l.c.): no decomposition occurs at 300°, 400°.

Le.); no decomposition occurs at 300-400°.

Sodium bromide (vol. v. p. 476). Panfil in (J. R. 25, 272 [1893]) obtained NaBr. 5aq by exposing cone. NaBrAq out of doors in winter in Russia; desomposed at -25° to the dihydrate

Sodium iodide (vol. iv. p. 481). NaJ. 5aq separates from a solution of 100 g. Par ni. 50 c.c. water at -14°; at -10° it gives NaI. 2aq and water (P., l.c.).

Sodium nitride (vol. j., p. 482). NaN, is not formed by the interaction of Na or Na,O and NH,, or Na and N, according to Titherley (C. J. 25, 507; of. Sodium amide, supre-k

**S5,507; of. Sodium amide, suprek Sodium monoxide (vol iv. p. 482). Na₂O is formed by heating Na in a limited volume of O at the temperature below 180°; also by heating Na in a limited volume of N₂O at 180°-200° (Holt a. Sirsa₂C₁J. 65, 42 [1894]). Heated in excess of 0, the peroxide Na₂O₂ is formed. H. a. S. say Na₂O is greyish wlide. NH₃ reacts with gens. Theated Na₂O to form NaNH₂ and H₂O fittherley, O. J. 65, 510).

not combine with 0 when heated therein (H. s., s., s., B. Begarding the interestion of Ne. C. and an alcoholic solution of H.C., o. Take (B. 27, 916 [1894]). For reactions of Ne. C. Poleck, B. 27, 2051 (abstract in C. J. 66 [11], 116). 816)

STRONTIUM. For Strontium carbide, . v Moissan, C. R. 118, 683 (abstract in C. J. 66 [1].

Moissan, C. R. 118, 000 (abstract in C. 5, 00 [1]; 818 [1894]).

SULFAATES (vol. iz. pt 567).

Ohromium sulphates (vol. iv. p. 570). Double salts of Cr. (SO₁), and (NH.) SO₂, are described by Klobb (Bl. [3] 9, 663; abstract in C. J. 66 [11]; 95 [1894]).

Vanadium sulphates (v. this vol. pp. 847,

848, 850)

OXY-IMIDO SULPHONATES (vol. iv. p. 602). Divers a. Haga have published a lengthy com-

munication on these salts in C. J. 65, 523 [1894]. SULPHUR (vol. v. p. 606). For measurements of the viscosity of molten S at different temperatures, v. Brunhes a. Dussy, C. R. 118, 1045 (abstract in C. J. 66 [11], 343 [1894]).

THALLIUM (vol. iv. p. 674). The molecule of Tr in dilute solution in tin is probably monatomic (Heycock a. Neville, C. J. 57, 379 [1890]).

Thallium tri-iodide TII,. Wells a, Penfield (Zeit. f. anorg. Chemie, 6, 312; abstract in C. J. 66 [11], 318 [1894]) obtained this compound, in rhombic crystals, a:b:c=6828:::1217, by digesting TII and I with alcohol and evaporating over H2SO4.